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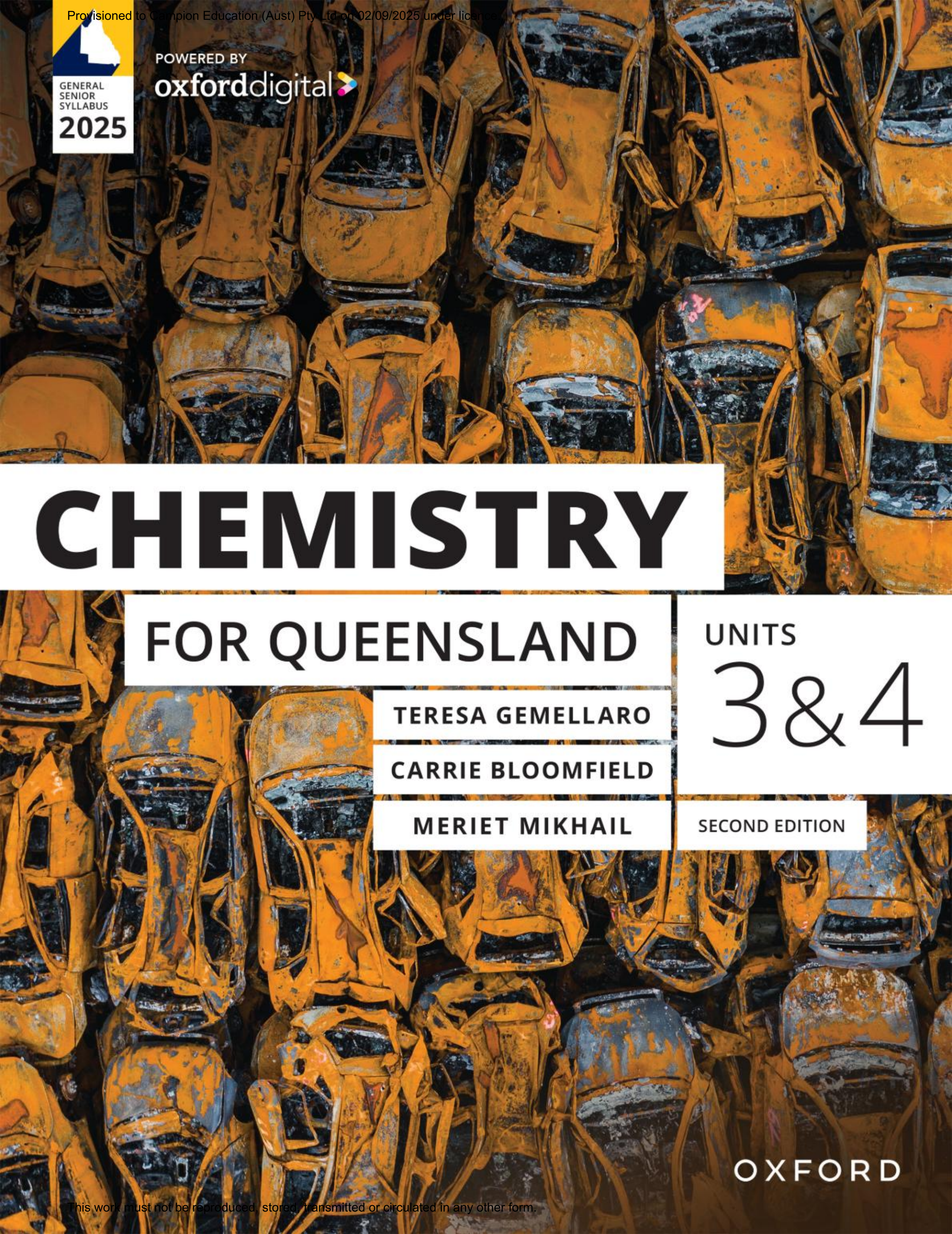


CHEMISTRY

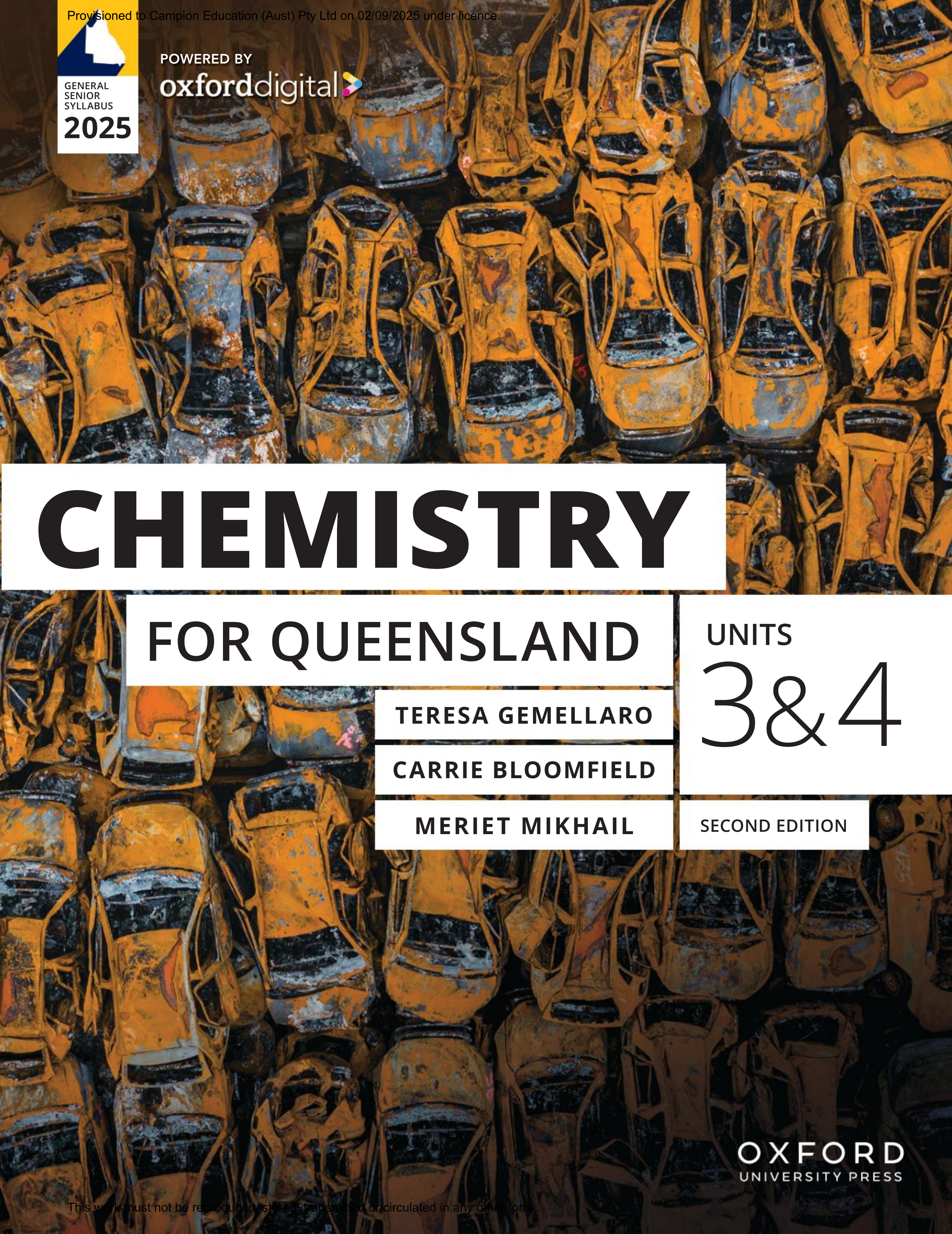
FOR QUEENSLAND

UNITS 3&4

TERESA GEMELLARO
CARRIE BLOOMFIELD
MERIET MIKHAIL

SECOND EDITION

OXFORD



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Contents

▶ Lessons available on Oxford Digital.

➤ Lessons available on Oxford Digital.

This module is available on Oxford Digital.

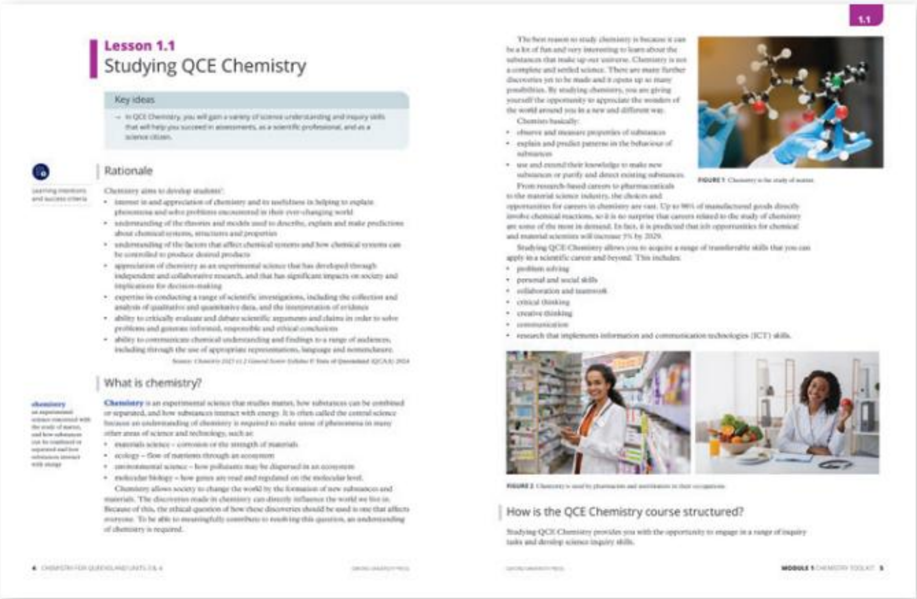
Introducing *Chemistry for Queensland Units 3 & 4* (Second edition)

Congratulations on choosing *Chemistry for Queensland Units 3 & 4* as part of your studies this year!

Chemistry for Queensland Units 3 & 4 has been purpose-written to meet the requirements of the QCAA Chemistry 2025 General senior syllabus. It includes a range of flexible print and digital products to suit your school and incorporates a wide variety of features designed to make learning fun, purposeful and accessible for all students!

Key features of the Student Books

The Chemistry toolkit module provides an overview of the syllabus, student-friendly guidance for every science inquiry skill and tips for success on assessment tasks.



Lesson 1.1

Studying QCE Chemistry

Key ideas

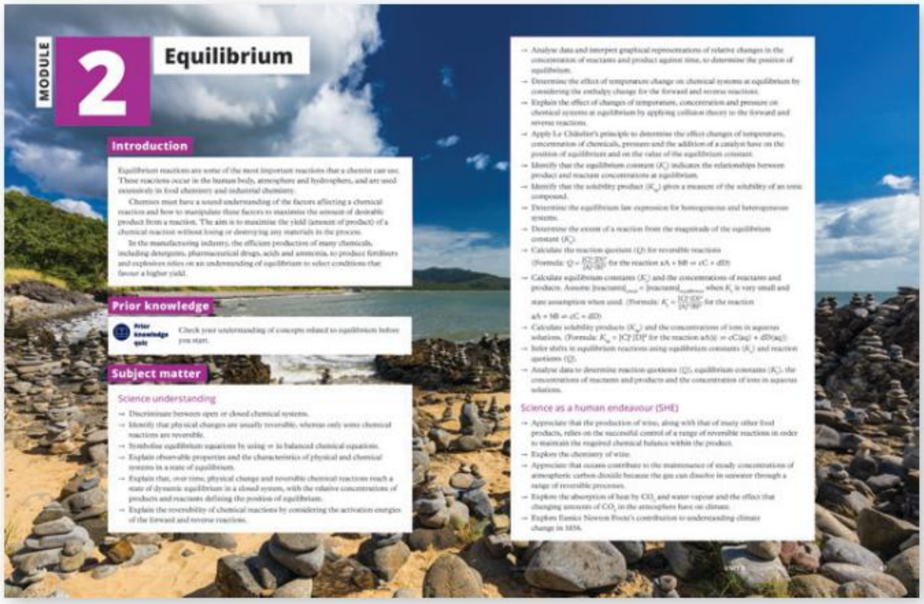
Rationale

What is chemistry?

How is the QCE Chemistry course structured?

Each module begins with a module opener that includes:

- QCAA subject matter
- reference to a supporting prior knowledge quiz that assesses and informs student understanding of prerequisite concepts
- a list of practical lessons that support science inquiry.



MODULE 2

Equilibrium

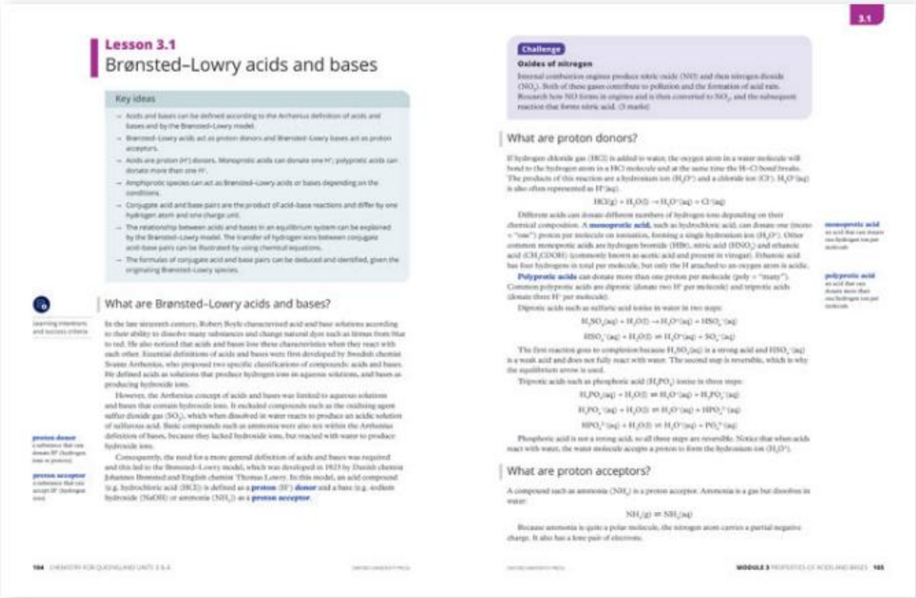
Introduction

Prior knowledge

Subject matter

Science understanding

Science as a human endeavour (SHE)



3.1

Lesson 3.1

Brønsted–Lowry acids and bases

Key ideas

What are Brønsted–Lowry acids and bases?

Challenge

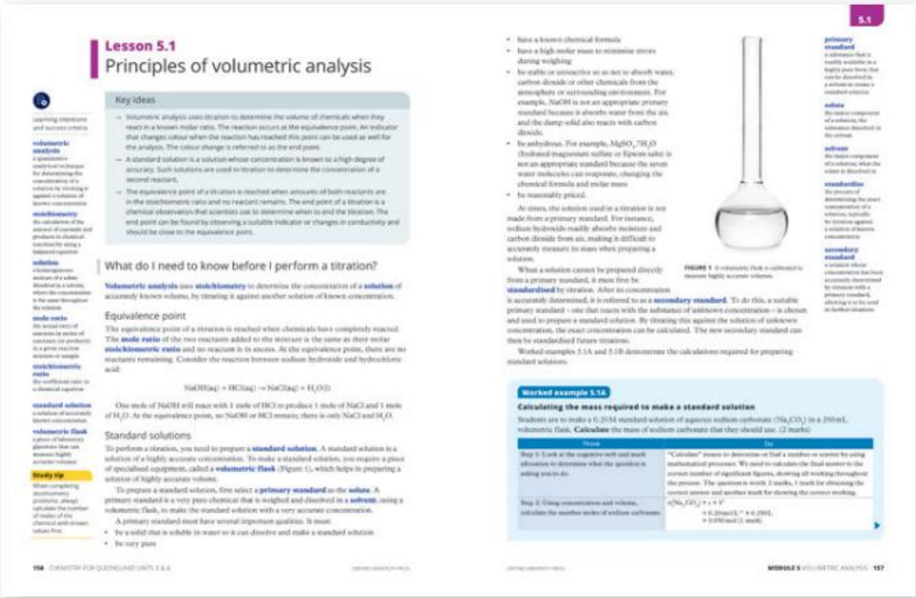
Oxides of nitrogen

What are proton donors?

What are proton acceptors?

Each lesson includes:

- **learning intentions and success criteria**
- clearly structured content written in clear, concise language
- definitions for all key terms on the page
- engaging, relevant and informative images and illustrations
- a range of tips and features designed to bring course content to life, including **study tips, worked examples, skill drills** and examples of **real-world science applications**
- references to supporting **digital resources**
- **Check your learning** activities organised according to **Marzano and Kendall's taxonomy** and incorporating **cognitive verbs**.



5.1

Lesson 5.1

Principles of volumetric analysis

Key ideas

What do I need to know before I perform a titration?

Equivalence point

Standard solutions

Study tip

Worked example 5.1A

Calculating the mass required to make a standard solution

Each module contains a range of practical activities designed to meet the requirements of science understanding and science inquiry subject matter and develop science inquiry skills.

Find out more

For a complete overview of all the features and benefits of this Student Book:

> activate your digital access (using the instructions on the inside front cover of this book) and click on "Introducing *Chemistry for Queensland Units 3 & 4*" in the "About this course" menu.

Key features of Oxford Digital

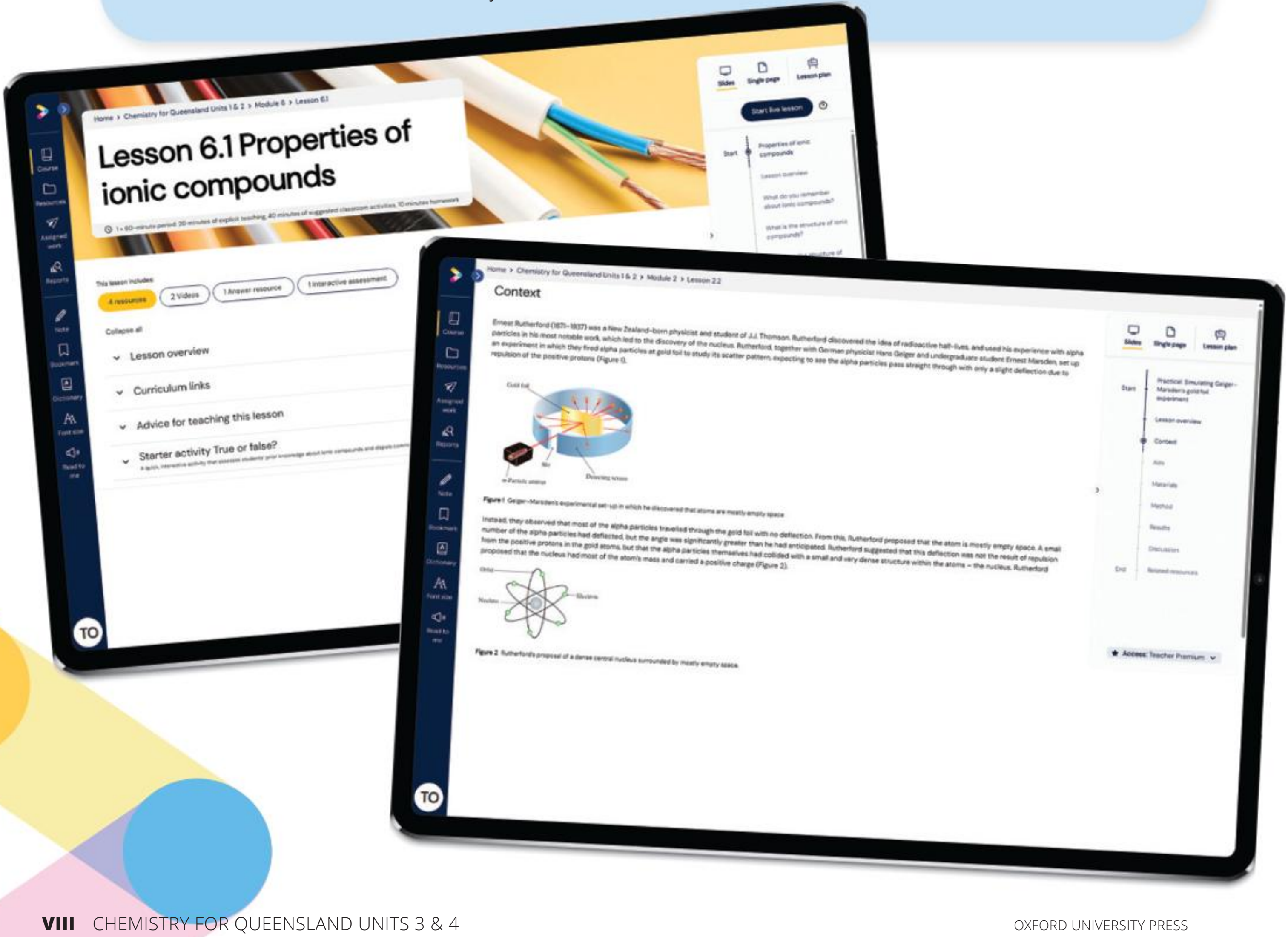
Oxford Digital has been designed in consultation with Australian teachers for Australian classrooms. The new platform delivers fully accessible, reflowable course content with videos, auto-marking activities, interactives and more embedded right where you need them.

There's also a range of unique features designed to improve learning outcomes.

Key features for students

As a student, you can:

- **view** all course content in a **fully accessible**, reflowable format that's delivered in bite-sized chunks so you can work at you own pace
- use the "Read to me" button to have any part of the course read aloud to you
- **highlight, take notes, bookmark pages**, or define words with the built-in **Australian Oxford Dictionary**
- **watch** short **content videos, worked example videos** and **practical demonstration videos** to help you revise anything you don't understand, catch up on things you've missed, or help you with your homework
- **complete** hundreds of interactive questions and quizzes as you work through the content and get the answers and results sent to you.



Home > Chemistry for Queensland Units 1 & 2 > Module 6 > Lesson 6.1

Lesson 6.1 Properties of ionic compounds

1 × 60-minute period: 20 minutes of explicit teaching, 40 minutes of suggested classroom activities, 10 minutes homework

This lesson includes:

4 resources | 2 Videos | 1 Answer resource | 1 Interactive assessment

Collapse all

Lesson overview

Curriculum links

Advice for teaching this lesson

Starter activity True or false?

Properties of ionic compounds
Lesson overview
What do you remember about ionic compounds?
What is the structure of ionic compounds?

Home > Chemistry for Queensland Units 1 & 2 > Module 2 > Lesson 2.2

Context

Ernest Rutherford (1871–1937) was a New Zealand-born physicist and student of J.J. Thomson. Rutherford discovered the idea of radioactive half-lives, and used his experience with alpha particles in his most notable work, which led to the discovery of the nucleus. Rutherford, together with German physicist Hans Geiger and undergraduate student Ernest Marsden, set up an experiment in which they fired alpha particles at gold foil to study its scatter pattern, expecting to see the alpha particles pass straight through with only a slight deflection due to repulsion of the positive protons (Figure 1).

Figure 1 Geiger–Marsden's experimental set-up in which he discovered that atoms are mostly empty space

Instead, they observed that most of the alpha particles travelled through the gold foil with no deflection. From this, Rutherford proposed that the atom is mostly empty space. A small number of the alpha particles had deflected, but the angle was significantly greater than he had anticipated. Rutherford suggested that this deflection was not the result of repulsion from the positive protons in the gold atoms, but that the alpha particles themselves had collided with a small and very dense structure within the atoms – the nucleus. Rutherford proposed that the nucleus had most of the atom's mass and carried a positive charge (Figure 2).

Figure 2 Rutherford's proposal of a dense central nucleus surrounded by mostly empty space.

Practical: Simulating Geiger–Marsden's gold foil experiment
Lesson overview
Context
Aim
Materials
Method
Results
Discussion
Related resources

Access: Teacher Premium

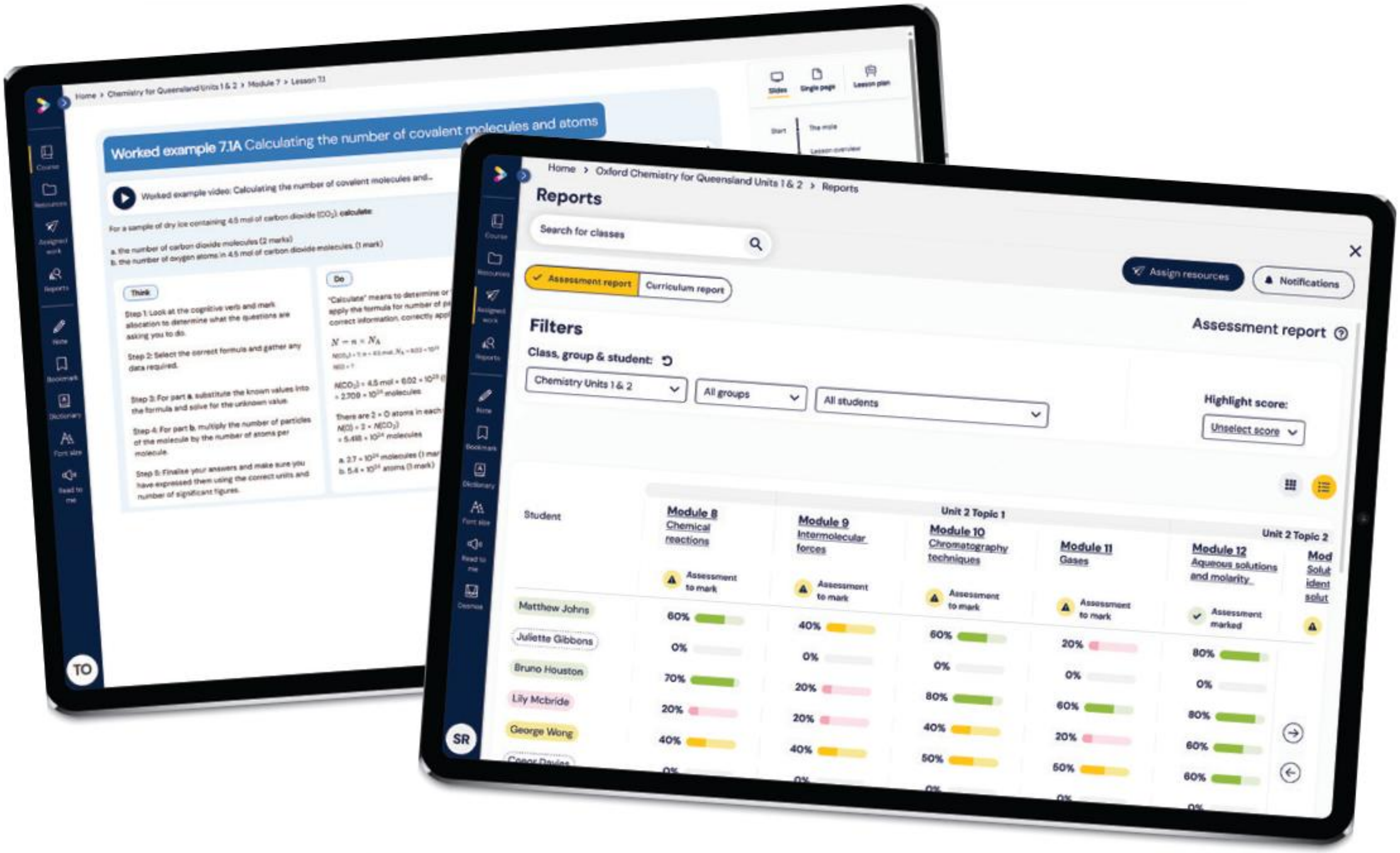
Key features for teachers

As a teacher, you can:

> **elevate** your teaching and **reduce planning and preparation time** with **Live Lesson mode**. This is an Australian first that lets you upgrade from traditional print-based lesson plans to **fully interactive, perfectly sequenced and timed interactive lessons complete with classroom activities** that are ready to go

> **personalise** learning for every student and **differentiate** content based on student strengths and weaknesses. Assign support or extension resources to any student using a range of differentiation resources

> **revolutionise** your planning, marking and reporting with powerful analytics on student performance and progress.



Worked example 7.1A Calculating the number of covalent molecules and atoms

Worked example video: Calculating the number of covalent molecules and...

For a sample of dry ice containing 4.5 mol of carbon dioxide (CO_2), **calculate**:

a. the number of carbon dioxide molecules (2 marks)
b. the number of oxygen atoms in 4.5 mol of carbon dioxide molecules. (1 mark)

Think

Step 1: Look at the cognitive verb and mark allocation to determine what the questions are asking you to do.

Step 2: Select the correct formula and gather any data required.

Step 3: For part **a**, substitute the known values into the formula and solve for the unknown value.

Step 4: For part **b**, multiply the number of particles of the molecule by the number of atoms per molecule.

Step 5: Finalise your answers and make sure you have expressed them using the correct units and number of significant figures.

Do

"Calculate" means to determine or apply the formula for number of p correct information, correctly app

$N = n \times N_A$

$N(CO_2) = 4.5 \text{ mol} \times 6.02 \times 10^{23}$
$= 2.709 \times 10^{24}$ molecules

There are $2 \times$ O atoms in each
$N(O) = 2 \times N(CO_2)$
$= 5.418 \times 10^{24}$ molecules

a. 2.7×10^{24} molecules (1 mar
b. 5.4×10^{24} atoms (1 mark)

Reports

Filters

Class, group & student: Chemistry Units 1 & 2 | All groups | All students

Highlight score: Unselect score

		Unit 2 Topic 1			Unit 2 Topic 2
Student	Module 8 Chemical reactions Assessment to mark	Module 9 Intermolecular forces Assessment to mark	Module 10 Chromatography techniques Assessment to mark	Module 11 Gases Assessment to mark	Module 12 Aqueous solutions and molarity ✓ Assessment marked
Matthew Johns	60%	40%	60%	20%	80%
Juliette Gibbons	0%	0%	0%	0%	0%
Bruno Houston	70%	20%	80%	60%	80%
Lily Mcbride	20%	20%	40%	20%	60%
George Wong	40%	40%	50%	50%	60%
Conor Davies	0%	0%	0%	0%	0%

Find out more

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Meet the authors & reviewers

Teresa Gemellaro

Author

Teresa holds a Bachelor of Science and Graduate Diploma in Education from the University of Queensland. She has taught chemistry, mathematics and science since 1980, with the majority of her career spent at Ayr State High School in North Queensland. In 2021 and 2022, Teresa was a chemistry teacher and facilitator in a vacation program at James Cook University, Townsville, helping Year 12 students revise Units 3 & 4 and prepare for the internal and external assessment tasks. She also contributed to editing course materials. Teresa is an experienced chemistry textbook author and has worked for the QCAA and its predecessor in many different roles – both chemistry-related and otherwise – since the mid-1980s.

Carrie Bloomfield

Author

Carrie has been teaching VCE Chemistry and science in secondary schools for the past 11 years and is currently a leading teacher at Mount Eliza Secondary College. She is a VCAA assessor for Chemistry and has presented on science inquiry skills at previous workshops for the Oxford Science series. Carrie co-authored the Oxford University Press's first editions of the *Chemistry for Queensland Units 1–4* and *Chemistry for VCE Units 1–4 series*.

Dr Meriet Mikhail

Author

Meriet was awarded a PhD in Medicine from the University of Sydney in 2005 and has received various awards and grants. She has presented at both national and international conferences on vaccine development and disease epidemiology. She is a QCE and IB senior chemistry teacher with over 12 years of experience teaching QCE Chemistry. Meriet is the Head of Chemistry at one of Brisbane's leading private schools and a QCAA Subject Matter Expert for Chemistry.

We would also like to acknowledge and thank the following authors for their contributions: Krystyle Kuipers, Martin Brabec and Philip Sharpe.

Bernice Zaro

First Nations reviewer

Bernice is a proud Aboriginal and Torres Strait Islander Woman with a strong passion for educational greatness through culturally inclusive learning. Bernice identifies with parents who are Traditionally connected to Aboriginal Communities of South East Queensland and Mer in Torres Strait Islands (Murray Island) and she is inspired to share and learn continuously. Bernice, along with her husband Aicey Zaro, a recognised traditional Artist, has been educating schools and communities through Cultural Awareness art workshops for over 15 years during their time managing the Zaro Cultural Gallery in the Burdekin region. Bernice has a passion for learning through her ongoing studies in Community Development, Child Wellbeing, Cultural Diversity and also sharing personal experiences through family, community and business, which inspire her to take on new opportunities.

Malcolm Corney

Reviewer

Malcolm holds a Bachelor of Applied Science (Applied Chemistry), a Graduate Diploma of Computer Science, a Master of Information Technology (Research) and a Graduate Diploma of Education (Secondary). He has worked as an analytical chemist in the fields of wastewater, pharmaceuticals and magnesium metal production for 20 years. He taught computer science and computer forensics at QUT for 15 years and has published in the fields of computer forensics and computer science education. He has taught STEM and senior chemistry at Kelvin Grove State College for nine years, where he leads the design of teaching and learning programs for these subjects.

Dr Philip Sharpe

Reviewer

Philip is a lecturer in Chemistry at the University of Queensland, teaching introductory, general, organic and biological inorganic chemistry since 2008 and is the immediate past Director of First Year Chemistry. He has received School and Faculty awards for his teaching and a national award for University Teaching as part of the First Year Chemistry teaching team. He has worked in Australia and the UK in the areas of macrocyclic coordination chemistry, electropolymers containing metal centres as nitrite sensors, amyloid formation in artificial proteins and iron-binding drugs for cancer treatment. He is a long-term member of the Royal Australian Chemical Institute (RACI) Queensland Chemistry Education group, which organises the long-standing and popular titration competition in Queensland.

MODULE 1

Chemistry toolkit

Introduction

Chemistry requires research skills to experiment and test theories in order to gain further knowledge. A true experiment always aims to discover natural laws of cause and effect – how do changes in one property cause changes in another?

This module will become a useful reference throughout Units 3 and 4 of Chemistry. It teaches you the principles that underpin how we approach investigating chemical phenomena and discovering new information about our natural world. It is only logical that it should come first!

This module is set out in a way that makes each piece of information easy to access. It is not meant to be read from beginning to end. Rather, it's like a toolbox – you dip your hand into it, get the tool you need and then apply it.

Prior knowledge

Prior knowledge quiz

Check your understanding of the science inquiry skills before you start.

oxforddigital Full lessons for this module are available on Oxford Digital.

Online-only lessons

Lesson 1.2	Considering First Nations perspectives in Chemistry
Lesson 1.3	Understanding the scientific method
Lesson 1.4	Planning investigations
Lesson 1.5	Considering safety and ethics
Lesson 1.6	Collecting data
Lesson 1.8	Evaluating evidence
Lesson 1.9	Communicating scientifically
Lesson 1.10	Preparing for your data test
Lesson 1.11	Conducting your student experiment
Lesson 1.12	Conducting your research investigation
Lesson 1.13	Preparing for your exams

Lesson 1.1

Studying QCE Chemistry

Key ideas

→ In QCE Chemistry, you will gain a variety of science understanding and inquiry skills that will help you succeed in assessments, as a scientific professional, and as a science citizen.

Learning intentions and success criteria

Rationale

Chemistry aims to develop students':

- interest in and appreciation of chemistry and its usefulness in helping to explain phenomena and solve problems encountered in their ever-changing world
- understanding of the theories and models used to describe, explain and make predictions about chemical systems, structures and properties
- understanding of the factors that affect chemical systems and how chemical systems can be controlled to produce desired products
- appreciation of chemistry as an experimental science that has developed through independent and collaborative research, and that has significant impacts on society and implications for decision-making
- expertise in conducting a range of scientific investigations, including the collection and analysis of qualitative and quantitative data, and the interpretation of evidence
- ability to critically evaluate and debate scientific arguments and claims in order to solve problems and generate informed, responsible and ethical conclusions
- ability to communicate chemical understanding and findings to a range of audiences, including through the use of appropriate representations, language and nomenclature.

Source: *Chemistry 2025 v1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

What is chemistry?

chemistry
an experimental science concerned with the study of matter, and how substances can be combined or separated and how substances interact with energy

Chemistry is an experimental science that studies matter, how substances can be combined or separated, and how substances interact with energy. It is often called the central science because an understanding of chemistry is required to make sense of phenomena in many other areas of science and technology, such as:

- materials science – corrosion or the strength of materials
- ecology – flow of nutrients through an ecosystem
- environmental science – how pollutants may be dispersed in an ecosystem
- molecular biology – how genes are read and regulated on the molecular level.

Chemistry allows society to change the world by the formation of new substances and materials. The discoveries made in chemistry can directly influence the world we live in. Because of this, the ethical question of how these discoveries should be used is one that affects everyone. To be able to meaningfully contribute to resolving this question, an understanding of chemistry is required.

The best reason to study chemistry is because it can be a lot of fun and very interesting to learn about the substances that make up our universe. Chemistry is not a complete and settled science. There are many further discoveries yet to be made and it opens up so many possibilities. By studying chemistry, you are giving yourself the opportunity to appreciate the wonders of the world around you in a new and different way.

Chemists basically:

- observe and measure properties of substances
- explain and predict patterns in the behaviour of substances
- use and extend their knowledge to make new substances or purify and detect existing substances.

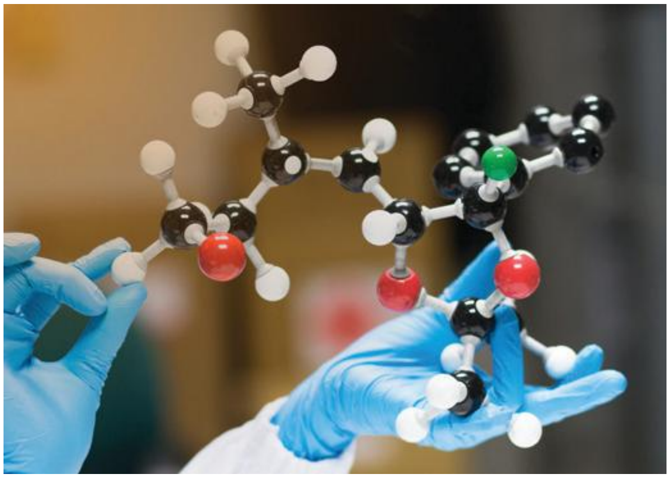

FIGURE 1 Chemistry is the study of matter.

From research-based careers to pharmaceuticals to the material science industry, the choices and opportunities for careers in chemistry are vast. Up to 96% of manufactured goods directly involve chemical reactions, so it is no surprise that careers related to the study of chemistry are some of the most in demand. In fact, it is predicted that job opportunities for chemical and material scientists will increase 5% by 2029.

Studying QCE Chemistry allows you to acquire a range of transferrable skills that you can apply in a scientific career and beyond. This includes:

- problem solving
- personal and social skills
- collaboration and teamwork
- critical thinking
- creative thinking
- communication
- research that implements information and communication technologies (ICT) skills.

FIGURE 2 Chemistry is used by pharmacists and nutritionists in their occupations.

How is the QCE Chemistry course structured?

Studying QCE Chemistry provides you with the opportunity to engage in a range of inquiry tasks and develop science inquiry skills.

Syllabus objectives

Like the other senior sciences, there are six syllabus objectives in QCE Chemistry.

1 **Describe ideas and findings.**

Students use scientific representations and language in appropriate genres to give a detailed account of scientific phenomena, concepts, theories, models and systems.

2 **Apply understanding.**

Students use scientific concepts, theories, models and systems within their limitations. They use algebraic, visual and graphical representations of scientific relationships and data to determine unknown scientific quantities or features. They explain phenomena, concepts, theories, models, systems and modifications to methodologies.

3 **Analyse data.**

Students consider scientific information from primary and secondary sources to identify trends, patterns, relationships, limitations and uncertainty. In qualitative data, they identify the essential elements, features or components. In quantitative data, they use mathematical processes and algorithms. They identify data to support ideas, conclusions or decisions.

4 **Interpret evidence.**

Students use their understanding of scientific concepts, theories, models and systems and their limitations to draw conclusions and develop scientific arguments. They compare, deduce, extrapolate, infer, justify and make predictions based on their analysis of data.

5 **Evaluate conclusions, claims and processes.**

Students critically reflect on the available evidence and make judgements about its application to research questions. They extrapolate findings to support or refute claims. They use the quality of the evidence to evaluate the validity and reliability of inquiry processes and suggest improvements and extensions for further investigation.

6 **Investigate phenomena.**

Students develop rationales and research questions for experiments and investigations. They modify methodologies to collect primary data and select secondary sources. They manage risks, environmental and ethical issues and acknowledge sources of information.

Study tip

Your assessments in QCE Chemistry are mapped to these syllabus objectives. The data test (Lesson 1.10) assesses objectives 2 to 4. The student experiment (Lesson 1.11) and research investigation (Lesson 1.12) assess objectives 1 to 6. The external exam (Lesson 1.13) assesses objectives 1 to 4.

Subject matter

The structure of the QCE Chemistry course is laid out in the Chemistry General Senior Syllabus. The course consists of four units. Units 1 and 2 are completed in the first year of the QCE Chemistry course and Units 3 and 4 in the second year. Each unit is divided into topics and each topic includes science understanding, science as a human endeavour and science inquiry subject matter. You should be familiar with these categories of understanding from your studies in years 7 to 10.

An overview of the QCE Chemistry units is shown in Figure 3, and Units 3 and 4 are summarised in Table 1. Each unit has its own specific objectives, which are outlined in the Unit 3 opener and Unit 4 opener.

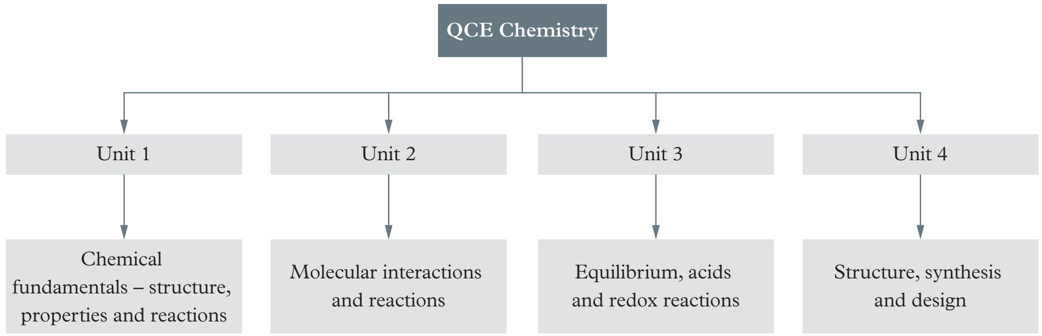

FIGURE 3 The structure of the QCE Chemistry course

TABLE 1 Topics in Units 3 and 4 Chemistry

Unit 3 Equilibrium, acids and redox reactions	
Topic	**Description**
1. Chemical equilibrium systems	In this topic, you will learn about: • chemical equilibrium • factors that affect equilibrium • equilibrium constants • properties of acids and bases • pH • Brønsted–Lowry model • dissociation constants • acid–base indicators • volumetric analysis.
2. Oxidation and reduction	In this topic, you will learn about: • redox reactions • electrochemical cells • galvanic cells • standard electrode potential • electrolytic cells.
Unit 4 Structure, synthesis and design	
Topic	**Description**
1. Properties and structure of organic materials	In this topic, you will learn about: • the structure of organic compounds • physical properties and trends • organic reactions and reaction pathways • organic materials: structure and function • analytical techniques.
2. Chemical synthesis and design	In this topic, you will learn about: • chemical synthesis • macromolecules: polymers, proteins and carbohydrates.

Source: *Chemistry 2025 v1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

Assessment in QCE Chemistry

In Units 3 and 4, you can be assessed in several ways across the different topics. The syllabus requires that you:

- complete three internal assessments:
  - a data test using data derived from practicals, activities or case studies from Unit 3, which assesses Objectives 2, 3 and 4
  - a student experiment in which students modify an experiment relevant to Unit 3 subject matter, which assesses Objectives 1, 2, 3, 4, 5 and 6
  - a research investigation in which students gather evidence related to a research question to evaluate a claim relevant to Unit 4 subject matter, which assesses Objectives 1, 2, 3, 4, 5 and 6
- complete a student experiment
- complete an external examination consisting of two papers with questions relating to Units 3 and 4, which assesses Objectives 1, 2, 3 and 4.

Many schools assess students studying Units 1 and 2 as they would for students studying Units 3 and 4. This means that you will probably have completed three assessment pieces and an end-of-year examination or examinations in Year 11.

TABLE 2 Units 3 and 4 assessments

Unit and assessment type	Assessment description	Assessment objectives
Unit 3 Equilibrium, acids and redox reactions: Data test	Students respond to items using qualitative data and/or quantitative data derived from practicals, activities or case studies relevant to Unit 3 subject matter.	1. Apply understanding of chemical equilibrium systems or oxidation and reduction to given algebraic, visual or graphical representations of scientific relationships and data to determine unknown scientific quantities or features. 2. Analyse data about chemical equilibrium systems or oxidation and reduction to identify trends, patterns, relationships, limitations or uncertainty in datasets. 3. Interpret evidence about chemical equilibrium systems or oxidation and reduction to draw conclusions based on analysis of datasets
Unit 3 Equilibrium, acids and redox reactions: Student experiment	Students modify (i.e. refine, extend or redirect) an experiment relevant to Unit 3 subject matter to address their own related hypothesis or question. This assessment provides opportunities to assess science inquiry skills.	1. Describe ideas and experimental findings about chemical equilibrium systems or oxidation and reduction. 2. Apply understanding of chemical equilibrium systems or oxidation and reduction to modify experimental methodologies and process data. 3. Analyse experimental data about chemical equilibrium systems or oxidation and reduction. 4. Interpret experimental evidence about chemical equilibrium systems or oxidation and reduction. 5. Evaluate experimental processes and conclusions about chemical equilibrium systems or oxidation and reduction. 6. Investigate phenomena associated with chemical equilibrium systems or oxidation and reduction through an experiment.
Unit 4 Structure, synthesis and design: Research investigation	Students gather evidence related to a research question to evaluate a claim relevant to Unit 4 subject matter. This assessment provides opportunities to assess science inquiry skills and science as a human endeavour (SHE) subject matter.	1. Describe ideas and findings about the properties and structure of organic materials or chemical synthesis and design. 2. Apply understanding of the properties and structure of organic materials or chemical synthesis and design to develop research questions. 3. Analyse research data about the properties and structure of organic materials or chemical synthesis and design. 4. Interpret research evidence about the properties and structure of organic materials or chemical synthesis and design. 5. Evaluate research processes, claims and conclusions about the properties and structure of organic materials or chemical synthesis and design. 6. Investigate phenomena associated with the properties and structure of organic materials or chemical synthesis and design through research.
Units 3 and 4 examination/s		

Source: *Chemistry 2025 v1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

You can use Lesson 1.10 Preparing for your data test, Lesson 1.11 Conducting your student experiment, Lesson 1.12 Conducting your research investigation and Lesson 1.13 Preparing for your exams to guide you through these assessments. Note that Science as a human endeavour content will not be directly assessed in your examinations.

What are the science inquiry skills?

In addition to developing your science understanding in Chemistry (which we will cover in Modules 2 to 14), the QCE course requires you to develop and apply a range of science inquiry skills. These skills are specified in the QCE Chemistry General Senior Syllabus and are listed on the opening pages of this module. This module will help you develop these skills.

The science inquiry skills are applicable to all areas of study in Units 1 to 4 of the QCE Chemistry course. They are especially important for preparing and planning for your data test, student experiment and research investigation assessment tasks.

FIGURE 4 Having good science inquiry skills prepares you for success in QCE Chemistry (and beyond!).

Check your learning 1.1

Check your learning 1.1: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Define** the term "chemistry" in 10 words or less. (1 mark)

2 **Recall** three transferrable skills that you can learn during your QCE Chemistry studies. (1 mark)

Analytical processes

3 **Judge** whether this is true: "Chemistry is said to be an experimental science, so all chemistry theories have to come from experiments". (2 marks)

Knowledge utilisation

4 **Investigate** how chemistry would be relevant to
  - **a** a veterinarian working on finding a cure for chlamydia in koalas (1 mark)
  - **b** a technician monitoring water quality for Queensland Urban Utilities at the South Pine Dam. (1 mark)
  - **c** an art conservator working in the Queensland Museum (1 mark)
  - **d** a wheat farmer from the Darling Downs (1 mark)
  - **e** a marine biologist working on the Great Barrier Reef (1 mark)
  - **f** an environmental toxicologist working in Mt Isa (1 mark)
  - **g** an architect designing shade structures for a park in Townsville (1 mark)
  - **h** a perfume maker from Noosa (1 mark)
  - **i** a council worker controlling mosquitoes in Cairns. (1 mark)

5 **Propose** how chemistry might be used in physics and biology; and how chemistry relies on mathematics. (3 marks)

Lesson 1.2

Considering First Nations perspectives in Chemistry

Key ideas

- → First Nations peoples have longstanding scientific knowledge.
- → First Nations peoples have developed knowledge about the world by observing using all the senses, predicting and hypothesising, testing (trial and error) and making generalisations within specific contexts such as the use of food, natural materials, navigation and sustainability of the environment.
- → Correctly acknowledging cultural and/or language groups, avoiding Eurocentrism and critically evaluating sources of information can help you to respectfully engage with First Nations' perspectives in QCE Chemistry.

Learning intentions and success criteria

Science inquiry skills

This lesson provides support for the following science inquiry skills:

- identify and implement strategies to manage risks, ethics and environmental impact, e.g.
    - cultural guidelines, protocols for working with the knowledges of First Nations peoples

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Lesson 1.3

Understanding the scientific method

Key ideas

- → The scientific method is a circular process that involves making observations, formulating a hypothesis that will often lead to performing experiments or simulations, developing models or theorems, retesting and trialling.
- → Research questions define the scope of an investigation. They can be used to develop hypotheses that predict the outcome of the investigation.

Science inquiry skills

This lesson provides support for the following science inquiry skills:

- identify, research and construct questions for investigation
- propose hypotheses and/or predict possible outcomes

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Learning intentions and success criteria

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Lesson 1.4

Planning investigations

Key ideas

→ A method outlines the steps followed in an experiment and lists all of the materials and equipment used.

→ Valid and reliable measurements can be obtained by carefully designing your investigation to collect sufficient data and minimise errors.

→ All measurements include errors or uncertainties, either systematic or random. It is important to consider these and implement strategies to minimise their effects when you plan your experiments.

Science inquiry skills

Learning intentions and success criteria

This lesson provides support for the following science inquiry skills:

- design investigations, including the procedure/s to be followed, the materials required, and the type and amount of primary and/or secondary data required to obtain valid and reliable evidence, e.g.
  - consider replicates, number of data points and quality of sources
  - identify the types of errors, extraneous variables or confounding factors that are likely to influence results and implement strategies to minimise systematic and random error
- use appropriate equipment, techniques, procedures and sources to systematically and safely collect primary and secondary data, e.g.
  - laboratory and field techniques: measurement, and equipment calibration
  - ICTs, scientific texts, databases, simulations, online sources
- suggest improvements and extensions to minimise uncertainty, address limitations and improve the overall quality of evidence, e.g.
  - analyse the impact of random error/measurement uncertainties and systematic errors in experimental work and determine how these errors/measurement uncertainties can be reduced
  - discriminate between random and systematic errors

  - identify that experimental design and procedure usually leads to systematic errors in measurement, which causes a deviation in a direction and that repeated trials and measurements will reduce random error but not systematic error

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Lesson 1.5
Considering safety and ethics

Key ideas

→ Good laboratory practices and laboratory safety allows you to identify risks and take measures to control them so that you and those sharing the laboratory space with you stay safe during scientific investigations.

→ Conducting experiments ethically involves considering the impacts of your investigation beyond the laboratory.

Learning intentions and success criteria

Science inquiry skills

This lesson provides support for the following science inquiry skills:

- identify and implement strategies to manage risks, ethics and environmental impact, e.g.
  - material safety data sheets
  - workplace health and safety guidelines
  - appropriate disposal methods
  - standard operating procedures

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Lesson 1.6
Collecting data

Key ideas

→ Single experimental measurements are reported using best estimates, indicators of measurement uncertainty and units.

→ Scientific notation is used to easily express extremely large or extremely small values.

→ Significant figures are digits in a number that are known with certainty plus the first digit that is uncertain.

→ All measurements, information and observations should be recorded in your logbook.

Science inquiry skills

Learning intentions and success criteria

This lesson provides support for the following science inquiry skills:

- use scientific language and representations to systematically record information, observations, data and measurement error, e.g.
  - symbols, units and prefixes
  - tables, graphs and diagrams
  - logbooks
- translate information between graphical, numerical and/or algebraic forms, e.g.
  - units and measurement conversions
  - ratios and percentages
  - symbols and notation

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Worked examples

This lesson is supported by the following Worked examples:

- **Worked example 1.6A** Writing numbers using scientific notation
- **Worked example 1.6B** Rounding answers to the correct number of significant figures
- **Worked example 1.6C** Converting between units for physical quantities

oxforddigital **This lesson is available on Oxford Digital.**

Lesson 1.7

Processing and analysing data

Key ideas

→ Data is processed and analysed to identify trends, patterns, relationships, limitations and uncertainty.

→ Absolute and percentage uncertainty give an idea of the precision of measurements.

→ Percentage error gives an idea of the accuracy of measurements.

→ Data can be summarised in a variety of ways, such as in a table, a scatterplot or a scientific diagram.

Science inquiry skills

Learning intentions and success criteria

This lesson provides support for the following science inquiry skills:

- use scientific language and representations to systematically record information, observations, data and measurement error, e.g.
  - indicators of measurement uncertainty and state measurement uncertainties as a range (±) to an appropriate precision, e.g. when adding or subtracting, the final answer should be given to the least number of decimal places, when multiplying or dividing, the final answer should be given to the least number of significant figures
  - identify that concentration can be represented in a variety of ways including, but not limited to, mol L^{-1}, g L^{-1} and ppm and that square brackets can be used to denote concentration
- use mathematical techniques to summarise data in a way that allows for identification of relevant trends, patterns, relationships, limitations and uncertainty, e.g.
  - mean
  - gradient analysis
  - scatterplots (with maximum and minimum trendlines and R^2)
  - propagate random error in data processing to show the impact of measurement uncertainties on the final result
  - apply simple treatment of error analysis, e.g. for functions such as addition and subtraction, absolute uncertainties should be added, for multiplication, division and powers, percentage uncertainties should be added
  - calculate the measurement uncertainties in processed data, including the use of absolute uncertainties of the mean (Formula: $\Delta\overline{x} = \pm\frac{(x_{\text{max}} - x_{\text{min}})}{2}$) and percentage uncertainties (Formula: percentage uncertainty (%) $= \frac{\text{absolute uncertainty}}{\text{measurement}} \times \frac{100}{1}$)
  - calculate the percentage error, when the experimental result can be compared with a theoretical or accepted result (value) (Formula: percentage error (%) $= \left|\frac{\text{measured value} - \text{true value}}{\text{true value}}\right| \times \frac{100}{1}$)
  - discriminate between absolute uncertainty and percentage error

- select and construct appropriate representations to present data and communicate findings, e.g.
  - summary tables
  - apply appropriate graphical representations to analyse data and draw conclusions
- analyse data to identify trends, patterns and relationships; recognising error, uncertainty and limitations of evidence
- interpret graphs in terms of the relationship between dependent and independent variables; draw and interpret best-fit lines or curves through data points, including evaluating when it can and cannot be considered as a linear function
- extrapolate findings to determine unknown values, predict outcomes and evaluate claims.

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What information does data analysis give us?

Once we have obtained our raw data, we are ready to process and analyse it. The goal of data analysis is to find patterns or trends, whereas data interpretation involves explaining those patterns. This typically involves completing calculations and constructing scatterplots. By transforming the data into more meaningful forms, we can then analyse it to quantify uncertainty, identify limitations, construct evidence-based arguments and draw conclusions.

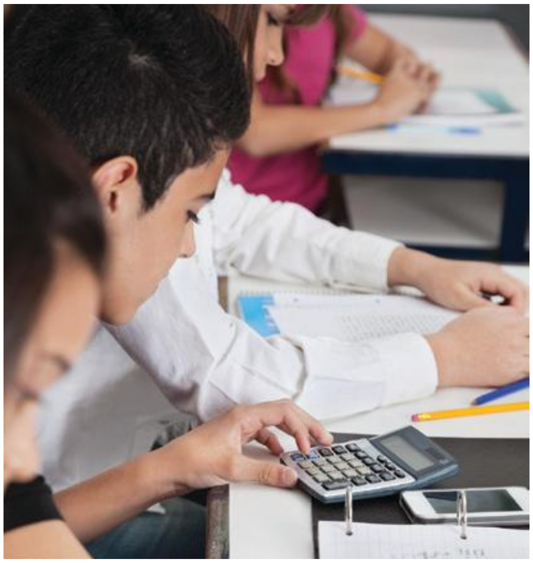


FIGURE 1 Analysing data (e.g. through mathematical techniques) helps us to draw conclusions from an investigation.

How do you use the measures of central tendency?

In the previous lesson, we talked about expressing measurements using a best estimate. This is straightforward when we are taking single measurements, but when there are a number of repeated measurements of the same value, there are some calculations we need to perform. These calculations allow us to better describe the measurement value and uncertainty.

To do this, we use measures of **central tendency**. When measurements involve random errors, the values tend to cluster around a central value. This is because random errors are just as likely to result in underestimates and overestimates of the "true" value. It is useful to discuss how close the values are to a central value using measures of central tendency.

The normal distribution

Many natural variables tend to have a normal distribution. This is also sometimes referred to as a bell curve (Figure 2). On a normal distribution, the most likely value is the central value, which is the arithmetic **mean** or average of the results. The curve is symmetrical, with the probability of a particular value becoming lower as that value gets further away from the mean, in either direction. The curve can be more or less stretched out. This variation or spread in the results can be quantified by a value known as the **standard deviation**.

central tendency
the tendency for repeated measurements of the same value to be grouped around the mean, mode or median

mean
the average of multiple values

standard deviation
a statistical value that expresses how spread out a group of values are or by how much they differ from the mean value for the group

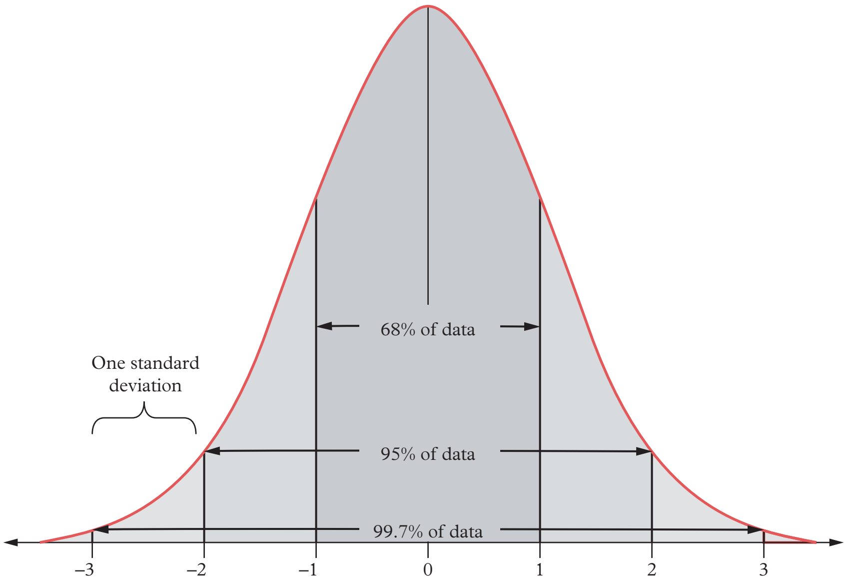


FIGURE 2 The normal distribution is also known as a bell curve.

For example, Table 1 shows the volume of aqueous hydrochloric acid needed to react with 20.0 mL of aqueous sodium hydroxide. Only six values are listed, but if the measurements were repeated several hundred times, then it is likely that a normal distribution of the values would be found around the mean.

TABLE 1 Volume of HCl(aq) required for reaction with 20.0 mL NaOH solution

Trial number	Volume of HCl(aq) (mL)
1	19.92
2	20.04
3	19.86
4	19.98
5	20.08
6	19.86

Calculating the mean

The arithmetic mean of a group of numbers is the sum of the numbers divided by the number of measurements. This can be expressed mathematically:

$$\overline{x} = \frac{\Sigma x}{n}$$

where $\overline{x}$ is the mean, x is a measured value, and n is the number of measurements (replicates) and Σ (capital sigma) means to add all the values (x) together.

This formula can be applied to the data in Table 1. The mean here should be reported to two decimal places, matching the precision in the original measurements.

$$\overline{x} = \frac{\Sigma x}{n} = \frac{19.92\,\text{mL} + 20.04\,\text{mL} + 19.86\,\text{mL} + 19.98\,\text{mL} + 20.08\,\text{mL} + 19.86\,\text{mL}}{6}$$
$$= 19.96\,\text{mL}$$

outlier
a value that is much smaller or larger than most of the other values in a set of data; it is greater than three standard deviations away from the mean

One problem with the mean value is that it is sensitive to **outlier** values (those that are much larger or smaller than the other values). If there was an additional measurement of 40.00 mL, it would shift the average to 22.82 mL, which is quite far from the other values. In practice, a value of 40.00 mL would probably be rejected as an outlier.

Outliers are typically attributed to mistakes or random errors. Once identified, they should be omitted from data analysis.

Mode

The **mode** is another way of describing a group of values. The mode is the value that appears most often in a set of measurements. For the data in Table 1, this is 19.86 mL, because this value appears twice, but all the other values appear only once.

mode
the value that appears the most often in a dataset

Median

The **median** value is the value that appears in the middle of a sorted list of numbers, if there is an odd number of items. Therefore, there is an equal number of values above and below the median value. If there is an even number of measurements, then the median is the average value of the middle pair of values. For the data in Table 1 (19.86, 19.86, 19.92, 19.98, 20.04, 20.08), these are 19.92 and 19.98 mL, and the median value is their average, 19.95 mL.

median
the value that appears in the middle when the dataset is sorted from smallest to largest value

The median value can be very useful to report, particularly when there are extreme outliers in the data.

Standard deviation

The other parameter that describes a normal distribution is the standard deviation, which is a measure of how spread out the values are (Figure 3). Steeper bell curves have smaller standard deviations and a smaller spread of values. Flatter bell curves have a larger standard deviation and a larger spread of values.

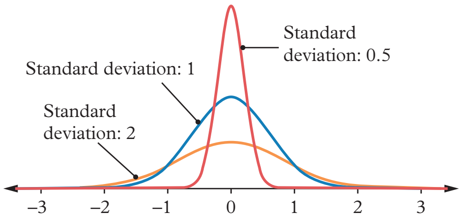


FIGURE 3 The effect of changing the standard deviation on the shape of normal curves

The experimental standard deviation s is defined in mathematical terms by the formula:

$$s = \sqrt{\frac{\Sigma(x - \bar{x})^2}{n - 1}}$$

where $\bar{x}$ is the mean, x is a measured value, n is the number of measurements and Σ (capital sigma) means to add all the values $(x_i - \bar{x})^2$ together.

Table 2 shows the results of these calculations on the experimental data given in Table 1.

TABLE 2 Steps for calculating the standard deviation of hydrochloric acid volumes

Trial number	Volume of aqueous hydrochloric acid solution (mL)	$(x_i - \bar{x})$ (mL)	$(x_i - \bar{x})^2$ (mL^2)
1	19.92	19.92 – 19.957 = –0.037	0.001344
2	20.04	20.04 – 19.957 = 0.083	0.006944
3	19.86	19.86 – 19.957 = –0.0967	0.009344
4	19.98	19.98 – 19.957 = 0.0233	0.000544
5	20.08	20.08 – 19.957 = 0.12337	0.015211
6	19.86	19.86 – 19.957 = –0.0967	0.009344

$$\begin{aligned} s &= \sqrt{\frac{0.001344 + 0.006944 + 0.009344 + 0.000544 + 0.015211 + 0.009344}{6 - 1}} \\ &= \sqrt{\frac{0.042733}{5}} \\ &= \sqrt{8.5466 \times 10^{-3}} \\ &= 0.09245 \text{ mL} \end{aligned}$$

This means that, on average, each data value deviates from the mean of 19.96 mL by 0.09 mL. The full working out has been shown here, but many calculators and spreadsheet programs also have statistical functions that will calculate these values more quickly and conveniently.

Standard deviation is a useful measurement to help you identify errors, outliers and evaluate the reliability of your results.

How do you calculate absolute uncertainty?

Using measures of central tendency helps you to be more certain of your data, but the reality is that you introduce another source of uncertainty through replication. When you report your result, you must therefore consider absolute or percentage uncertainty.

absolute uncertainty
the exact magnitude of difference between the mean and the range of measurements; an indicator of the precision of measurements

Absolute uncertainty ($\Delta\overline{x}$) quantifies how values deviate around a mean. It is the half-range of the measurements, meaning that it indicates the highest measured value and the lowest measured value. It is calculated using:

$$\Delta\overline{x} = \pm\frac{(x_{\text{max}} - x_{\text{min}})}{2}$$

where x_{max} is the largest value and x_{min} is the smallest value. It is expressed to the same number of decimal places as the value with the fewest significant figures (s.f.).

For single measurements, uncertainty is reported based on the uncertainty of the measurement instrument. What if this value is larger than the absolute uncertainty? Which value should you use?

The rule is, the uncertainty value that you report should be the largest one. This is because we don't want to underestimate the uncertainty of the result. This would make the result appear more precise and reliable than is justified or warranted.

Worked example 1.7A

Calculating the mean and absolute uncertainty

An acid–base titration was conducted using a burette with an uncertainty of ±0.02 mL. The titre volumes obtained were 5.80, 6.00 and 6.05 mL. **Calculate** the mean and the absolute uncertainty and express your answer correctly. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We are being asked to calculate the mean and absolute uncertainty. The question is worth 2 marks, so we must correctly apply the formulas to complete the calculations and express the answers correctly.

Think	Do
Step 2: Select the appropriate formulas and gather any data required.	$\bar{x} = \frac{\Sigma x}{n}$ $\Delta\bar{x} = \pm\frac{(x_{\max} - x_{\min})}{2}$ $x_{\max} = 6.05\,\text{mL};\ x_{\min} = 5.80\,\text{mL};\ n = 3$
Step 3: Substitute the known values into the formulas and solve for the mean.	$\bar{x} = \frac{5.80\,\text{mL} + 6.00\,\text{mL} + 6.05\,\text{mL}}{3}$ $= 5.95\,\text{mL}$
Step 4: Substitute the known values into the formulas and solve for the absolute uncertainty. Compare the absolute uncertainty to the uncertainty of the instrument. The larger uncertainty is the one to be reported in the final answer.	$\Delta\bar{x} = \pm\frac{6.05\,\text{mL} - 5.80\,\text{mL}}{2}$ $= \pm\ 0.125\,\text{mL}$ The absolute uncertainty of 0.125 mL is larger than the instrument uncertainty of 0.02 mL.
Step 5: Finalise your answer. Report it as the best estimate (mean), uncertainty and correct units. Make sure you use the correct number of significant figures in the mean and the same number of decimal places in the uncertainty.	The measurements are to 3 s.f. The mean is currently expressed also as 3 s.f., so we do not need to round it up or down. Absolute uncertainty must be presented to the same number of decimal places (d.p.), i.e. 2. Thus, 0.125 rounds up to 0.13. The final answer is: 5.95 ± 0.13 mL. (1 mark for correct mean; 1 mark for correct absolute uncertainty)

Your turn

The mass of a solid substance was measured using an electronic balance with an uncertainty of ±0.05 g. The recorded masses were 25.20, 25.20 and 25.15 g. **Calculate** the mean and the absolute uncertainty and express your answer correctly. (2 marks)

How do you calculate percentage uncertainty?

After data is collected, you may need to transform it in some way or apply a formula to it calculate other quantities. For example, if you gather mass, amount (in moles) or volume, you can calculate the number of particles, concentration or molar mass, and compare these calculated values with accepted (true) values.

If you add, subtract, multiply or divide the data, you can propagate uncertainty through your calculations. Often, this can involve different units and measurement instruments, so absolute uncertainty may no longer be useful. You will need to make adjustments to take into account the calculations you have performed, and the value you use may instead be percentage uncertainty.

Percentage uncertainty is calculated by dividing the absolute uncertainty by the observed measurement and multiplying the result by 100 to give a percentage:

$$\text{percentage uncertainty (\%)} = \frac{\text{absolute uncertainty } (\Delta\bar{x})}{\text{measurement } (x)} \times 100\%$$

$$= \frac{\Delta\bar{x}}{x} \times 100\%$$

percentage uncertainty
an indicator of uncertainty in which the range of values for a measurement result (the absolute uncertainty) is expressed as a percentage of the measurement

Worked example 1.7B

Calculating the percentage uncertainty

Calculate the percentage uncertainty of a 0.10 M solution of NaOH with a titre volume of 26.18 mL. The calibrated burette used in the titration had an absolute uncertainty of 0.02 mL. (1 mark)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We are being asked to calculate the percentage uncertainty. The question is worth 1 mark, so we must correctly apply the formula to complete the calculations.
Step 2: Select the appropriate formulas and gather any data required.	percentage uncertainty (%) = $\frac{\Delta \overline{x}}{x} \times 100\%$ $\Delta \overline{x} = \pm 0.02\,\text{mL}$, $x = 26.18\,\text{mL}$
Step 3: Substitute the known values into the formula and solve for the percentage uncertainty.	percentage uncertainty (%) = $\frac{0.02\,\text{mL}}{26.18\,\text{mL}} \times 100\%$ $= 0.07639\%$
Step 4: Finalise your answer.	±0.08% (1 mark)

Your turn

A calibrated burette used in titration has an absolute uncertainty of ±0.02 mL. It is used in an acid–base titration between sodium hydroxide and acetic acid. The titre volume was 13.25 mL. **Calculate** the percentage uncertainty. (1 mark)

How is uncertainty propagated in calculations?

When completing calculations involving two or more quantities, the uncertainties of each measurement must be combined. This is called propagation of uncertainty. There are some simple rules that can be used to calculate the final uncertainty:

1. If the measured values are added or subtracted, the absolute uncertainties must be added. For example:

$$5.0 \pm 0.2\,\text{g} - 2.3 \pm 0.2\,\text{g} = 2.7 \pm 0.4\,\text{g}$$

2. If the measured value is multiplied or divided, the percentage uncertainties must be added together. For example:

$$3\,\text{g} + 4\% \times 5.2\,\text{g} + 2\% = 15.6\,\text{g} + 6\%$$

3. If powers are applied to the measured value, the percentage uncertainties must be added together. For example:

$$(5.0\,\text{g} \pm 2\%)^3 = (5.0\,\text{g} \pm 2\%) \times (5.0\,\text{g} \pm 2\%) \times (5.0\,\text{g} \pm 2\%) = 125\,\text{g} \pm 6\%$$

Study tip

For addition and subtraction, add the **absolute** uncertainties. For multiplication, division and powers, add the **percentage** uncertainties.

Worked example 1.7C

Calculating absolute uncertainty involving subtraction or addition

During a titration, the following titres were recorded for a 0.10 M solution of HCl:

Initial titre = 6.05 ± 0.02 mL
Final titre = 23.35 ± 0.02 mL

Calculate the difference in volume and the absolute uncertainty and report it correctly. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We are being asked to calculate the difference in volume and absolute uncertainty. The question is worth 2 marks, so we must complete the calculations and express the answer correctly.
Step 2: Find the difference in volume.	difference in volume = 23.35 mL − 6.05 mL = 17.30 mL
Step 3: Determine how to propagate the uncertainties.	We are dealing with subtraction, so we need to add the absolute uncertainties.
Step 4: Solve for the final uncertainty by adding the absolute uncertainties.	0.02 mL + 0.02 mL = 0.04 mL
Step 5: Finalise your answer. Report it as the best estimate, uncertainty and correct units. Make sure you use the correct number of significant figures in the mean and the same number of decimal places in the uncertainty.	17.30 ± 0.04 mL (1 mark for correct volume; 1 mark for correct uncertainty)

Your turn

A chemistry student prepared three solutions using different pieces of glassware to measure the required quantities and reported their volumes:

Solution A: 25.00 ± 0.02 mL
Solution B: 36.1 ± 0.1 mL
Solution C: 48.2 ± 0.2 mL

Calculate the total volume of the three solutions and **determine** the absolute uncertainty in the total volume, reporting it correctly. (2 marks)

Worked example 1.7D

Calculating percentage uncertainty involving division

Calculate the concentration in g L^{-1} when 15.7 ± 0.1 g is fully dissolved in a flask of water to make 2.0 ± 0.1 L of solution. Report your answer correctly. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We are being asked to calculate the concentration and percentage uncertainty. The question is worth 2 marks, so we must complete the calculations and express the answer correctly.
Step 2: Find the concentration using $c = \frac{m}{V}$.	$c = \frac{15.7\,\text{g}}{2.0\,\text{L}}$ $= 7.85\,\text{g}\,\text{L}^{-1}$
Step 3: Determine how to propagate the uncertainties.	We are dealing with division, so we need to add the percentage uncertainties. percentage uncertainty (%) = $\frac{\Delta\overline{x}}{x} \times 100\%$ For the mass: $\overline{x} = 0.1\,\text{g}$, $x = 15.7\,\text{g}$ For the volume: $\overline{x} = 0.1\,\text{L}$, $x = 2.0\,\text{L}$

Think	Do
Step 4: Substitute the known values into the formula and solve for the percentage uncertainties.	For the mass: percentage uncertainty (%) $= \frac{0.1\,\text{g}}{15.7\,\text{g}} \times 100\%$ $= 0.6369\%$ For the volume: percentage uncertainty (%) $= \frac{0.1\,\text{L}}{2.0\,\text{L}} \times 100\%$ $= 5.0\%$
Step 5: Solve for the final uncertainty by adding the percentage uncertainties.	0.6369 + 5.0 = 5.6369% This can also be converted back into an absolute uncertainty, by multiplying the percentage by the calculated concentration. $5.6369\% \times 7.85\,\text{g L}^{-1} = 0.4425\,\text{g L}^{-1}$
Step 4: Finalise your answer. Report it as the best estimate, uncertainty and correct units. Make sure you use the correct number of significant figures in the mean and the same number of decimal places in the uncertainty.	$7.9 \pm 0.4\,\text{g L}^{-1}$ or $7.9\,\text{g L}^{-1} \pm 5.6\%$ (1 mark for correct concentration; 1 mark for correct uncertainty)

Your turn

Calculate the total concentration in grams per litre (g L^{-1}) when 28.4 ± 0.2 g of solute is fully dissolved in a flask of water to make 3.5 ± 0.1 L of solution. Report your answer correctly. (2 marks)

percentage error the percentage difference between the accepted (true or theoretical) value and the measured (experimental) value

Study tip

Absolute and percentage uncertainty are indicators of precision of measurements, whereas percentage error is an indicator of accuracy.

Study tip

Percentage error is reported to one significant figure.

How do you calculate percentage error?

So far, we have talked about uncertainties, which are a way of expressing the level of precision of measurements. To indicate the accuracy of experimental results, we use **percentage error**. This is the percentage difference between the measured experimental value and the known true (or theoretical) value:

$$\text{percentage error (\%)} = \left|\frac{\text{measured value} - \text{true value}}{\text{true value}}\right| \times \frac{100}{1}$$

The straight lines (|, modulus signs) in the equation indicate the “absolute value”, which means the sign (+ or –) of the answer is ignored. Percentage error is reported to one significant figure.

Worked example 1.7E

Calculating percentage error

In an experiment, the enthalpy of combustion for propanol was determined to be $-1{,}978\ \text{kJ mol}^{-1}$ but the theoretical enthalpy of combustion is $-2{,}021\,\text{kJ mol}^{-1}$. **Calculate** the percentage error for the enthalpy of combustion. (1 mark)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	“Calculate” means to determine or find a number or answer by using mathematical processes. We are being asked to calculate the percentage error. The question is worth 1 mark, so we must correctly apply the formula and complete the calculation.

Think	Do
Step 2: Select the appropriate formulas and gather any data required.	$\text{percentage error (\%)} = \left\lvert \dfrac{\text{measured value} - \text{true value}}{\text{true value}} \right\rvert \times 100\%$ measured value = $-1{,}978\,\text{kJ}\,\text{mol}^{-1}$ true value = $-2{,}021\,\text{kJ}\,\text{mol}^{-1}$
Step 3: Substitute the known values into the formulas and solve for the percentage error.	$\text{percentage error (\%)} = \left\lvert \dfrac{-1{,}978\,\text{kJ}\,\text{mol}^{-1} - (-2{,}021\,\text{kJ}\,\text{mol}^{-1})}{-2{,}021\,\text{kJ}\,\text{mol}^{-1}} \right\rvert \times 100\%$ $= \left\lvert \dfrac{43\,\text{kJ}\,\text{mol}^{-1}}{-2{,}021\,\text{kJ}\,\text{mol}^{-1}} \right\rvert \times 100\%$ $= 2.128\%$
Step 4: Finalise your answer. Percentage error is rounded to 1 s.f.	2% (1 mark)

Your turn

A student measures the density of an object to be $8.63\,\text{g}\,\text{mL}^{-1}$, but the accepted value is $8.96\,\text{g}\,\text{mL}^{-1}$. **Calculate** the student's percentage error. (1 mark)

Study tip

Generally, we allow a 5% threshold for percentage uncertainty and percentage error. If percentage uncertainty is 5% or lower, we consider the result to be precise. If percentage error is 5% or lower, we consider the result to be accurate.

How can you present your results?

After you have collected measurements and processed the data, they must be presented in a useful way. It is important to consider the best way to display the data. The information needs to be clear and easy to read, and relationships between variables should be straightforward to identify. Common types of data representation used in chemistry include summary tables and scatterplots.

Summary tables

Tables are often used to summarise and organise data. While a data table states what has been measured and presents the raw data, a summary table can bring together processed data. A summary table should have a heading, and column and row headings. Where quantities are being reported, appropriate units should appear in the headings.

Tables are best where there is a relatively small amount of data and the values are individually important, as shown in Table 3.

TABLE 3 Change in average reaction temperature with time

Time (min)	Average temperature (°C)
5	43.5
10	37.8
15	35.7
20	24.2

Scatterplots

Graphs are often more useful than summary tables when investigating trends in data. They are visual displays of how one variable changes either over time or in response to changes in another variable. x–y scatterplots are often used where there is a continuous trend in a measured value as one value is altered in a systematic way.

For example, the change in temperature of honey as it is heated over time can be shown in a scatterplot (Figure 4).

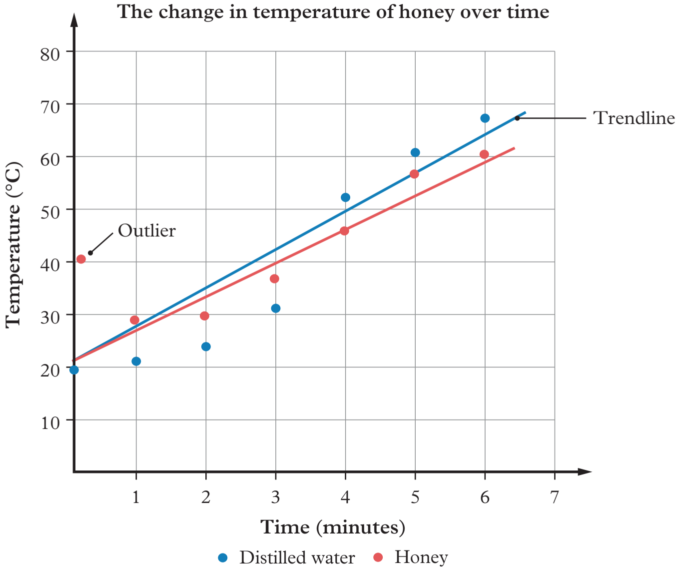


FIGURE 4 An *x*–*y* scatterplot showing how the temperature of a reaction (the dependent variable) changes with time (the independent variable)

Study tip

The trendline can allow you to predict values beyond and between the set of data points collected. This is called extrapolation and interpolation, respectfully. You will learn about this later.

All graphs should include:

- a graph title that succinctly describes what the graph is showing (typically includes the independent variable (IV) and dependent variable (DV))
- clearly labelled axes, including units of measurement
- equally spaced units of measurement along the axes (scaling)
- axes that start at zero (where possible)
- data plotted within the confines of each axis
- distinguishing symbols, colours or keys when more than one dataset is plotted on a single graph
- measurement uncertainty (where relevant) as error bars (see below)
- a trendline that fits between the error bars (see below).

By analysing the shape of your graphs, you can construct arguments about the relationship between variables.

How do you graph linear relationships?

trendline (line of best fit)
a line drawn on a graph joining as many points as possible and showing the general direction of the data; should be drawn with an approximately equal number of points above and below the line

gradient
the slope of a graph

Graphing the (x, y) pairs of values can visually reveal the relationship between the variables. Where there is a linear relationship, a **trendline** (or line of best fit) can be added to the graph. This is a line drawn through the middle of the plotted data so that the points are evenly spread on either side of the line. It does not connect all the data points on a graph. You can see two trendlines in Figure 4.

It is rare for the data to be perfectly linear, so drawing a trendline allows you to identify the proportionality relationship between the two variables. A straight trendline can be mathematically represented by a linear equation in the general form of:

$$y = mx + c$$

where x and y are the IV and DV, respectfully, m is the **gradient** or the slope of the line and c is the y-intercept or the point at which the line cuts the y-axis at $x = 0$.

Gradient

The slope of any straight line is defined as the change in y divided by the change in x:

$$\begin{aligned} m &= \frac{\text{change in } y}{\text{change in } x} \\ &= \frac{\Delta y}{\Delta x} \\ &= \frac{y_2 - y_1}{x_2 - x_1} \end{aligned}$$

Therefore, the slope of the trendline can be calculated by choosing two points on the line, (x_1, y_1) and (x_2, y_2). Let's consider the trendline in Figure 5. The two points are (0, 1) and (2, 4). We can calculate m:

$$\begin{aligned} m &= \frac{4 - 1}{2 - 0} \\ &= \frac{3}{2} \end{aligned}$$

Three important points to remember are:

- don't force the line to go through the origin; it should go through the middle of the data points, with as many points above it as below it
- use the x and y coordinates of points on the trendline to calculate the gradient
- use points as widely separated as possible to get the most accurate value for the gradient.

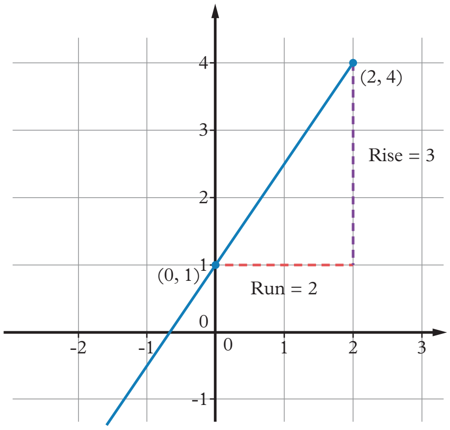


FIGURE 5 An example of linear data

The direction in which the gradient slopes tells you about the relationship between the variables. An incline in the positive direction of the x-axis means that the gradient is a positive value and this indicates that as the IV increases, the DV also increases. The opposite is also true: a decline in the positive direction of the x-axis means the gradient of the line has a negative value and this indicates that as the IV increases, the DV decreases.

This can also be described using **correlations**. Variables can be positively or negatively correlated. Positive correlation is when the value of one variable increases as the other variable increases (gradient slopes upwards). Negative correlation is when the value of one variable decreases, as the other variable increases (gradient slopes downwards). Figure 5 displays a positive correlation.

correlation
a link between a change in the independent variable and a change in the dependent variable; this does not mean that the changing independent variable caused the change in the dependent variable

y-intercept

The y-intercept is the point on the graph where the trendline intercepts or cuts the y-axis at $x = 0$. This data point can be found in two ways:

1. Extending the trendline and reading the y-intercept from the graph. Consider Figure 5 again. We have found that the gradient m is $\frac{3}{2}$. We can already tell that the y-intercept is +1, so $y = \frac{3}{2}x + 1$.
2. Calculating the y-intercept using the equation for the trendline and using algebra to find c. From Figure 5, we have the equation $y = \frac{3}{2}x + c$. To find c, we can select any point along the line. Let's use (2, 4). If we substitute these x and y coordinates into the equation for the trendline, we get $4 = \frac{3}{2}(2)+c4$ or $4 - 3 = c$. Therefore, $c = 1$.

Study tip

You may find it easier to remember the gradient as "rise over run", where "rise" refers to the y-axis and "run" refers to the x-axis.

How can you infer data by extrapolation and interpolation?

extrapolation the prediction of values beyond the range of data points by extending the trendline

interpolation the prediction of values between data points using a trendline

If the equation for a trendline is known, it is possible to determine unknown values. Extending and reading a graph beyond the last plotted point is called **extrapolation**. Inferring a reading between plotted points is called **interpolation**.

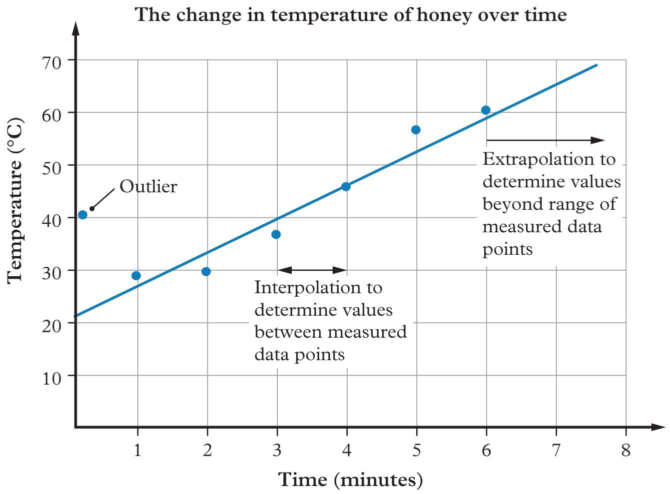


FIGURE 6 Extrapolation and interpolation of data to determine unknown values

In Figure 6, the data points are only at 0, 1, 2, 3, 4, 5 and 6 minutes. You can extrapolate the trendline past 6 minutes to 7 minutes and read off the temperature as 65°C. You can also interpolate the data to read off values between points. For example, at 1.5 minutes, the temperature is 30°C.

In QCE Chemistry, you will use standard curves to find unknown values. This involves interpolation. Worked example 1.7F shows you how to construct a standard curve (scatterplot with a trendline) for an atomic absorption spectroscopy experiment, and then use interpolation to find the concentration of an unknown sample.

Worked example 1.7F

Constructing and analysing linear scatterplots

A student wants to determine the concentration of a copper sulfate solution. They use atomic absorption spectroscopy to measure the concentration of various copper sulfate standard solutions, as well as their sample (Table 4).

TABLE 4 Data obtained from the experiment (AU = absorbance units)

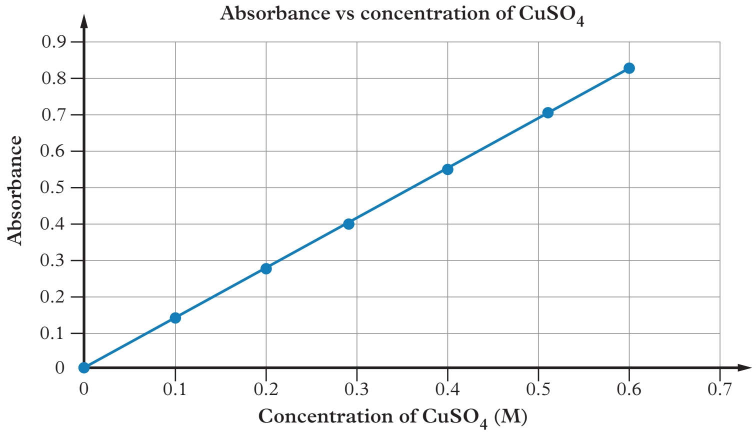
Concentration of copper sulfate (M)	Absorbance (AU)
0.0000	0.000
0.1007	0.157
0.2009	0.290
0.2902	0.400
0.3999	0.550
0.5094	0.705
0.5999	0.825
unknown	0.460

a **Sketch** a scatterplot for the copper sulfate standard solutions. (3 marks)

b **Calculate** the gradient, *m*, of the trendline. (1 mark)

c **Derive** the equation for the trendline. (2 marks)

d **Calculate** the concentration (in M) of the unknown solution of copper sulfate solution. (1 mark)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	“Sketch” means to represent using a diagram or graph. “Calculate” means to determine or find a number or answer by using mathematical processes. “Derive” means manipulate a mathematical relationship to give a new equation. These questions are worth a variety of marks. We must graph the data, find the equation for the trendline and use it to find the unknown value.
Step 2: For part **a,** sketch the graph by drawing and labelling the axes with the IV (concentration) on the *x*-axis and DV (absorbance) on the *y*-axis – this includes units! Plot each data point and draw a trendline.	**a**  (1 mark for correct axes and labels; 1 mark for correct data points; 1 mark for trendline)
Step 3: For part **b,** find the gradient by selecting the appropriate equation. Determine the change in *y* and change in *x* for two widely separated points on the line.	**b** $m = \frac{y_2 - y_1}{x_2 - x_1}$ using the two points (0.4, 0.55) and (0.2, 0.28). $m = \frac{0.55 - 0.28}{0.4\,M - 0.2\,M}$ (1 mark) $= 1.35\,M^{-1}$
Step 4: For part **c,** read the intercept off the *y*-axis and include the units. Alternatively, we can calculate this more accurately using the *m* value and one (*x*, *y*) datapoint.	**c** From the graph, $c = 0$. From calculating, using $m = 1.35$ and (0.4, 0.55). $0.55 = 1.35(0.4) + c$ (1 mark) $c = 0.01$ Putting it altogether: $y = 1.35x + 0.01$ (1 mark)
Step 5: For part **d,** use the equation for the trendline and substitute in the value for absorbance (*y*) to solve for concentration (*x*).	**d** $0.460 = 1.35x + 0.01$ $0.450 = 1.35x$ $x = 0.333\,M$ (1 mark)

Your turn

A student conducted an experiment to investigate the density of copper by measuring the masses of samples of known volume. The results were tabulated (Table 5). A linear graph can then be used to determine the volume of an irregularly shaped copper ornament with a mass of 113.25 g.

TABLE 5 Results from experiment measuring mass and volume of Cu

Volume (cm^3)	Mass (g)
2	17.83
3	26.84
4	35.64
8	71.66
16	143.11
unknown	113.25

a **Sketch** a scatterplot for the mass of Cu as a function of volume, including a linear trendline. (3 marks)

b **Calculate** the gradient of the trendline. (1 mark)

c **Derive** the equation for the trendline. (2 marks)

d **Calculate** the volume of 113.25 g of Cu metal. (1 mark)

How do you graph non-linear relationships?

linearising the process of transforming non-linear data by applying a mathematical function to one of the variables so that the relationship between the variables becomes closer to a straight line

Not all relationships between variables are linear. Initially, these relationships may appear more complex to analyse. However, sometimes a linear relationship can be found by applying a mathematical operation to one or both variables. This is called **linearising** the data.

One example of an experiment in which linearising is necessary is when the rate of reaction is measured in response to a change in concentration of a reactant. This is an exponential relationship given by the equation $y = e^x$.

When x is plotted against y, the graph is non-linear (Figure 7A). To linearise the relationship, the function must be undone. For an exponential relationship, we take the natural logarithm (ln or $\log_e$) of both sides to "undo" the exponential: $\ln y = x$. If the relationship is indeed exponential, plotting x against $\ln y$ should give a linear relationship (Figure 7B).

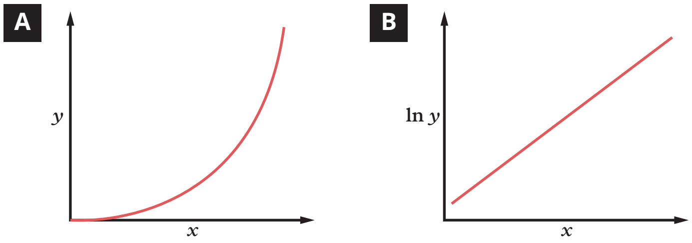
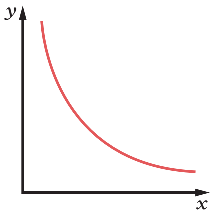
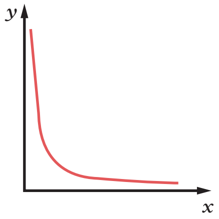
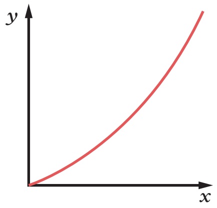
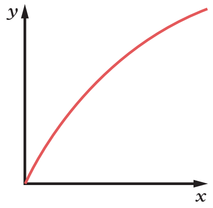
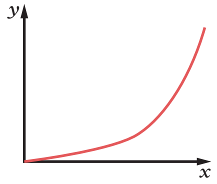
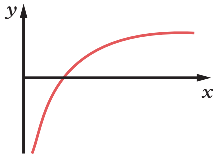


FIGURE 7 (A) The x versus y graph of the data does not give a straight line. (B) The straight line indicates that this is an exponential relationship.

The trendline for the linearised graph can be determined by using the methods described earlier. This can enable you to extrapolate or interpolate the data to predict values not captured by direct measurement.

The same strategy can be applied to other non-linear relationships. Table 6 summarises the functions that must be applied to different relationships.

TABLE 6 Mathematical functions to apply to linearise different non-linear relationships

Type of relationship	Relationship	What to graph
Inverse 	$y = \frac{1}{x}$	y vs $\frac{1}{x}$
Inverse-square 	$y = \frac{1}{x^2}$	y vs $\frac{1}{x^2}$
Square or parabolic 	$y = x^2$	y vs x^2
Square root 	$y = \sqrt{x}$	y vs $\sqrt{x}$
Exponential 	$y = e^x$	$\ln y$ vs x
Logarithmic 	$y = 10^x$	$\log_{10} y$ vs x

How are error bars used to represent uncertainty?

The measurement uncertainty associated with a particular mean value can be easily displayed on a graph as error bars. These are vertical or horizontal lines that are added to each data point that represent the absolute uncertainty at that point. For example, Figure 8 shows a student experiment that investigates the effect of increasing temperature on the solubility of a salt (in grams of salt per 100 g of water). The vertical error bars reflect a small degree of uncertainty for the dependent variable measured which in this case, is the solubility of the salt.

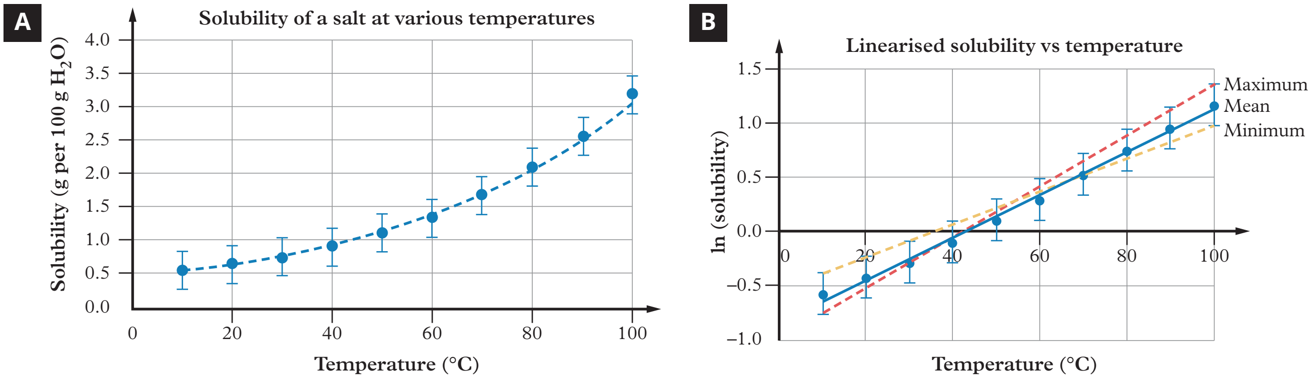


FIGURE 8 (A) Vertical error bars show the zone of uncertainty for the solubilities of salt in water (g per 100 g H_2O). (B) Maximum and minimum trendlines can be added to the graph to show the uncertainty in the gradient for the linearised curve.

Figure 8A shows vertical error bars for the measurement of solubility of a salt (*y*-axis). Figure 8B shows the linearised solubility over time. The gradient of the trendline (or mean trendline) is 0.0195. Two other trendlines have been added.

maximum trendline
a line of best fit of maximum gradient within the bounds of the error bars

minimum trendline
a line of best fit of minimum gradient within the bounds of the error bars

- The **maximum trendline** has the highest possible gradient. It connects the bottom of the error bar of the first data point (10, –0.6500) with the top of the error bar for the last data point (100, 1.4125) but must not go beyond any of the error bars in between.
- The **minimum trendline** has the smallest possible gradient. It connects the top of the error bar of first data point (10, –0.3500) with the bottom of the error bar for the last data point (100, 0.9625) but must not go beyond any of the error bars in between.

To calculate the maximum and minimum gradients, it is good practice to use points spaced as wide apart as possible. Ideally, try to use the full line between $x = 10°\text{C}$ and $x = 100°\text{C}$.

- The maximum trendline (red) gradient is: $\frac{1.4125 - (-0.6500)}{100 - 10} = 0.023$.
- The minimum trendline (yellow) gradient is: $\frac{0.9625 - 0.3500}{100 - 10} = 0.015$.

The uncertainty in the gradient is calculated using the following formula:

$$\Delta\overline{x} = \pm\frac{(x_{\text{max}} - x_{\text{min}})}{2}$$

$$= \pm\frac{0.023 - 0.015}{2}$$

$$= \pm 0.0042\,\text{g}\,\text{mL}^{-1}\,°\text{C}^{-1}$$

Thus, the gradient can be stated using absolute uncertainty as $m = 0.0195 \pm 0.0042$.

Worked example 1.7G

Analysing minimum and maximum trendlines

Calculate the uncertainty of the slope of the trendline in Figure 9 using the maximum and minimum best fit lines and express the gradient correctly. (2 marks)

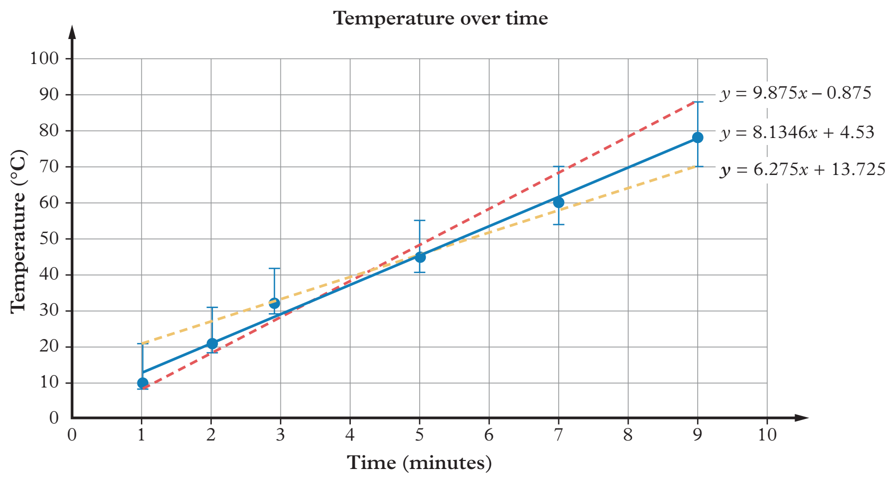


FIGURE 9 The change in temperature over time

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We are being asked to calculate the uncertainty of the gradient. The question is worth 2 marks, so we must correctly apply the formulas to complete the calculations and express the answer correctly.
Step 2: Select the appropriate formulas and gather any data required.	$\Delta\bar{x} = \pm\frac{(x_{max} - x_{min})}{2}$ x_{max} is the maximum trendline gradient = 9.875 x_{min} is the minimum trendline gradient = 6.275
Step 3: Substitute the known values into the formula and solve for the uncertainty of the gradients.	$\Delta\bar{x} = \pm\frac{9.875°\text{C min}^{-1} - 6.275°\text{C min}^{-1}}{2}$ $= \pm 1.8°\text{C min}^{-1}$ (1 mark)
Step 4: Finalise your answer. Report it as the best estimate, uncertainty and the correct units. Make sure you use the correct number of significant figures in the mean and the same number of decimal places in the uncertainty.	8.135 ± 1.800°C min^{-1} (1 mark)

Your turn

Given the equations of the mean, maximum, and minimum trendlines below, **calculate** the uncertainty of the gradient and express the gradient correctly. (2 marks)

Mean trendline: $y = 1.98x + 47.9$

Maximum trendline: $y = 2.35x + 53.2$

Minimum trendline: $y = 1.18x + 51.6$

How do you interpret graphs?

Scatterplots allow scientists to describe the relationship between the IV and DV. The description of the graph should include the:

- IV and DV
- type of correlation shown by the graph
- the shape of the graph (type of relationship, e.g. linear, exponential).

When interpreting the data shown on a graph, it is important to remember that correlation does not imply **causation**; you may not be able to make the claim that an IV *is the result of* a change in the DV. Instead, you can describe them as being correlated – a change in the IV *is related to* a change in the DV but does not necessarily cause it to change.

causation
when a change in a single variable causes a change in a second variable

Check your learning 1.7

Check your learning 1.7: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Define** the following terms: absolute uncertainty, percentage uncertainty, percentage error. (3 marks)

2 The titres of an acid–base titration were measured in triplicate and found to be: 24.3 mL, 24.7 mL, 23.8 mL. **Calculate** the
  a average titre volume. (1 mark)
  b absolute uncertainty of the mean titre value. (1 mark)
  c percentage uncertainty of the titre value. (1 mark)

3 A student obtained a value of 3.74 mL s^{-1} for the rate of hydrogen production in a metal–acid displacement reaction, whereas the accepted value for the same reaction is 3.85 mL s^{-1}. **Calculate** the percentage error. (1 mark)

4 **Explain** what it means to "linearise" a relationship. (2 marks)

Analytical processes

5 **Determine** the mean, mode and median of the following dataset. (3 marks)
12.5, 12.7, 13.1, 13.4, 13.4, 13.8, 13.9, 14.8 mg

6 **Contrast** positive and negative correlation. **Sketch** two graphs to support your answer. (3 marks)

7 **Contrast** correlation and causation. (1 mark)

8 A student combines two liquid reactants they have measured in a measuring cylinder. Reactant A has a volume of 15.3 ± 0.5 mL and reactant B has a volume of 18.5 ± 0.5 mL.
  a **Determine** the combined volume of the reactants. (1 mark)
  b **Calculate** the absolute uncertainty of the combined volume of reactants. (1 mark)

9 A student wants to determine the volume of a rectangular container. They use a ruler with an absolute uncertainty of ±0.2 cm to obtain the following measurements: length 4.5 cm, width 2.3 cm, height 1.0 cm.
  a **Analyse** the information to **determine** the percentage uncertainty of each measurement. (3 marks)
  b To calculate the volume, the student multiplies the length, width and height of the container. **Determine** the volume. (1 mark)
  c **Determine** the percentage uncertainty of the volume of the container. (1 mark)
  d If the accepted true volume of the container is 10.7 cm^3, **determine** the percentage error of the experiment. (1 mark)

10 A chemistry class sets up an apparatus to measure how changes in temperature affect a sample of air trapped in a long thin glass tube. The air is trapped at the upper end by a droplet of oil that can move up or down as temperature changes. The assembly is immersed in hot water, allowing the air to reach the same temperature as the water. The temperature and the length of

the sample of air is measured and recorded. Length is proportional to volume. The hot water is allowed to cool gradually, and further measurements are made at a number of temperatures as it cools.

Temperature (°C)	70	65	60	55	50	45	40	35	30
Length (cm)	35.3	34.7	34.1	33.8	33.4	32.5	32.1	31.5	31.1

a **Construct** a graph of the results on Excel. Draw a linear trendline, displaying the equation, R^2 and appropriate error bars. (3 marks)

b **Determine** the length of the column of air that would be expected if the assembly could be cooled to –100°C, using the equation for the trendline in part **a**. (1 mark)

11 A student experiment investigated how the pressure of air in a syringe sealed at one end changed as the volume of the syringe was decreased by pushing in the plunger. Three trials were conducted for each volume. The results are shown in the table.

Volume of air (mL)	Pressure (kPa)		
	Trial 1	Trial 2	Trial 3
60	101	101	101
55	109	111	110
50	121	118	121
45	133	130	133
40	147	143	148
35	167	160	168
30	191	186	193

a **Calculate** the mean pressures for each volume value. (7 marks)

b **Sketch** a scatterplot for the average data using Excel. (2 marks)

c **Compare** the shape of the scatterplot in part **b** to the shapes of various non-linear functions shown in the table. **Determine** which type of relationship best matches the shape of the scatterplot, and what variable should be graphed to linearise the data. (2 marks)

d **Calculate** $\frac{1}{V}$ for each volume in the table. (7 marks)

e Sketch a scatterplot of P as a function of $\frac{1}{V}$ using Excel, including the trendline, equation for the trendline, and R^2. Set the intercept at (0, 0). (4 marks)

Knowledge utilisation

12 A decomposition reaction of reagent X was carried out and the concentration of reagent over time was monitored and recorded in the table.

Time (s)	Concentration of reagent X (M)
4.00×10^2	3.30×10^{-3}
1.00×10^3	2.50×10^{-3}
2.00×10^3	2.00×10^{-3}
3.00×10^3	1.50×10^{-3}
5.00×10^3	5.00×10^{-4}

a **Construct** a suitable scatterplot for the results and **determine** the equation of the trendline that best represents the relationship between the decomposition of X over time. (5 marks)

b **Predict** the initial concentration of reagent X (time = 0 s) and the concentration at 4.0×10^3 s. Include units. (1 mark)

Lesson 1.8
Evaluating evidence

Key ideas

→ Evidence is evaluated to determine its validity and reliability.
→ Goodness of fit (R^2) provides information about the precision of the data.
→ Random and systematic errors can be identified by assessing the trendline of a graph.
→ Not all secondary sources are reliable; they must be evaluated before use.

Learning intentions and success criteria

Science inquiry skills

This lesson provides support for the following science inquiry skills:

- identify and implement strategies to manage risks, ethics and environmental impact, e.g.
    - acknowledgement of sources and referencing
- interpret graphs in terms of the relationship between dependent and independent variables; draw and interpret best-fit lines or curves through data points, including evaluating when it can and cannot be considered as a linear function
- discriminate between precision and accuracy
    - identify that all measurements have limits to the precision and accuracy that must be considered when evaluating experimental results
    - identify that quantitative data obtained from measurements is associated with random error/measurement uncertainties
- use data and reasoning to discuss and evaluate the validity and reliability of evidence, e.g.
    - discuss ways in which measurement error, instrumental uncertainty, the nature of the methodology or other factors influence uncertainty and limitations in the data
    - evaluate information sources and compare ideas, information and opinions presented within and between texts, considering aspects such as bias, appropriateness and reasonableness
    - compare findings to theoretical models or expected values
    - discriminate between validity and reliability
- appreciate the role of peer review in scientific research.

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Lesson 1.9

Communicating scientifically

Key ideas

→ Different communication conventions are used depending on the target audience.

→ Evidence-based arguments bring together scientific ideas and primary and/or secondary data obtained from scientific investigation.

→ Sources can be acknowledged using in-text referencing and a bibliography.

Science inquiry skills

Learning intentions and success criteria

This lesson provides support for the following science inquiry skills:

- select, synthesise and use evidence to construct scientific arguments and draw conclusions
- communicate to specific audiences and for specific purposes using appropriate language, nomenclature, genres and modes
- acknowledge sources of information and use standard scientific referencing conventions

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Lesson 1.10

Preparing for your data test

Key ideas

→ The data test is an assessment task where you respond to items using qualitative data and/or quantitative data derived from practicals, activities or case studies.

→ In your data test, you will apply your understanding, analyse data and interpret evidence.

Assessment objectives

Learning intentions and success criteria

This lesson provides support for achieving the assessment outcomes for the data test:

Objective 2. Apply understanding of chemical equilibrium systems or oxidation and reduction to given algebraic, visual or graphical representations of scientific relationships and data to determine unknown scientific quantities or features.

Objective 3. Analyse data about chemical equilibrium systems or oxidation and reduction to identify trends, patterns, relationships, limitations or uncertainty in datasets.

Objective 4. Interpret evidence about chemical equilibrium systems or oxidation and reduction to draw conclusions based on analysis of datasets.

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Worked examples

This lesson is supported by the following Worked example:

- **Worked example 1.10A** Responding to the data test

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Lesson 1.11

Conducting your student experiment

Key ideas

→ The student experiment is an assessment task where you modify (i.e. refine, extend or redirect) an experiment to address your own related hypothesis or question.

→ You will research and plan your experiment, analyse, interpret and evaluate your evidence, and communicate your findings.

Learning intentions and success criteria

Assessment objectives

This lesson provides support for achieving the assessment outcomes for the student experiment:

Objective 1. Describe ideas and experimental findings about chemical equilibrium systems or oxidation and reduction.

Objective 2. Apply understanding of chemical equilibrium systems or oxidation and reduction to modify experimental methodologies and process data.

Objective 3. Analyse experimental data about chemical equilibrium systems or oxidation and reduction.

Objective 4. Interpret experimental evidence about chemical equilibrium systems or oxidation and reduction.

Objective 5. Evaluate experimental processes and conclusions about chemical equilibrium systems or oxidation and reduction.

Objective 6. Investigate phenomena associated with chemical equilibrium systems or oxidation and reduction through an experiment.

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Lesson 1.12

Conducting your research investigation

Key ideas

→ The research investigation is an assessment task where you gather evidence related to a research question to evaluate a claim about an issue in chemistry.

Assessment objectives

Learning intentions and success criteria

This lesson provides support for achieving the assessment outcomes for the research investigation:

Objective 1. Describe ideas and findings about the properties and structure of organic materials or chemical synthesis and design.

Objective 2. Apply understanding of the properties and structure of organic materials or chemical synthesis and design to develop research questions.

Objective 3. Analyse research data about the properties and structure of organic materials or chemical synthesis and design.

Objective 4. Interpret research evidence about the properties and structure of organic materials or chemical synthesis and design.

Objective 5. Evaluate research processes, claims and conclusions about the properties and structure of organic materials or chemical synthesis and design.

Objective 6. Investigate phenomena associated with the properties and structure of organic materials or chemical synthesis and design through research.

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Lesson 1.13

Preparing for your exams

Key ideas

→ Your external exam requires you to demonstrate your understanding of the QCE Chemistry course by completing multiple-choice and short-response questions.

→ Exam questions are typically written using cognitive verbs, which tell you what information you need to provide in your answer to the question.

Learning intentions and success criteria

Assessment objectives

This lesson provides support for achieving the assessment outcomes for the examination:

Objective 1. Describe ideas and findings about chemical equilibrium systems, oxidation and reduction, properties and structure of organic materials, and chemical synthesis and design.

Objective 2. Apply understanding of chemical equilibrium systems, oxidation and reduction, properties and structure of organic materials, and chemical synthesis and design.

Objective 3. Analyse data about chemical equilibrium systems, oxidation and reduction, properties and structure of organic materials, and chemical synthesis and design to identify trends, patterns, relationships, limitations or uncertainty.

Objective 4. Interpret evidence about chemical equilibrium systems, oxidation and reduction, properties and structure of organic materials, and chemical synthesis and design to draw conclusions based on analysis.

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MODULE 1

Lesson 1.14

Review: Chemistry toolkit

Summary

1.1
- In QCE Chemistry, you will gain a variety of science understanding and inquiry skills that will help you succeed in assessments, as a scientific professional, and as a science citizen.

1.2
- First Nations peoples have longstanding scientific knowledge.
- First Nations peoples have developed knowledge about the world by observing using all the senses, predicting and hypothesising, testing (trial and error), and making generalisations within specific contexts such as the use of food, natural materials, navigation and sustainability of the environment.
- Correctly acknowledging cultural and/or language groups, avoiding Eurocentrism and critically evaluating sources of information can help you to respectfully engage with First Nations perspectives in QCE Chemistry.

1.3
- The scientific method is a circular process that involves making observations, formulating a hypothesis that will often lead to performing experiments or simulations, developing models or theorems, retesting and trailing.
- Research questions define the scope of an investigation. They can be used to develop hypotheses that predict the outcome of the investigation.

1.4
- A method outlines the steps followed in an experiment and lists all of the materials and equipment used.
- Valid and reliable measurements can be obtained by carefully designing your investigation to collect sufficient data and minimise errors.
- All measurements include errors or uncertainties, either systematic or random. It is important to consider these and implement strategies to minimise their effects when you plan your experiments.

1.5
- Good laboratory practices and laboratory safety allows you to identify risks and take measures to control them so that you and those sharing the laboratory space with you stay safe during scientific investigations.
- Conducting experiments ethically involves considering the impacts of your investigation beyond the laboratory.

1.6
- Single experimental measurements are reported using best estimates, indicators of measurement uncertainty and units.
- Scientific notation is used to easily express extremely large or extremely small values.
- Significant figures are digits in a number that are known with certainty plus the first digit that is uncertain.
- All measurements, information and observations should be recorded in your logbook.

1.7
- Data is processed and analysed to identify trends, patterns, relationships, limitations and uncertainty.
- Absolute and percentage uncertainty give an idea of the precision of measurements.
- Percentage error gives an idea of the accuracy of measurements.
- Data can be summarised in a variety of ways, such as in a table, a scatterplot or a scientific diagram.

1.8
- Evidence is evaluated to determine its validity and reliability.
- Goodness of fit (R^2) provides information about the precision of the data.
- Random and systematic errors can be identified by assessing the trendline of a graph.
- Not all secondary sources are reliable; they must be evaluated before use.

1.9
- Different communication conventions are used depending on the target audience.
- Evidence-based arguments bring together scientific ideas and primary and/or secondary data obtained from scientific investigation.
- Sources can be acknowledged using in-text referencing and a bibliography.

1.10
- The data test is an assessment task where you respond to items using qualitative data and/or quantitative data derived from practicals, activities or case studies.
- In your data test, you will apply your understanding, analyse data and interpret evidence.

1.11
- Your student experiment requires you to modify an experiment you have conducted in Units 3 and 4 to address your own related hypothesis or question.
- You will research and plan your experiment, analyse, interpret and evaluate your evidence and communicate your findings.

1.12
- The research investigation is an assessment task where you gather evidence related to a research question to evaluate a claim about an issue in chemistry.

1.13
- Your external exam requires you to demonstrate your understanding of the QCE Chemistry course by completing multiple-choice and short-response questions.
- Exam questions are typically written using cognitive verbs, which tell you what information you need to provide in your answer to the question.

Review questions 1.14A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

1 How many significant figures are in 0.0034 g?

A 4
B 2
C 5
D 3

2 How close a measurement is to its true value is called

A validity.
B accuracy.
C precision.
D reliability.

3 Two students experimentally determined the concentration of a copper(II) sulfate solution. They performed three trials. Their results are shown in the table.

Student 1	Student 2
0.893	0.884
0.897	0.882
0.889	0.883

The true value of the copper(II) sulfate solution was 0.893 M. Which student(s) produced results showing a systematic error?

A Student 1
B Student 2
C Both students
D Neither student

4 Consider the research question: “How does concentration of acid affect the rate of hydrogen gas production?” The independent variable is

A concentration of acid.
B rate of gas production.
C volume of gas produced.
D time taken to produce gas.

5 A student adds 4.92 g of sodium chloride to 7.587 g of copper metal. What is the final total mass of the two substances correct to 2 s.f.?

A 13 g
B 12.5 g
C 12.51 g
D 12.50 g

6 A piece of metallic magnesium with a mass of 6.431 g was found to have a volume of 3.70 cm^3. A student carried out the following calculation to determine the density: density = $\frac{6.431\,\text{g}}{3.70\,\text{cm}^3}$. What is the best estimate the student could report for the density of magnesium?

- **A** 1.7 g cm^{-3}
- **B** 1.74 g cm^{-3}
- **C** 1.738 g cm^{-3}
- **D** 1.7381 g cm^{-3}

7 The document that a seller of chemicals in Australia must supply with a chemical is called a

- **A** risk assessment.
- **B** safety data sheet.
- **C** certificate of analysis.
- **D** fitness for use warranty.

8 Which are likely to be reduced when an experiment is repeated several times?

- **A** Random errors only
- **B** Systematic errors only
- **C** Both random and systematic errors
- **D** Neither random nor systematic errors

9 Which term is defined as "a value closest to the true value, usually found by taking repeated measurements and averaging"?

- **A** Average
- **B** Uncertainty
- **C** Best estimate
- **D** Accepted value

10 Students are using a poorly calibrated electronic balance to measure the mass of a watch glass. They repeat the measurement three times to be sure of the answer. Their measurements could be described as having

- **A** low accuracy and low precision.
- **B** low accuracy and high precision.
- **C** high accuracy and low precision.
- **D** high accuracy and high precision.

11 How close a measurement is to other replicates in the same experiment is referred to as

- **A** validity.
- **B** accuracy.
- **C** precision.
- **D** relevance.

12 Which of the following expresses the answer to the calculation using the correct number of significant figures?

$$\frac{1.47 \times 10^{-5}}{6.538 \times 10^{-3}}$$

- **A** 2.3 × 10^{-3}
- **B** 2.25 × 10^{-3}
- **C** 2.225 × 10^{-3}
- **D** 2.2248 × 10^{-3}

13 Which of the following expresses the answer to the calculation using the correct number of significant figures?
$(0.335 \pm 0.001) + (0.279 \pm 0.002)$

- **A** 0.614
- **B** 0.614 ± 0.003
- **C** 0.614 ± 0.001
- **D** 0.614 ± 0.002

14 Convert 237.8 metres to millimetres.

- **A** 200,000 mm or 2 × 10^5 mm
- **B** 240,000 mm or 2.4 × 10^5 mm
- **C** 238,000 mm or 2.38 × 10^5 mm
- **D** 237,800 mm or 2.378 × 10^5 mm

Review questions 1.14B Short response

Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

15 **Explain** the difference between significant figures and scientific notation. (2 marks)

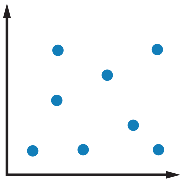
16 **Explain** how a "systematic error" differs from a "random error". (2 marks)

17 **Explain** what is meant by "propagation of errors" when performing a calculation. (1 mark)

18 **Explain** the reasons for making repeated measurements in an experiment. (2 marks)

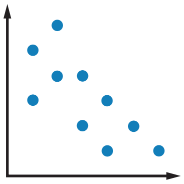
19 **Describe** the correlation (if any) in the following graphs.

a



(1 mark)

b



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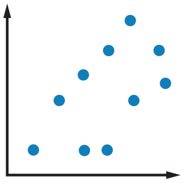
c



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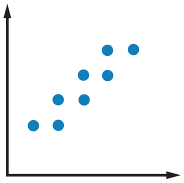
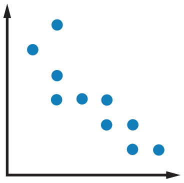
d



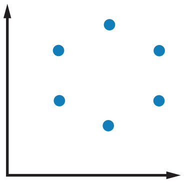
(1 mark)

e



(1 mark)

f



(1 mark)

20 **Calculate** the following to the correct number of significant figures.

- **a** 12.39 + 1.4 (1 mark)
- **b** 0.4329 ÷ 0.031 (1 mark)
- **c** 0.043 – 0.03 (1 mark)
- **d** 340 × 0.3402 (1 mark)

21 Four students weigh a standard 10 g mass on the same balance. All four students achieve a measurement of 8.9 g for the mass of the standard. **Describe** the accuracy and precision of the measurement. (2 marks)

22 A chemist decides to increase the number of replicates in their experiment. **Identify** the type of error they are trying to reduce. **Explain** your answer. (2 marks)

23 In an acid–metal reaction, 46.9 ± 0.2 cm^3 of hydrogen gas was produced in 20 ± 1 seconds. **Calculate** the rate of reaction in $cm^3\ s^{-1}$ and express your answer with an uncertainty correct to the appropriate number of significant figures. (3 marks)

Analytical processes

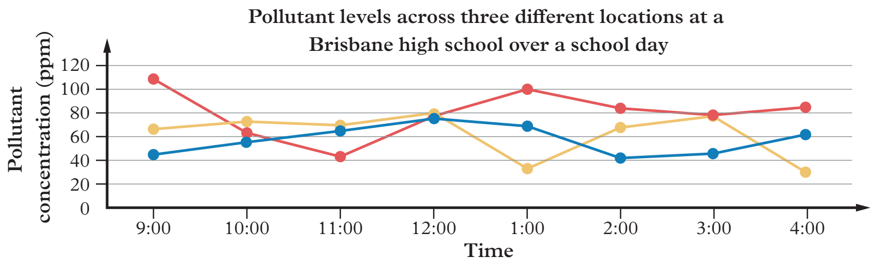
24 **Determine** the diameter of the bauble shown. **Calculate** the absolute uncertainty of your measurement. Provide reasoning to support the measurement. Provide reasoning to support the uncertainty you have shown. (3 marks)

25 A scientist used an electronic balance that consistently measured mass as 0.05 g above the true value. **Identify** an error that would result from using this electronic balance. **Consider** how the scientist could minimise this error in the future. (2 marks)

Knowledge utilisation

26 The accepted boiling point of water is 100°C. The following boiling point values were measured by a student during an experiment under standard laboratory conditions:
89°C, 90°C, 91°C, 88°C, 91°C, 95°C, 97°C, 93°C, 91°C, 90°C.
Comment on the accuracy and precision of the data.

27 As part of a Year 12 science project, the concentration of air pollutants at different locations around a school located in midtown Brisbane was investigated. Air quality sensors were positioned at varying locations and pollutant levels were recorded over a 4-hour period during a weekday. The graph of hourly pollutant levels is shown.



Library	45	56	64	76	69	43	47	62
Playground	108	65	45	79	100	85	79	84
Classroom	67	73	69	79	34	68	78	32

- **a** **Determine** the time during the school day when the concentration of pollutants is highest. (1 mark)
- **b** Briefly **describe** the trend in pollution over the course of a school day and the relationship between pollution and location. (2 marks)
- **c** Provide a hypothesis explaining the trend in location and pollution over the course of the day. (3 marks)
- **d** **Propose** a possible experiment that can test your hypothesis. (4 marks)

28 The density of an aluminium block was experimentally determined as 2.53 g cm^{-3}. The true density is 2.70 g cm^{-3}. **Calculate** the percentage error and **evaluate** the validity of the experimental results obtained if 5% is the cut-off. (3 marks)

29 As part of a student investigation, 12 copper coins were weighed. The recorded masses are displayed in the table.

Mass of copper coin (g)		
3.113	3.109	3.049
2.456	2.786	3.053
3.101	3.121	3.024
2.789	3.063	3.098

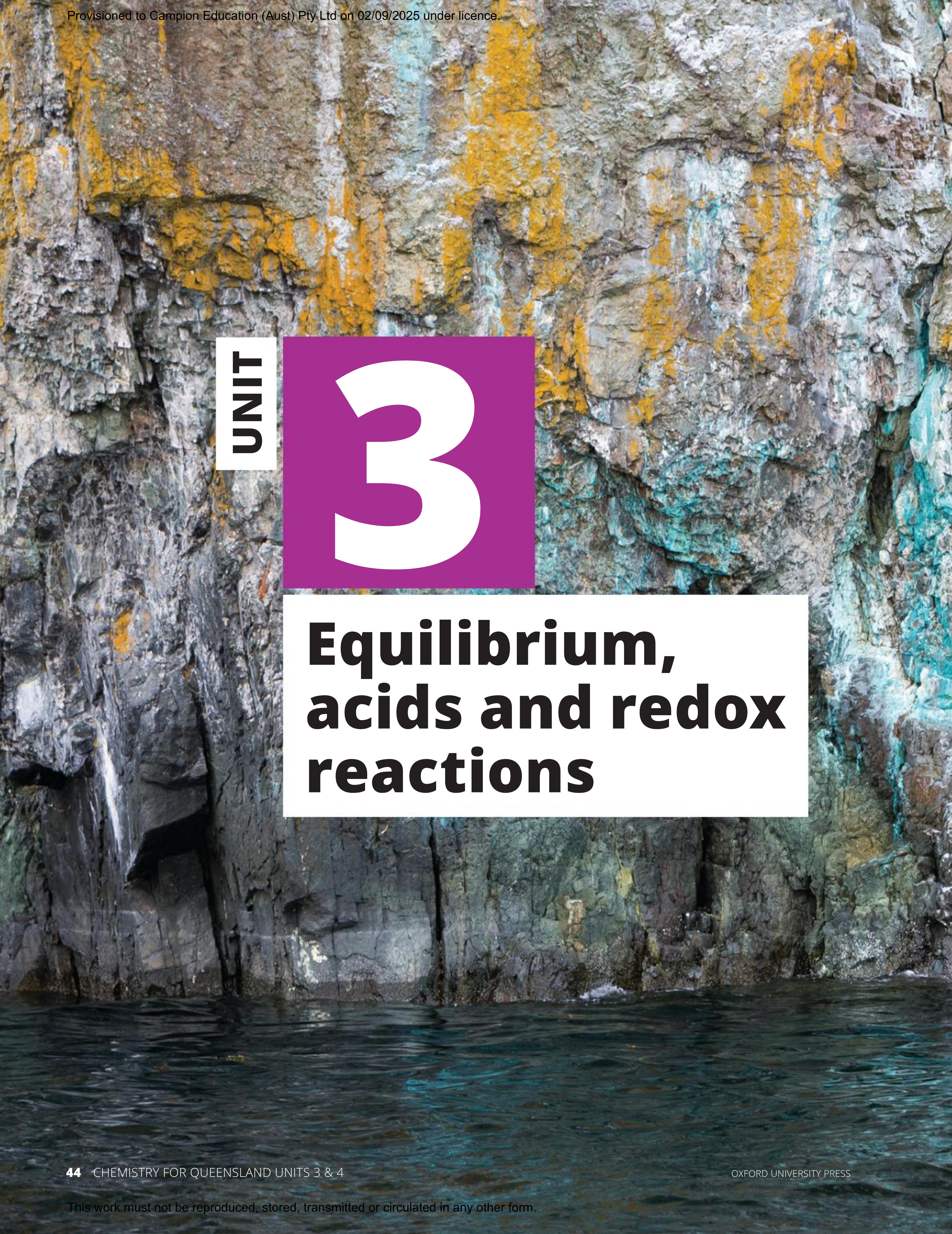
After further investigation into the dates on each of the coins, it was revealed that:

- two of the lightest coins were minted between 1950 and 1966
- two of the heaviest coins were minted between 1970 and 1980.

- **a** **Propose** a possible explanation for why coins appear to be lighter with time. (1 mark)
- **b** The student calculated the average mass of the 12 coins and expressed her answer as: 2.9802 g ± 0.3325 g. **Explain** why this is incorrect, then rewrite her answer to fix the error. (2 marks)

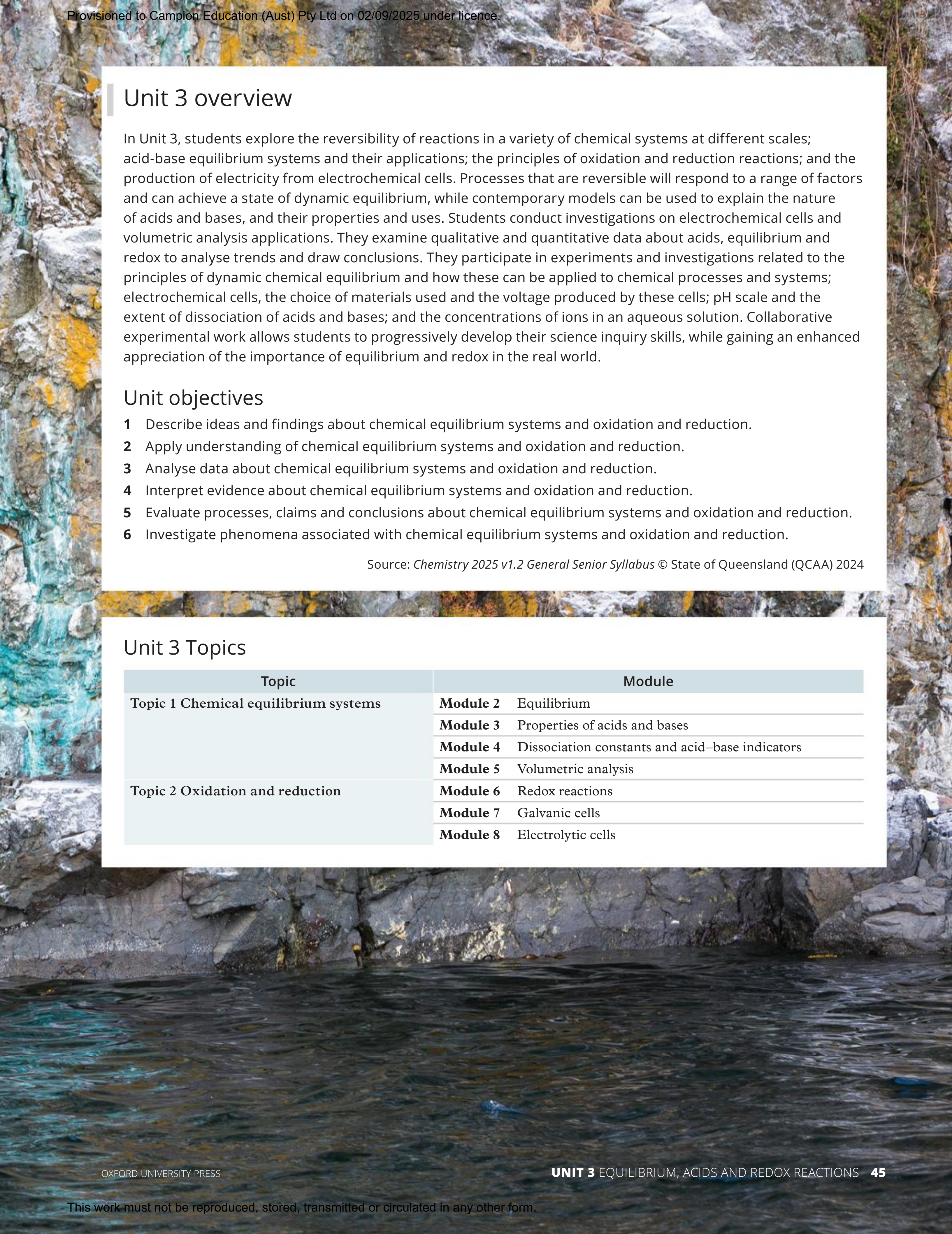
30 Use two different online chemistry sources to **investigate** basic information about caffeine (including its melting point, proper chemical name and type of elements it contains). **Consider** which database was easier to use and why. **Discuss** which is more reliable or trustworthy. (2 marks)

Module 1 checklist: Chemistry toolkit



UNIT 3

Equilibrium, acids and redox reactions



Unit 3 overview

In Unit 3, students explore the reversibility of reactions in a variety of chemical systems at different scales; acid-base equilibrium systems and their applications; the principles of oxidation and reduction reactions; and the production of electricity from electrochemical cells. Processes that are reversible will respond to a range of factors and can achieve a state of dynamic equilibrium, while contemporary models can be used to explain the nature of acids and bases, and their properties and uses. Students conduct investigations on electrochemical cells and volumetric analysis applications. They examine qualitative and quantitative data about acids, equilibrium and redox to analyse trends and draw conclusions. They participate in experiments and investigations related to the principles of dynamic chemical equilibrium and how these can be applied to chemical processes and systems; electrochemical cells, the choice of materials used and the voltage produced by these cells; pH scale and the extent of dissociation of acids and bases; and the concentrations of ions in an aqueous solution. Collaborative experimental work allows students to progressively develop their science inquiry skills, while gaining an enhanced appreciation of the importance of equilibrium and redox in the real world.

Unit objectives

1 Describe ideas and findings about chemical equilibrium systems and oxidation and reduction.
2 Apply understanding of chemical equilibrium systems and oxidation and reduction.
3 Analyse data about chemical equilibrium systems and oxidation and reduction.
4 Interpret evidence about chemical equilibrium systems and oxidation and reduction.
5 Evaluate processes, claims and conclusions about chemical equilibrium systems and oxidation and reduction.
6 Investigate phenomena associated with chemical equilibrium systems and oxidation and reduction.

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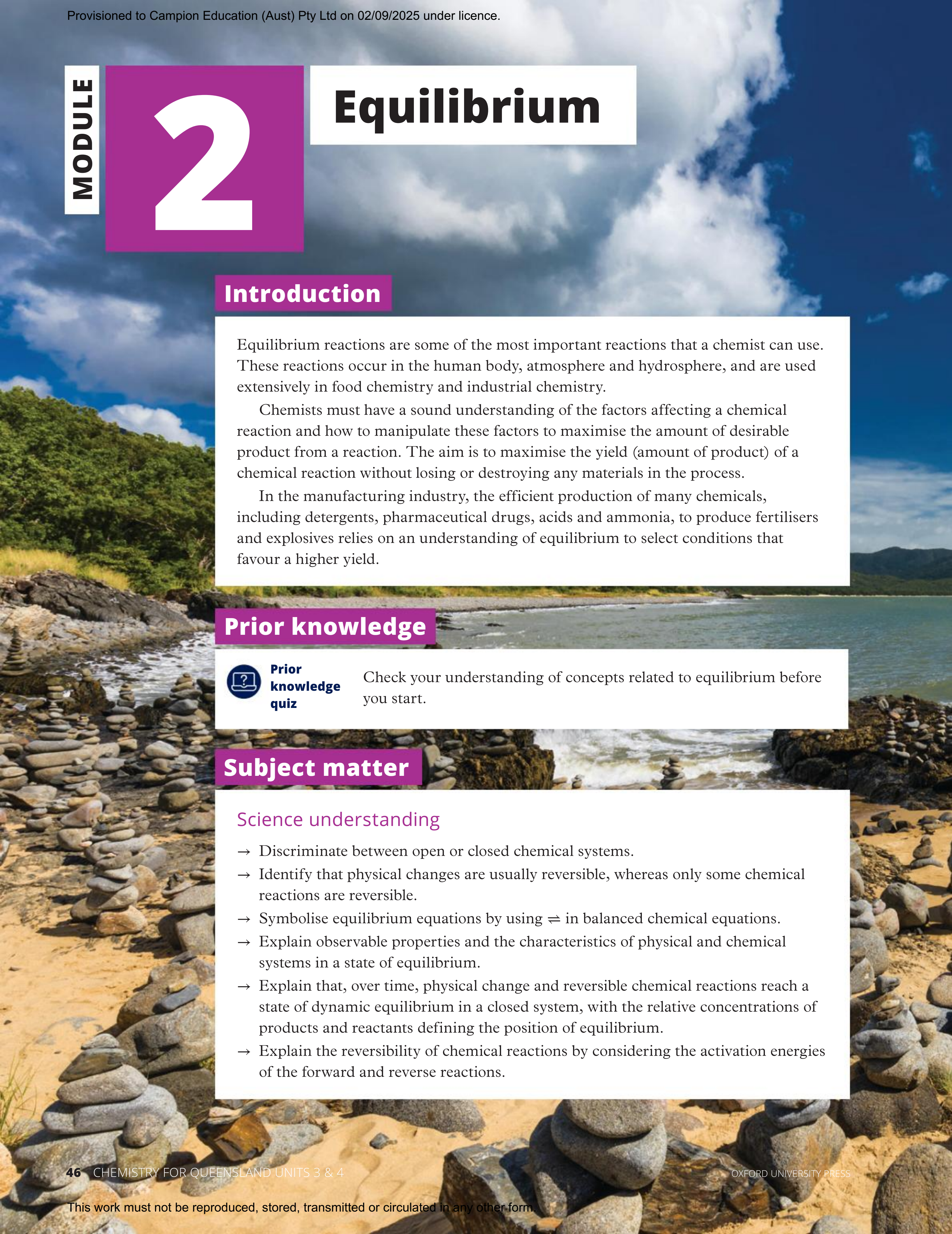
Unit 3 Topics

Topic	Module	
Topic 1 Chemical equilibrium systems	**Module 2**	Equilibrium
	Module 3	Properties of acids and bases
	Module 4	Dissociation constants and acid–base indicators
	Module 5	Volumetric analysis
Topic 2 Oxidation and reduction	**Module 6**	Redox reactions
	Module 7	Galvanic cells
	Module 8	Electrolytic cells



MODULE 2 Equilibrium

Introduction

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 (amount of product) of a chemical reaction without losing or destroying any materials in the process.

In the manufacturing industry, the efficient production of many chemicals, including detergents, pharmaceutical drugs, acids and ammonia, to produce fertilisers and explosives relies on an understanding of equilibrium to select conditions that favour a higher yield.

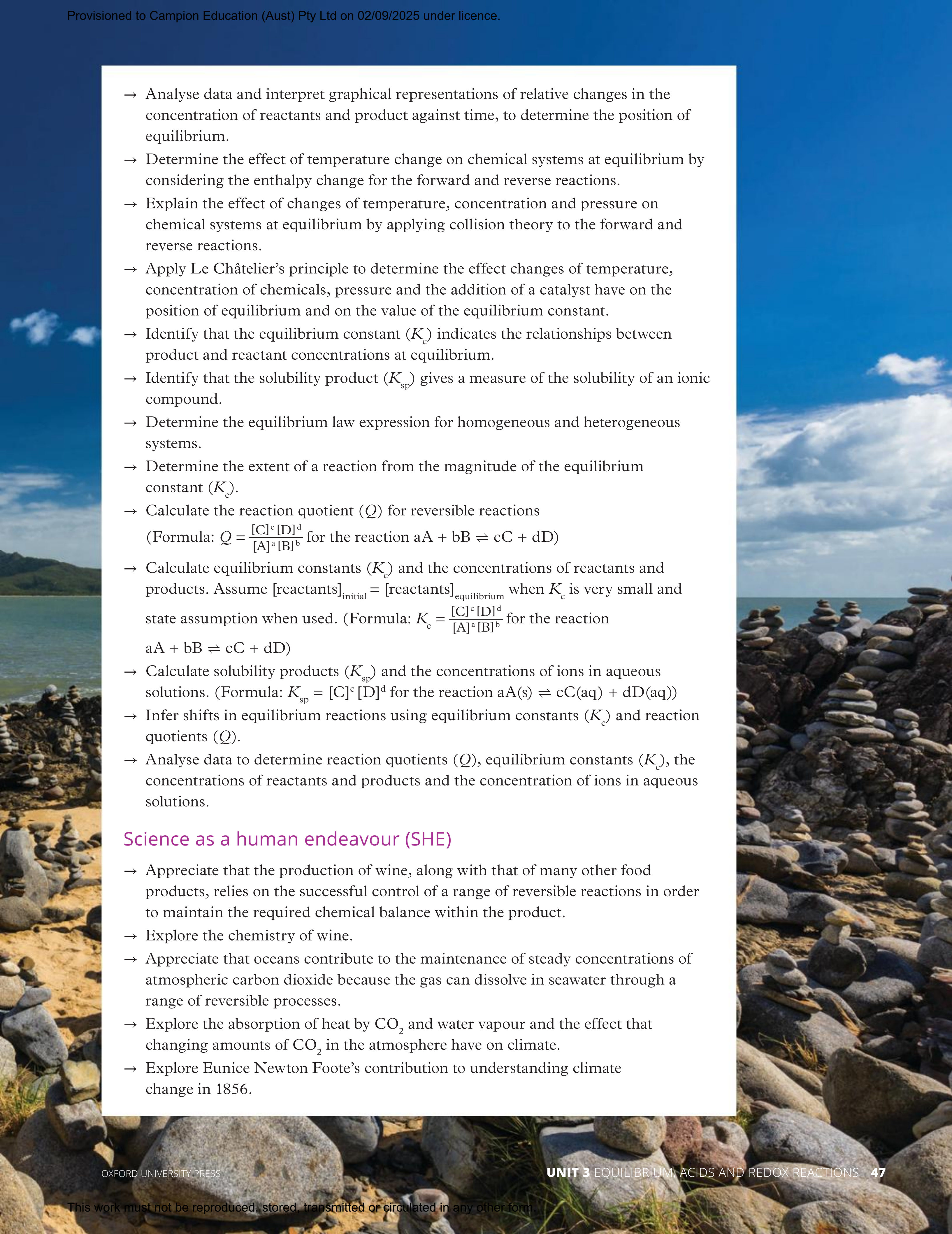
Prior knowledge

Prior knowledge quiz Check your understanding of concepts related to equilibrium before you start.

Subject matter

Science understanding

- → Discriminate between open or closed chemical systems.
- → Identify that physical changes are usually reversible, whereas only some chemical reactions are reversible.
- → Symbolise equilibrium equations by using $\rightleftharpoons$ in balanced chemical equations.
- → Explain observable properties and the characteristics of physical and chemical systems in a state of equilibrium.
- → Explain that, over time, physical change 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 data and interpret graphical representations of relative changes in the concentration of reactants and product against time, to determine the position of equilibrium.
- Determine the effect of temperature change on chemical systems at equilibrium by considering the enthalpy change for the forward and reverse reactions.
- Explain the effect of changes of temperature, concentration and pressure on chemical systems at equilibrium by applying collision theory to the forward and reverse reactions.
- Apply Le Châtelier's principle to determine 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.
- Identify that the equilibrium constant (K_c) indicates the relationships between product and reactant concentrations at equilibrium.
- Identify that the solubility product (K_{sp}) gives a measure of the solubility of an ionic compound.
- Determine the equilibrium law expression for homogeneous and heterogeneous systems.
- Determine the extent of a reaction from the magnitude of the equilibrium constant (K_c).
- Calculate the reaction quotient (Q) for reversible reactions (Formula: $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ for the reaction $aA + bB \rightleftharpoons cC + dD$)
- Calculate equilibrium constants (K_c) and the concentrations of reactants and products. Assume $[\text{reactants}]_{\text{initial}} = [\text{reactants}]_{\text{equilibrium}}$ when K_c is very small and state assumption when used. (Formula: $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ for the reaction $aA + bB \rightleftharpoons cC + dD$)
- Calculate solubility products (K_{sp}) and the concentrations of ions in aqueous solutions. (Formula: $K_{sp} = [C]^c[D]^d$ for the reaction $aA(s) \rightleftharpoons cC(aq) + dD(aq)$)
- Infer shifts in equilibrium reactions using equilibrium constants (K_c) and reaction quotients (Q).
- Analyse data to determine reaction quotients (Q), equilibrium constants (K_c), the concentrations of reactants and products and the concentration of ions in aqueous solutions.

Science as a human endeavour (SHE)

- Appreciate that the production of wine, along with that of many other food products, relies on the successful control of a range of reversible reactions in order to maintain the required chemical balance within the product.
- Explore the chemistry of wine.
- Appreciate that oceans contribute to the maintenance of steady concentrations of atmospheric carbon dioxide because the gas can dissolve in seawater through a range of reversible processes.
- Explore the absorption of heat by CO_2 and water vapour and the effect that changing amounts of CO_2 in the atmosphere have on climate.
- Explore Eunice Newton Foote's contribution to understanding climate change in 1856.

Science inquiry

→ Investigate factors that affect equilibrium (Le Châtelier’s principle).
→ Investigate solubility.

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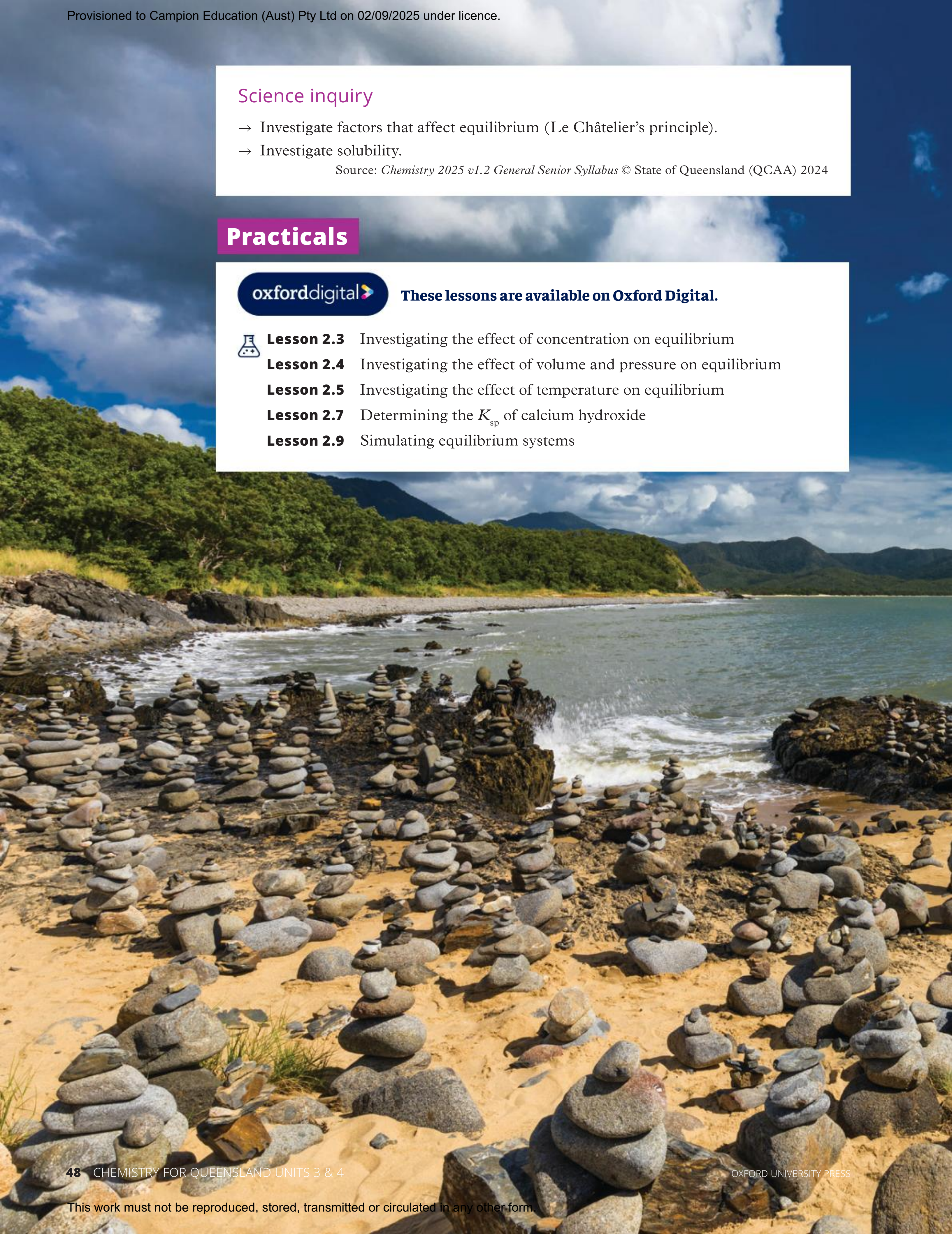
Practicals

These lessons are available on Oxford Digital.

Lesson 2.3	Investigating the effect of concentration on equilibrium
Lesson 2.4	Investigating the effect of volume and pressure on equilibrium
Lesson 2.5	Investigating the effect of temperature on equilibrium
Lesson 2.7	Determining the K_{sp} of calcium hydroxide
Lesson 2.9	Simulating equilibrium systems



Lesson 2.1
Equilibrium systems

Key ideas

→ Chemical reactions occur in open systems where particles can escape into the atmosphere or be added and removed during the reaction.

→ Chemical reactions occur in closed equilibrium systems where all reactants and products are kept within the same container and cannot escape into the environment.

→ Chemical reactions that proceed both forwards and backwards become equilibrium reactions.

→ Dynamic equilibrium is reached when the rates of the forward and reverse reactions are equal. At this point, the concentrations of reactants and products are constant.

→ The reversibility of a reaction depends on the activation energy of the forward and reverse reactions, which can be identified from an energy profile diagram.

How do we represent reactions that are reversible?

Learning intentions and success criteria

Until now, you have seen chemical reactions that go completely to the products, and you have used a forward reaction arrow to indicate that all reactants collide successfully with sufficient activation energy to form products. The exception to this has been weak acids and bases, which only partially ionise in water; we indicate this by using the $\rightleftharpoons$ arrows. In this case, not all reactants form products.

In this module, we will explore this concept further.

Why are some changes reversible and others are not?

A **chemical system** is a broad term used to describe the environment that a chemical is reacting in. This may be a beaker sitting on a laboratory bench at room temperature, or a gas cylinder at high pressures.

chemical system
the reaction mixture, including reactants, products, catalysts and any solvents

open system
a chemical system that allows both matter and energy to move into and out of the system

closed system
a chemical system that allows energy to move into and out of the system but does not allow the transfer of matter

Open and closed systems

Chemical systems can be classified as open or closed according to their ability to exchange matter and energy with their surroundings. The system is the mixture of reactants, products, catalysts and any solvents contained within a reaction vessel. The surroundings are the reaction vessel and the wider environment around the chemical system. In **open systems**, both matter and energy can freely move between the system and its environment.

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 a **closed system**. Energy can freely move in and out of the bottle.

Inside the water bottle, the energy of some 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 space above the liquid 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. Condensation on the outer surface causes energy to be transferred into the system, warming the water in the bottle.

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.

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. As the products are lost in an open system, the following equation can be used:

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

where the forward reaction arrow indicates that, once the liquid water forms a gas, the gas does not form the liquid in the bottle again.

In a closed system, where liquid water evaporates, then condenses later on the side of the water bottle and then trickles back down into the liquid, the following equation can be used:

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

This equation uses equilibrium arrows ($\rightleftharpoons$), which indicate that the reaction or change can be reversed. Because higher temperatures allow liquid water to turn into a gas more readily, we say that the forward reaction is favoured at higher temperatures.

Reversibility in physical and chemical change

Physical changes, such as melting, boiling and dissolving, are typically reversible because they involve changes in the state or appearance of a substance without altering its chemical composition.

For example, water can freeze into ice and then melt back into liquid form. In this case, equilibrium arrows are used to indicate its reversibility:

$$H_2O(s) \rightleftharpoons H_2O(l)$$

Not all chemical reactions are reversible. Some reactions, such as the combustion of fuel, are irreversible under normal conditions because the reactants are completely converted into products. In this case, the reaction arrow is used to indicate that it is not reversible:

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

Certain chemical reactions, such as the formation of ammonia from nitrogen and hydrogen in the Haber process, are reversible and can proceed both forwards and backwards under appropriate conditions. Again, equilibrium arrows are used to indicate its reversibility:

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

It is for these reasons that we say that physical changes are usually reversible, whereas only some chemical reactions are reversible.

Worked example 2.1A

Writing equilibrium reactions

Write the following reactions as equilibrium reactions and **identify** whether they are physical or chemical changes.

a An aqueous system of carbonic acid forms hydrogen ions and hydrogencarbonate ions. (2 marks)

b Liquid hydrogen forms gaseous hydrogen. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the questions are asking you to do.	"Identify" means distinguish; locate, recognise and name. We need to write a balanced chemical equation using equilibrium arrows for 1 mark and then identify whether a physical or chemical change has occurred. If a chemical change has occurred, reactants and products have different chemical formulas. If a physical change has occurred, the reactants and products have the same chemical formula but different states.
Step 2: For part **a**, write the equation for the reaction.	**a** $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ (1 mark)
Step 3: Identify the change as physical or chemical.	This is a chemical change. (1 mark)
Step 4: For part **b**, write the equation for the reaction.	**b** $H_2(l) \rightleftharpoons H_2(g)$ (1 mark)
Step 5: Identify the change as physical or chemical.	This is a physical change. (1 mark)

Your turn

Write the following reactions as equilibrium reactions and **identify** whether they are physical or chemical changes.

a The gaseous decomposition of sulfur trioxide forms sulfur dioxide and oxygen. (2 marks)

b Gaseous nitrogen forms liquid nitrogen. (2 marks)

What is dynamic equilibrium?

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

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 a closed 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 1).

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

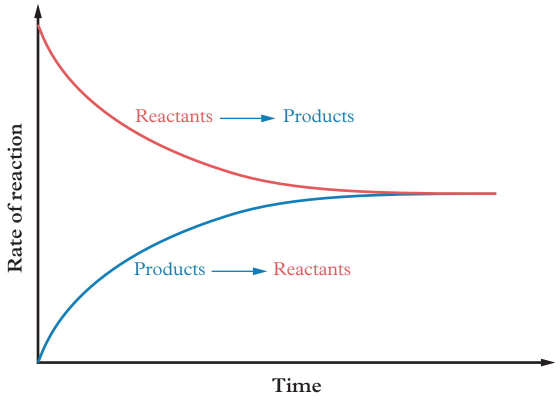


FIGURE 1 Dynamic equilibrium is reached when the rates of the forward and reverse reactions are equal.

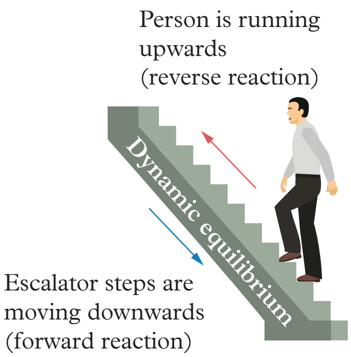


FIGURE 2 The person is at dynamic equilibrium: the rate at which he is going up the escalator equals the rate at which he is going down.

The rates of the forward and reverse reactions being equal can be visualised using the escalator analogy (Figure 2). The escalator steps are moving downwards (forward reaction) while you are running up (reverse reaction). If your running speed matches that of the escalator, you get stuck in the middle running upwards but not moving. This is analogous to dynamic equilibrium. The concentrations of reactants and products are constant 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. This is the forward reaction:

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

However, as ammonia is forming, its bonds are also breaking to re-form the nitrogen and hydrogen molecules. This is the reverse reaction:

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

Note that the individual forward and reverse reactions have been written with forward arrows because we are only examining half of the reaction process. The overall reaction combining the two directions uses the equilibrium arrows.

When the rate of formation of ammonia is equal to the rate of formation of nitrogen and hydrogen, the system has reached equilibrium. This can also be detected by measuring concentrations. When the concentrations of the reactants and products are constant, each is reacting as fast as they are formed, and they are in equilibrium. There is no apparent change at the macroscopic level, but at the particle level, both the forward and reverse reactions continue.

Reversibility using activation energy

In a chemical reaction, energy is required to initiate the reaction. This energy is known as the **activation energy (E_a)**. The smaller the activation energy, the more readily the reaction forms products. Over time, as the chemicals react, the concentrations of the reactants decrease and the concentrations of the products increase.

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

The products of some chemical reactions escape into the atmosphere. For example, in the reaction between a solution of hydrochloric acid and a solution of sodium hydrogencarbonate, one of the products is gaseous and is lost after it is formed:

$$HCl(aq) + NaHCO_3(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

The gas is released into the atmosphere and therefore can no longer take part in the reaction system. The concentrations of hydrochloric acid and sodium hydrogencarbonate decrease as they react. However, the concentration of the carbon dioxide product does not increase because this product is being lost to the atmosphere. Due to the continual removal of one product from the mixture, 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 at the end. This is an open system, and dynamic equilibrium cannot be reached in an open system.

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

Figure 3A shows the energy profile for an exothermic reaction. The activation energy for the reaction is 40 kJ. The **change in enthalpy** for the reaction 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.

change in enthalpy
the amount of heat absorbed or released by a system during a process at constant pressure, usually during a chemical reaction

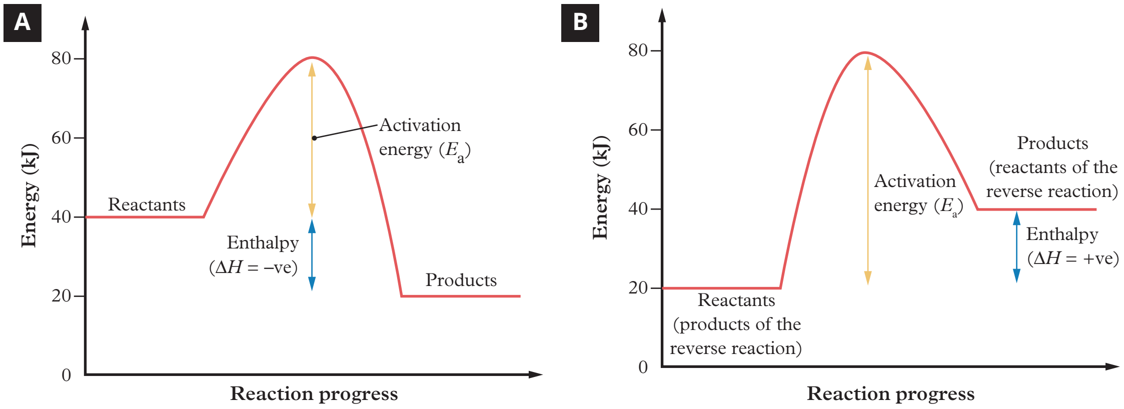


FIGURE 3 (A) The energy profile for an exothermic reaction. (B) The energy profile for the reverse endothermic reaction.

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 3B). The reverse reaction has an activation energy of 60 kJ and a change in enthalpy of 20 kJ. The change in enthalpy is positive because the total energy of the products is greater than the total energy of the reactants, and heat is absorbed from the surroundings.

Provided that the reaction has enough energy to overcome the activation energy in both the forward and reverse reactions, the reaction proceeds readily in both directions, and equilibrium is maintained. It is thus considered to be a reversible reaction.

forward reaction
the reaction between reactants to form products

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

Worked example 2.1B

Analysing energy profiles

Figure 4 shows the energy profile for the forward reaction between hydrogen and oxygen to form water.

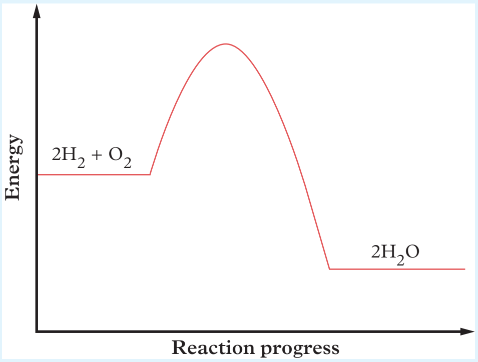


FIGURE 4 The energy profile diagram for the forward reaction of the formation of water

The activation energy is 1370 kJ and the enthalpy is −482 kJ.

a **Calculate** the activation energy for the reverse reaction. (1 mark)

b **Calculate** the enthalpy for the reverse reaction. (1 mark)

c Using the data, **justify** whether the reaction can be considered to be reversible. (2 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. "Justify" means to give reasons or evidence to support an answer. We need to calculate the values and then use them as evidence in the justification. This is why the justification is worth 2 marks, If your response is justified without data, it is only worth 1 mark.
Step 2: For part **a**, calculate the activation energy for the reverse reaction.	**a** The reverse reaction's activation energy is from the water to the top of the energy profile where bonds are broken. This is calculated at E_a for the forward reaction + ΔH = 1,370 + 482 = 1,852 kJ (1 mark)
Step 3: For part **b**, calculate the enthalpy for the reverse reaction.	**b** The enthalpy of the reverse reaction is the same as that of the forward reaction but with the opposite sign. So, –482 kJ becomes +482 kJ (1 mark)
Step 4: For part **c**, based on the activation energy, justify whether the forward or reverse reaction occurs more readily.	**c** The forward reaction has an E_a of 1,370 kJ. The reverse reaction has an E_a of 1,852 kJ. Response: The forward reaction has an activation energy of 1,370 kJ, which is lower than but similar to the reverse reaction's 1,852 kJ. (1 mark) Therefore, provided sufficient energy is provided to overcome the activation energy, the reaction is reversible. (1 mark)

Your turn

Figure 5 demonstrates the energy profile for the decomposition of hydrogen chloride gas into its elements.

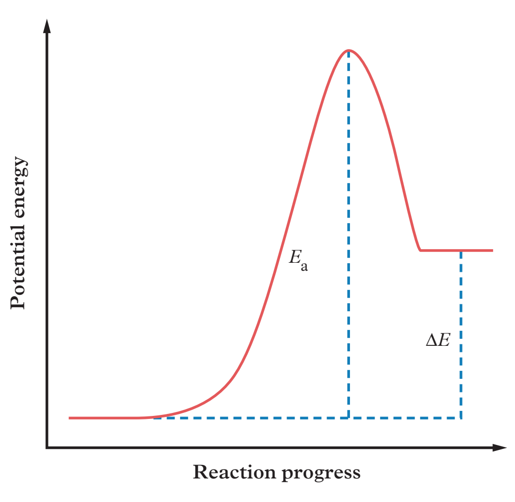


FIGURE 5 An energy profile diagram for the decomposition of hydrogen chloride

The activation energy is 864 kJ and the enthalpy is +185 kJ.

a **Calculate** the activation energy for the reverse reaction. (1 mark)

b **Calculate** the enthalpy for the reverse reaction. (1 mark)

c Using the data, **justify** whether the reaction can be considered to be reversible. (2 marks)

How are changes to reactions measured and observed?

A change to an equilibrium system can be measured as a change in concentration. As mentioned previously, when the concentrations of the reactants and products are constant, they are being broken down as fast as they are formed, and they are in equilibrium. If the concentrations are changing, the system is not at equilibrium. Once a system reaches equilibrium, the concentration of one or more reactants or products can be determined, allowing the concentrations of the remaining reactants and products to be calculated.

It is easy to measure the concentration of a specific substance within a reaction by spectroscopy, such as UV–visible spectroscopy; for example, if the specific chemical is the only one absorbing light at a particular wavelength.

The most common methods of measuring concentration of a species in an equilibrium system rely on observation of a property that can be related to the concentration of a **chemical species**, either directly, such as the colour of a solution, or indirectly, by measuring a different species such as by pH.

chemical species
a general term that refers to any identifiable entity involved in a chemical reaction or present in a chemical system; can include atoms, ions, molecules and complexes; in a chemistry context, the word "species" may be used interchangeably with the term "chemical species"

Observation

The colour of a solution can indicate the extent of some reactions, if one of the species is coloured. Consider the reaction of iron(III) ions with thiocyanate ions to form the iron(III) thiocyanate ion. Initially, the iron(III) solution is yellow. When the solutions are mixed, the iron(III) ions react with the thiocyanate ions to produce iron(III) thiocyanate, which has an intense a blood-like red colour (Figure 6). The solution becomes darker red, indicating that the reaction has moved forward to reach equilibrium:

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

pH measurements

When an equilibrium reaction involves either an acid or a base, you can measure the **pH** to determine the concentration of hydronium ions in solution. Recall from Units 1 & 2, that pH can be measured using universal indicator or with a pH metre. In Module 3, you will learn how the concentrations of hydronium ions (H_3O^+) and hydroxide ions (OH^-) can be calculated from the measured pH. By determining the concentrations of hydronium or hydroxide ions at equilibrium, the equilibrium concentrations of other chemical species can also be found.

FIGURE 6 The addition of yellow iron(III) ions to thiocyanate ions produces the red iron(III) thiocyanate ions.

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 pH and use it to calculate the concentration of the H_3O^+ ion (also written as $H^+(aq)$ ion) and then use simple stoichiometry to determine the concentration of all other chemicals in the reaction.

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

Other methods for monitoring equilibrium involve measuring properties of the system. These include:

- pressure data for equilibrium reactions involving different amounts of gas molecules on each side. Equilibrium is reached when the gas pressure of the system is constant

- electrical conductivity, used typically for equilibria in aqueous ion systems because they involve ions and conduct electricity in solution. The higher the concentration of ions, the greater the conductivity. Some ions are more conductive than others, with H^+ being the most conductive in aqueous solution. (This will be discussed in more detail in Module 5.)

Analyse graphical representations

Graphs can be used to represent reactions as they reach dynamic equilibrium. To analyse these graphs, it is essential to understand that, at equilibrium:

- the rates of the forward and reverse reactions are equal
- concentrations of reactants and products are constant (but they are not necessarily the same concentration as each other).

In both graphing examples below, we will analyse the reaction between hydrogen and iodine to form hydrogen iodide:

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

Rate versus time graphs

This was first introduced to you when dynamic equilibrium was discussed. Consider the rate–time graph in Figure 7. We can note from the graph that:

- the forward reaction rate starts high because H_2 and I_2 are abundant. It decreases as their concentrations decrease
- the reverse reaction rate starts at zero (no HI initially) and increases as HI forms
- at equilibrium, the rates of the forward and reverse reactions are equal
- the graph shape indicates that:
  - the forward reaction rate decreases over time
  - the reverse reaction rate increases over time
  - both curves meet and remain constant at equilibrium.

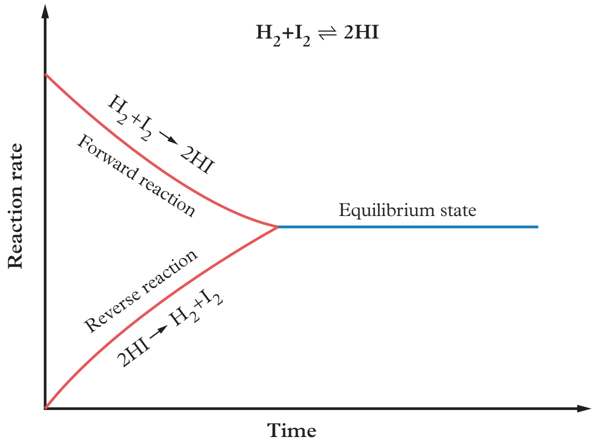


FIGURE 7 A rate–time graph for the reaction between hydrogen and iodine

Concentration versus time graphs

Because we know that concentration is constant at equilibrium, we can ascertain from the graph (Figure 8A) that:

- the concentrations of H_2 and I_2 start high and decrease over time
- the concentration of HI starts at zero and increases until equilibrium is reached. If the reaction starts with HI, the concentration of HI decreases and the concentrations of H_2 and I_2 increase, with the equilibrium concentrations reaching the same values if other conditions are the same

- the concentration of HI increases twice as rapidly as the concentrations of H_2 and I_2 decrease
- at equilibrium, all concentrations remain constant.

Figure 8B shows the reverse reaction, in which only HI was present initially.

- The concentration of HI starts high and decreases over time.
- The concentrations of H_2 and I_2 start at zero and increase until equilibrium is reached.
- The concentration of HI decreases twice as rapidly as the concentrations of H_2 and I_2 increase.
- At equilibrium, all concentrations remain constant.

The equilibrium concentrations of all three components of the reaction mixture are the same in both Figure 8A and Figure 8B, showing that the same equilibrium point is reached regardless of the direction of the reaction.

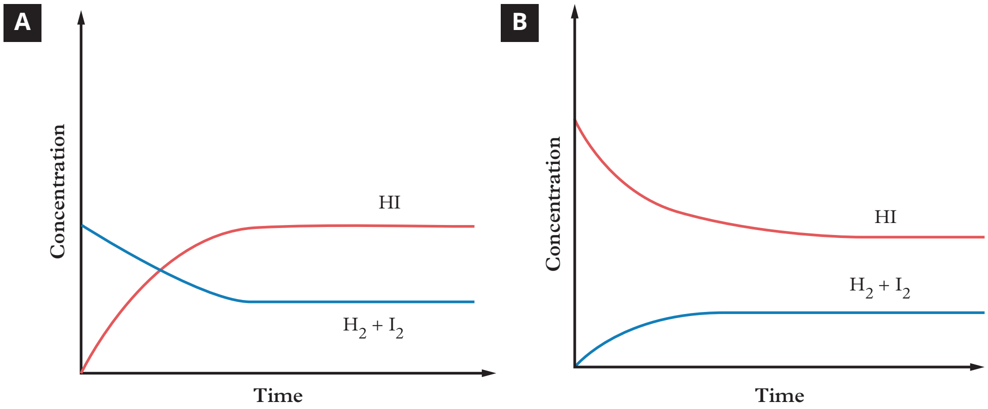


FIGURE 8 A concentration–time graph for the reaction between hydrogen and iodine. Notice that the *y*-axis shows concentration not rate, unlike Figure 7.

Worked example 2.1C

Analysing rate–time and concentration–time graphs

In a reaction between hydrogen and nitrogen to form ammonia, the graph in Figure 9 is obtained. Initially, ammonia is pumped into an empty sealed container and then allowed to reach equilibrium. The following reaction represents this process:

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

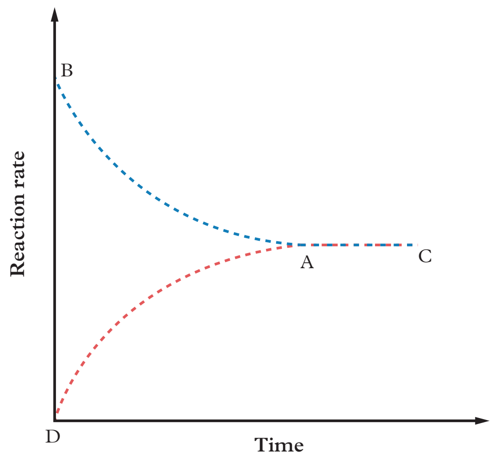


FIGURE 9 A rate–time equilibrium graph for the reaction between hydrogen and nitrogen to form ammonia

1 **Identify** where on the graph the following are represented and **explain** why this section of the graph represents them.

- **a** The forward reaction (1 mark)
- **b** The reverse reaction (1 mark)
- **c** Equilibrium (1 mark)

2 **Identify** what is represented by the following.

- **a** B (1 mark)
- **b** D (1 mark)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Identify" means distinguish; locate, recognise and name. "Explain" means make an idea or situation plain or clear by describing it in more detail or revealing relevant facts. We need to analyse the graph and explain which aspects of equilibrium are represented in various spaces.
Step 2: For part **1a**, the forward reaction occurs when H_2 reacts with N_2. As there is neither initially, it must start at the bottom of the graph	**1a** The bottom curve that arches up is the rate of reaction of hydrogen and nitrogen to form ammonia. Because initially there is no hydrogen and nitrogen, the rate of reaction starts at zero and only commences after ammonia starts breaking down. As more hydrogen and nitrogen are formed, their concentration increases and their rate increases. (1 mark)
Step 3: For part **1b**, the reverse reaction occurs when ammonia breaks down. Initially, only ammonia is present so it must start at the top of the graph.	**b** The top curve that progresses down is the rate of the reaction of ammonia breaking down into its elements. Due to its high concentration, the reaction of ammonia to form hydrogen and nitrogen has a high rate initially, which decreases over time as its concentration decreases. (1 mark)
Step 4: For part **1c**, equilibrium is reached when the two rates are equal.	**c** The section of the graph represented by the horizontal line is where both reactions have the same rate. (1 mark)
Step 5: For part **2a**, B representation	**2a** Initial rate of reaction of NH_3 breaking down into its elements. (1 mark)
Step 6: For part **2b**, D representation	**b** Initial rate of reaction of H_2 and N_2 reacting to form NH_3 (1 mark)

Your turn

In a reaction between hydrogen and nitrogen to form ammonia, the graph in Figure 10 is obtained. Initially, hydrogen and nitrogen are pumped into an empty sealed container and then allowed to reach equilibrium. The following reaction represents this process:

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

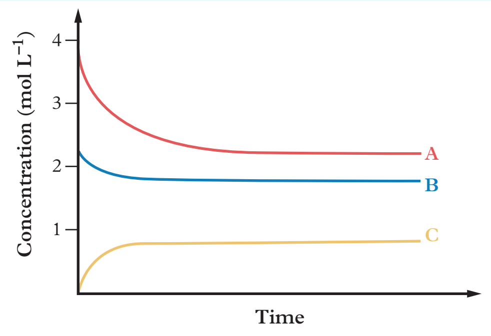


FIGURE 10 A concentration–time equilibrium graph for the reaction between hydrogen and nitrogen to form ammonia

1 **Identify** where on the graph the following are represented and **explain** why this section of the graph represents them.
   - **a** The forward reaction (1 mark)
   - **b** The reverse reaction (1 mark)
   - **c** Equilibrium (1 mark)

2 **Identify** what is represented by the following.
   - **a** A (1 mark)
   - **b** B (1 mark)
   - **c** C (1 mark)

Check your learning 2.1

Check your learning 2.1: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Define** "dynamic equilibrium". (1 mark)

2 **Explain** what is required for a reaction to reach dynamic equilibrium. (3 marks)

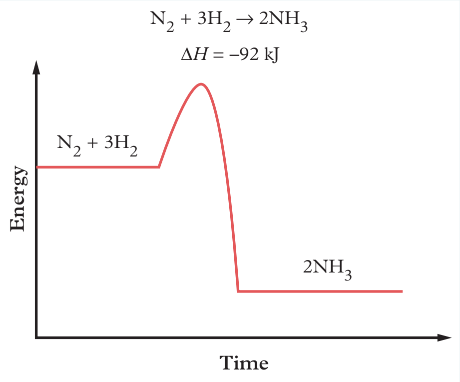
Analytical processes

3 Write equilibrium equations for the following changes and **determine** whether they are physical processes or chemical reactions.
   - **a** Dry ice (solid carbon dioxide) forms gaseous carbon dioxide. (2 marks)
   - **b** Hydrogen and iodine gases form hydrogen iodide. (2 marks)
   - **c** Gaseous carbon monoxide and water form gaseous carbon dioxide and hydrogen. (2 marks)
   - **d** In an aqueous system, copper(II) ion reacts with ammonia, forming the complex ion $[Cu(NH_3)_4]^{2+}$. (2 marks)
   - **e** In a liquid system, ethanoic acid (CH_3COOH) and methanol (CH_3OH) form methyl ethanoate (CH_3COOCH_3) and water. (2 marks)

Knowledge utilisation

4 The following energy profile represents the forward reaction between nitrogen and hydrogen to form ammonia. It is not drawn to scale.

The reaction profile has an activation energy of 2160 kJ.



   - **a** **Calculate** the activation energy for the reverse reaction. (1 mark)
   - **b** **Calculate** the enthalpy for the reverse reaction. (1 mark)
   - **c** This reaction is reversible but will only proceed towards equilibrium at high temperatures and pressures. Using the data, **justify** why the reaction is considered reversible and why it will only reach equilibrium under the stated conditions. (2 marks)

5 A student claims that Earth is an open equilibrium system. **Evaluate** this claim and justify whether you believe the student to be correct. (3 marks)

6 **Investigate** homogeneous and heterogeneous equilibria and explain what these terms mean, giving an example of each. (4 marks)

Lesson 2.2

Factors that affect equilibrium – Le Châtelier's principle

Key ideas

→ The position of equilibrium indicates whether a reaction is favouring the forward or reverse reactions and whether there will be more reactants or more products at equilibrium.

→ Le Châtelier laid the foundation for equilibrium understanding in his principle, which states that any change to a system will be partially opposed until equilibrium is re-established.

→ Enthalpy changes can be used to determine the effect of temperature on an equilibrium system and whether the position of equilibrium will shift forwards or backwards.

→ Le Châtelier's principle can also be used to predict the effect of changing temperature, concentration and pressure on equilibrium systems and whether the position of equilibrium will shift forwards or backwards.

→ Graphs can be used to represent changes to equilibrium systems.

Learning intentions and success criteria

What is Le Châtelier's principle and how is it used?

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.

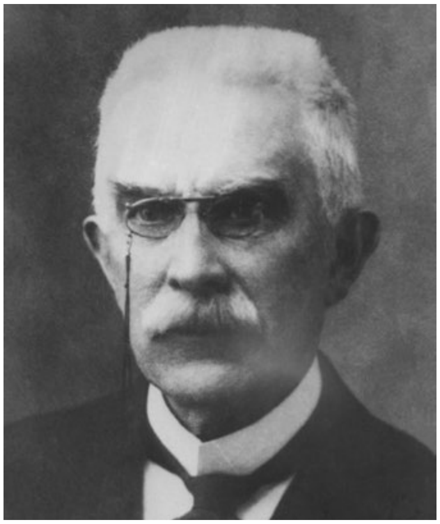


FIGURE 1 French chemist Henry Louis Le Châtelier (1850–1936) developed his principle, which predicts the effect of changes on a chemical equilibrium.

How is Le Châtelier's principle essential to an understanding of equilibrium?

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 affect 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.

How do changes in concentration affect equilibrium?

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

- adding or removing a reactant or product
- changing **pressure** and **volume** for equilibria involving substances in the gas phase
- 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-response questions about equilibrium and changes in concentration

When answering short-response 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 almost 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. The only time a change to a system at equilibrium may be fully opposed rather than partially opposed is in the case of an equilibrium occurring in more than one phase, such as solid and solution.

TABLE 1 The structure for answering short-response 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* reverse 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* reverse 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. →

concentration
the amount of a chemical species in a given volume in a solution

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 on another substance

volume
a measure of the space occupied by a substance

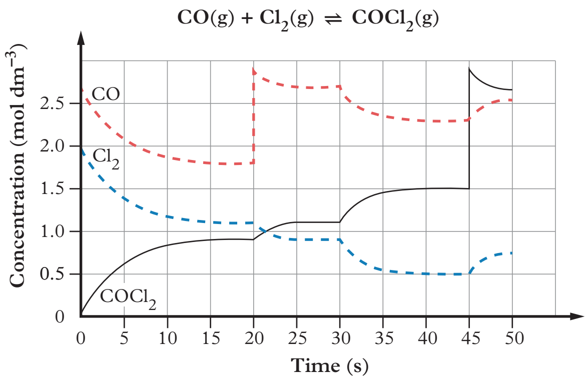


FIGURE 2 A graph showing a reaction reaching equilibrium, followed by a series of changes, and the reaction returning to equilibrium after each change

Graphing

You can also represent changes to equilibrium systems graphically. Plot time on the *x*-axis and concentration on the *y*-axis. Figure 2 shows a graph of a reaction system depicting a number of sequential changes made, followed by the response of the reaction system to return to equilibrium. The reaction is for the formation of $COCl_2$ from CO and Cl_2. Equilibrium is first reached at 15 seconds, as shown by the unchanging concentrations of all chemical species following this time. The first change occurs at 20 seconds, when the concentration of CO is increased. The system partially opposes this change by using some of the added CO. Cl_2 is also used and $COCl_2$ is produced, and the system reaches equilibrium once more at 25 seconds. At this time, the concentrations of all three chemical species exhibit a gradual change until a new equilibrium is reached at 40 seconds. This is indicative of a temperature change. At 45 seconds, the concentration of $COCl_2$ is increased. Subsequently, the system responds to use some of the added $COCl_2$ to return to a new equilibrium position by 50 seconds.

Worked examples 2.2A–E demonstrate these explanations and the corresponding graphs. Each example focuses on a single change, rather than a number of sequential changes.

Worked example 2.2A

Graphing an increase in reactant concentration

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

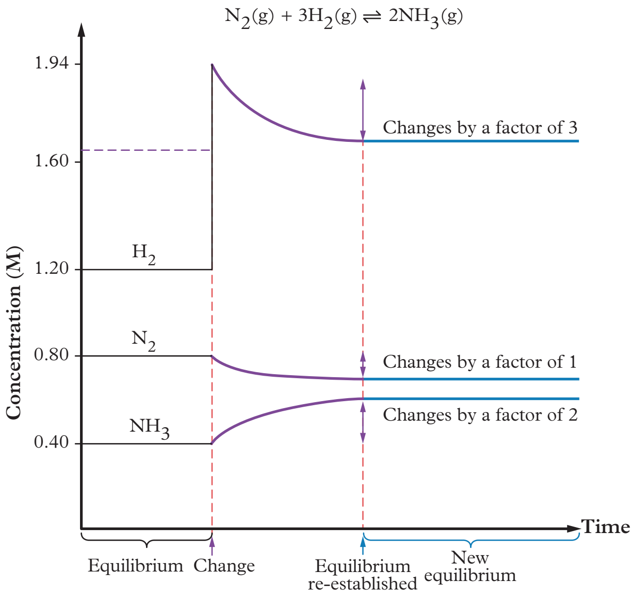
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The concentration of hydrogen is increased by 0.74 M. At equilibrium, the concentration of hydrogen is 1.64 M.

a **Explain** the effect of this increase in concentration on the equilibrium system. (2 marks)

b **Construct** a graph of the equilibrium change. (3 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Explain" means make an idea or situation plain or clear by describing it in more detail or revealing relevant facts. "Construct" means display information in a diagrammatic or logical form. We need to use Le Châtelier's principle and the short-response structure to explain the effect of the change and then represent this diagrammatically in a graph by following the graphing rules.
Step 2: For part **a**, use Le Châtelier's principle to determine what will happen in the system.	**a** As the concentration of hydrogen is increased, Le Châtelier's principle states that the system will partially oppose this change by moving to the side to decrease the concentration of hydrogen, the product side. (1 mark) Therefore, a net forward reaction results. (1 mark)
Step 3: For part **b**, initial equilibrium – before the change.	**b** At equilibrium, the lines are horizontal, indicating a constant concentration before the change is made.
Step 4: Initial change	Hydrogen concentration increases by 0.74 M; therefore, the increase line starts at 1.2 M and extends to 1.94 M. It is represented as a vertical line, indicating it was increased suddenly.

<table>
<tr><th>Think</th><th>Do</th></tr>
<tr><td>Step 5: Direction of movement after the change is made (hydrogen). Calculations are all conveniently summarised in a table showing the reaction, the initial concentrations, the changes in concentrations and the equilibrium concentrations.</td><td>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 1.64 M. Note: 1.64 M is higher than the original concentration of 1.2 M but lower than the 1.94 M immediately following addition of extra hydrogen – 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.
<table>
<tr><th>R</th><th>N_2</th><th>$3H_2$</th><th>$2NH_3$</th></tr>
<tr><td>I</td><td>0.8</td><td>1.2 + 0.74 = 1.94</td><td>0.4</td></tr>
<tr><td>C</td><td>−0.10</td><td>−0.30</td><td>+0.20</td></tr>
<tr><td>E</td><td>0.70</td><td>1.64 (given)</td><td>0.6</td></tr>
</table></td></tr>
<tr><td>Step 6: Direction of movement after the change is made (nitrogen and ammonia)</td><td>Because there is a net forward reaction, the concentration of nitrogen will also decrease, and the concentration of ammonia will increase.</td></tr>
<tr><td>Step 7: How large are the concentration changes?</td><td>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.</td></tr>
<tr><td>Step 8: Final equilibrium – after the change</td><td>When equilibrium is re-established, the lines on the graph must be horizontal again.</td></tr>
<tr><td>Step 9: Final answer: put all of the information together into a graph.</td><td>

Marks are awarded for:

- the initial concentrations and the changes (1 mark)
- the direction of movement of all reactants and products after the change is made (i.e. $[H_2]$ and $[N_2]$ decrease while $[NH_3]$ increases) (1 mark)</td></tr>
</table>

Think	Do
	• all of the little bits and pieces, including: – horizontal lines at equilibrium – changes occurring according to the molar ratio – change lines reaching equilibrium together – change lines having a steeper change at the start and plateauing moving towards equilibrium (as rate is greatest after the change is made). (1 mark)

Your turn

A reaction vessel contains 1.0 M nitrogen, 1.5 M hydrogen and 2.0 M ammonia at equilibrium:

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

The concentration of nitrogen is increased by 0.4 M and, at equilibrium, its concentration is measured to be 1.36 M.

a **Explain** the effect of this increase in concentration on the equilibrium. (2 marks)

b **Construct** a graph of the equilibrium change. (3 marks)

How do changes to pressure and volume in gaseous systems affect equilibrium?

Recall from Units 1 & 2 that gases can exist in fixed-volume (e.g. rigid-wall container) and variable-volume systems (e.g. balloon). According to Boyle's 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 in a smaller volume, the concentrations of all particles, both reactants and products, increase.

Consider the following reaction between gases:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

In this reaction, the forward reaction reduces the number of gas particles present, and the reverse reaction increases the number of gas particles present. If the reaction has reached equilibrium, then the volume is reduced and the pressure increased, then the volume is held constant, the system is no longer at equilibrium. In order to return to equilibrium, Le Châtelier's principle predicts that the system partially opposes this change. The way that this can be achieved is to decrease the pressure, by moving to the side with fewer particles. In this case, this corresponds to a net forward reaction. Table 2 summarises the structure for answering similar questions.

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 or removal of a reactant or product in a fixed-volume system corresponds to changing the concentration of that species; Table 1 can be used as a guide for answering questions of this type.

The addition of an inert (unreactive) gas, such as argon, can also increase the total 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, regardless of the increase in pressure caused by the inert gas. The partial pressures of the reactants and products is unchanged by adding a non-reacting gas. Therefore, the addition of an inert gas has no effect on a gaseous equilibrium system.

TABLE 2 The structure for answering short-response questions about equilibrium

Change (what has happened?)	Le Châtelier's principle says (how does the system partially oppose the change?)	Effect (on equilibrium position)
When the volume decreases/pressure increases	the system *partially opposes* the change by moving to the side with fewer particles	resulting in a *net* forward/reverse reaction (depending on the reaction equation).
When the volume increases/pressure decreases	the system *partially opposes* the change by moving to the side with more particles	resulting in a *net* forward/reverse reaction (depending on the reaction equation).

Study tip

When working through equilibrium questions, write the reaction equation, the initial concentrations, change in concentrations and final equilibrium concentrations. This is conveniently done in a table often referred to as a RICE table, or sometimes an ICE table. The reaction (or ratio) (R) is listed in the top row, the initial concentrations (I) in the second row, the change in concentrations (C) in the third row, and the equilibrium concentrations (E) in the fourth row.

Worked example 2.2B

Graphing an increase in volume

At equilibrium, nitrogen dioxide has a concentration of 1.0 M and dinitrogen tetroxide has a concentration of 0.3 M:

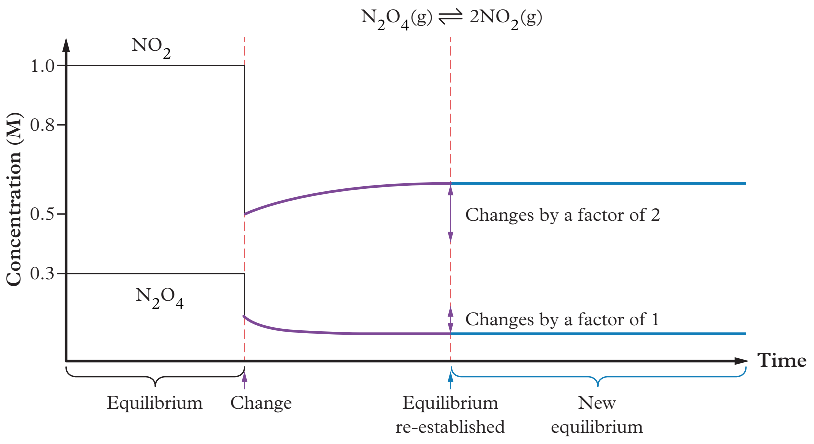
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

After some time, the volume of the system is doubled. When equilibrium is re-established, the concentration of nitrogen dioxide is 0.6 M.

a **Explain** the effect of this increase in volume on the equilibrium system. (2 marks)

b **Construct** a graph of the equilibrium change. (3 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Explain" means make an idea or situation plain or clear by describing it in more detail or revealing relevant facts. "Construct" means display information in a diagrammatic or logical form. We need to use Le Châtelier's principle and the short-response structure to explain the effect of the change and then represent this diagrammatically in a graph by following the graphing rules.
Step 2: For part **a**, use Le Châtelier's principle to determine what will happen in the system.	**a** When the volume of the system is doubled, all concentrations decrease by half and pressures are halved. Le Châtelier's principle states that 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. (1 mark) This results in a net forward reaction. (1 mark)
Step 3: For part **b**, initial equilibrium – before the change	**b** At equilibrium, the lines are horizontal, indicating a constant concentration before the change is made.
Step 4: Initial change	When the volume is doubled, the concentration of particles within the system is halved. At equilibrium, $[NO_2]$ is 1.0 M, which is halved to 0.5 M, whereas $[N_2O_4]$ is 0.3 M, which is halved to 0.15 M. (1 mark) All concentrations decrease sharply, as indicated by the vertical lines, as the volume increases.

<table>
<tr><th>Think</th><th>Do</th></tr>
<tr><td>Step 5: Direction of movement after the change is made</td><td>After the change, [NO_2] increases to 0.6 M and [N_2O_4] decreases in concentration.</td></tr>
<tr><td>Step 6: How large are the concentration changes? A RICE table allows Steps 4 to 6 to be more conveniently summarised.</td><td>As the chemicals are in a 2:1 ratio, [N_2O_4] will decrease by half the amount that [NO_2] increases.
<table>
<tr><th>R</th><th>N_2O_4</th><th>$2NO_2$</th></tr>
<tr><td>I</td><td>0.15</td><td>0.5</td></tr>
<tr><td>C</td><td>−0.05</td><td>+0.1</td></tr>
<tr><td>E</td><td>0.10</td><td>0.6 (given)</td></tr>
</table>
</td></tr>
<tr><td>Step 7: Final equilibrium – after the change</td><td>When equilibrium is re-established, the lines on the graph must be horizontal again.</td></tr>
<tr><td>Step 8: Final answer: put all of the information together into a graph.</td><td>


Marks are awarded for:

- the initial concentrations and the changes (1 mark)
- the direction of movement of all reactants and products after the change is made (i.e. [NO_2] increases while [N_2O_4] decreases) (1 mark)
- all of the little bits and pieces, including:
  - horizontal lines at equilibrium
  - changes occurring according to the molar ratio
  - change lines reaching equilibrium together
  - change lines having a steeper change at the start and plateauing moving towards equilibrium (as rate is greatest after the change is made). (1 mark)
</td></tr>
</table>

Your turn

A gaseous system at equilibrium contains 0.7 M sulfur dioxide, 0.1 M oxygen and 0.3 M sulfur trioxide:

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

The volume is halved, and equilibrium is re-established. The concentration of sulfur dioxide is found to be 1.3 M.

a **Explain** the effect of this decrease in volume on the equilibrium system. (2 marks)

b **Construct** a graph of the equilibrium change. (3 marks)

How does dilution in aqueous systems affect equilibrium?

The concentrations of particles in an aqueous system can be decreased by diluting the system with water (Table 3). 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.

TABLE 3 The structure for answering short-response questions about equilibrium

Change (what has happened?)	Le Châtelier says (how does the system partially oppose the change?)	Effect (on equilibrium position)
When the system is diluted, concentration of all species decreases	the system *partially opposes* the change by moving to the side with more particles	resulting in a *net* forward/reverse reaction (depending on the reaction equation).

Note: Dilution cannot increase the concentration, so the system cannot move to the side of the reaction with fewer particles.

Worked example 2.2C

Graphing the dilution of a system

A reaction between aqueous iron(III) ions and thiocyanate ions to form iron(III) thiocyanate ions is at equilibrium:

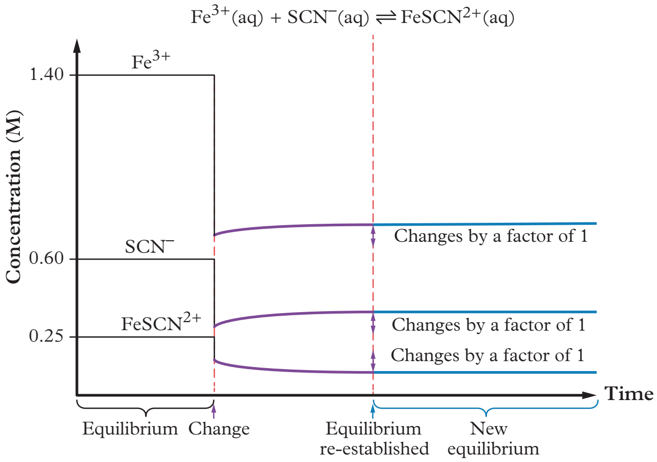
$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

Initially, their concentrations are 1.4 M, 0.6 M 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 0.35 M.

a **Explain** the effect of this increase in volume on the equilibrium system. (2 marks)

b **Construct** a graph of the equilibrium change. (3 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Explain" means make an idea or situation plain or clear by describing it in more detail or revealing relevant facts. "Construct" means display information in a diagrammatic or logical form. We need to use Le Châtelier's principle and the short-response structure to explain the effect of the change and then represent this diagrammatically in a graph by following the graphing rules.
Step 2: For part **a**, use Le Châtelier's principle to determine what will happen in the system.	**a** Doubling the volume by diluting it with water will halve the concentration of all ions in the aqueous solution. Le Châtelier's principle states that 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. (1 mark) Therefore, a net reverse reaction results. (1 mark)
Step 3: For part **b**, initial equilibrium – before the change	**b** At equilibrium, the lines are horizontal, indicating a constant concentration before the change is made.
Step 4: Initial change	When the reaction is diluted by doubling the volume, all concentrations decrease by half because there are fewer particles per volume of water. This results in a steep decrease in all concentrations, represented as vertical lines.
Step 5: Direction of movement after the change is made	After the change, [SCN^{-}] increases to 0.35 M, [Fe^{3+}] also increases and [$FeSCN^{2+}$] decreases.

<table>
<tr><th>Think</th><th>Do</th></tr>
<tr><td>Step 6: How large are the concentration changes? The calculations of these changes are summarised in a RICE table.</td><td>Any change to the system to partially oppose the change will occur in a 1:1:1 ratio. They must all change by the same amount.
<table>
<tr><th>R</th><th>Fe^{3+}</th><th>SCN^-</th><th>$FeSCN^{2+}$</th></tr>
<tr><td>I</td><td>0.7</td><td>0.3</td><td>0.125</td></tr>
<tr><td>C</td><td>+0.05</td><td>+0.05</td><td>−0.05</td></tr>
<tr><td>E</td><td>0.75</td><td>0.35 (given)</td><td>0.075</td></tr>
</table></td></tr>
<tr><td>Step 7: Final equilibrium – after the change</td><td>When equilibrium is re-established, the lines on the graph must be horizontal again.</td></tr>
<tr><td>Step 8: Final answer: put all of the information together into a graph.</td><td>

Marks are awarded for:

the initial concentrations and changes in concentrations (1 mark)
the direction of movement of all reactants and products after the change is made (i.e. $[Fe^{3+}]$ and $[SCN^-]$ increase while $[FeSCN^{2+}]$ decreases) (1 mark)
all of the little bits and pieces, including:

horizontal lines at equilibrium
changes occurring according to the molar ratio
change lines reaching equilibrium together
change lines having a steeper change at the start and plateauing moving towards equilibrium (as rate is greatest after the change is made). (1 mark)

</td></tr>
</table>

Your turn

A solution of aqueous cobalt chloride is at equilibrium according to the reaction:

$$Co(H_2O)_6^{\ 2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{\ 2-}(aq) + 6H_2O(l)$$

Initially, the concentrations of reactants and products are 1.5 M, 6.0 M and 1.8 M, respectively. (Note that the water concentration is not represented here. Water should be included in your response because it is a product and part of the system but excluded on the graph as it has a constant concentration.) The volume of the reaction is tripled by adding water. When equilibrium is re-established, the concentration of $CoCl_4^{\ 2-}$ is 0.17 M.

a **Explain** the effect of this increase in volume on the equilibrium system. (2 marks)

b **Construct** a graph of the equilibrium change. (3 marks)

How do changes in temperature affect equilibrium?

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 required for a reaction to occur depends on the size of the activation energy and whether the reaction is exothermic or endothermic. Changing the temperature alters the rate of both the forward and the reverse reactions. Changing the temperature also alters the equilibrium position.

Endothermic reactions

In an endothermic reaction, products have more energy than reactants. This means that energy must be absorbed from the surroundings for the reaction to proceed because the enthalpy value is positive (Figure 3).

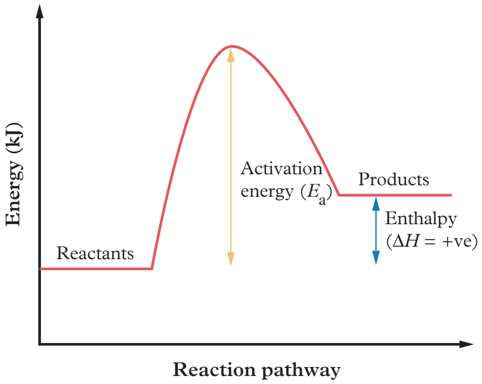


FIGURE 3 An endothermic reaction energy profile

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 in the direction that causes energy to be 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 (Table 4 and Worked example 2.2D).

It is worth noting that when constructing a graph for a change in temperature, there is a gradual change in reactants and products over time. This is because the concentration does not immediately change, i.e. a system will take time to reach a new equilibrium. This is the only graph where, in the initial change, all chemicals experience a gradual change, making a change in the temperature graph easy to identify.

TABLE 4 The structure for answering short-response questions about equilibrium

Change (what has happened?)	Le Châtelier says (how does the system partially oppose the change?)	Effect (on equilibrium position)
An increase in temperature in an endothermic system	causes the system to partially oppose the change by moving to the side that stores energy within product bonds	resulting in a net forward reaction. →
A decrease in temperature in an endothermic system	causes the system to partially oppose the change by moving to the side that releases energy from product bonds	resulting in a net reverse reaction. ←

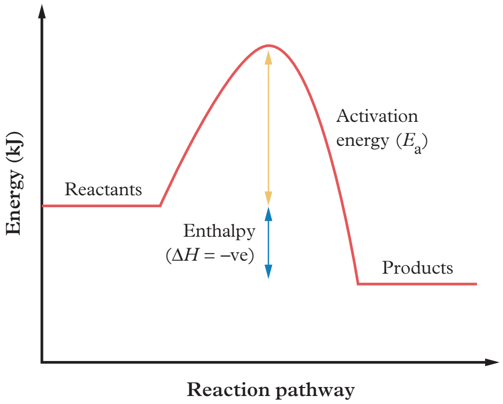


FIGURE 4 An exothermic reaction energy profile

Exothermic reactions

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 4).

In an exothermic reaction, energy is a product:

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

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

Table 5 will help you remember the effect of temperature on equilibrium. Table 6 will help you predict the effect of changes on endothermic and exothermic reactions.

TABLE 5 How changing temperature affects equilibrium reactions

Change (what has happened?)	Le Châtelier says (how does the system partially oppose the change?)	Effect (on equilibrium position)
An increase in temperature in an exothermic system	causes the system to partially oppose the change by moving to the side that stores energy within reactant bonds	resulting in a net reverse reaction. ←
A decrease in temperature in an exothermic system	causes the system to partially oppose the change by moving to the side that releases energy from reactant bonds	resulting in a net forward reaction. →

TABLE 6 An overall guide to predict the effect of changes in endothermic and exothermic systems

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 2.2D

Graphing temperature changes

Nitrogen and oxygen are in equilibrium with nitrogen monoxide:

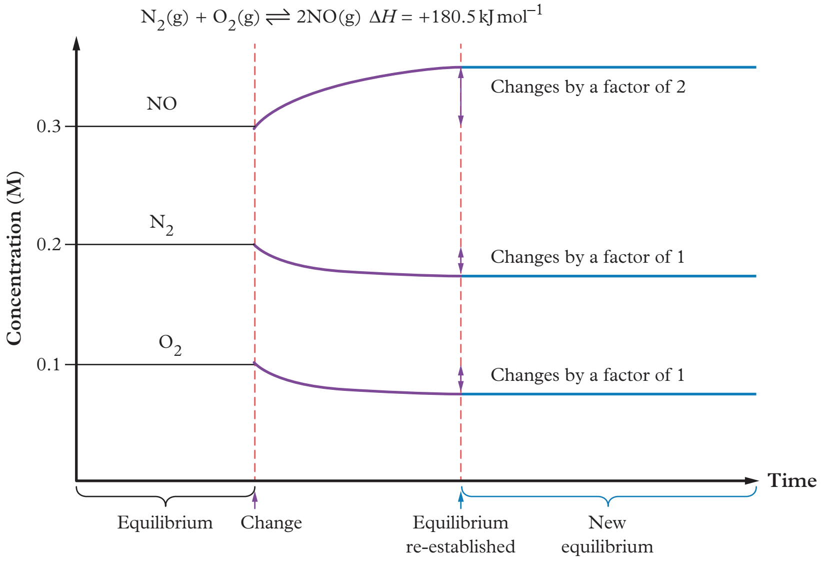
$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = +180.5\,\text{kJ mol}^{-1}$$

Initially, their concentrations are 0.2 M, 0.1 M and 0.3 M, respectively. The temperature of the system is increased and when equilibrium is re-established, the concentration of oxygen is found to be 0.05 M.

a **Explain** the effect of this increase in temperature on the equilibrium system. (2 marks)

b **Construct** a graph of the equilibrium change. (3 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	“Explain” means make an idea or situation plain or clear by describing it in more detail or revealing relevant facts. “Construct” means display information in a diagrammatic or logical form. We need to use Le Châtelier’s principle and the short-response structure to explain the effect of the change and then represent this diagrammatically in a graph by following the graphing rules.

<table>
<tr><th>Think</th><th>Do</th></tr>
<tr><td>Step 2: For part **a**, use Le Châtelier's principle to determine what will happen in the system.</td><td>**a** If temperature is increased in an endothermic system, Le Châtelier's principle states that the system will partially oppose an increase in energy by moving to the side where energy is stored within the bonds of the molecules. This is the product side because the products have more energy that the reactants. (1 mark)
Therefore, a net forward reaction results. (1 mark)</td></tr>
<tr><td>Step 3: For part **b**, initial equilibrium – before the change</td><td>**b** At equilibrium, the lines are horizontal, indicating a constant concentration before the change is made.</td></tr>
<tr><td>Step 4: Initial change</td><td>There is no initial change because there is no immediate increase or decrease in concentration.</td></tr>
<tr><td>Step 5: Direction of movement after the change is made</td><td>The system will move net forward, meaning that the reactants will decrease in concentration as the product increases in concentration.</td></tr>
<tr><td>Step 6: How large are the concentration changes?</td><td>The reaction changes by the molar ratio of $1N_2:1O_2:2NO$.</td></tr>
<tr><td>Step 7: Final equilibrium – after the change. Calculations to support this are included in a RICE table.</td><td>When equilibrium is re-established, the lines on the graph must be horizontal again.
<table>
<tr><th>R</th><th>N_2</th><th>O_2</th><th>2NO</th></tr>
<tr><td>I</td><td>0.2</td><td>0.1</td><td>0.3</td></tr>
<tr><td>C</td><td>−0.05</td><td>−0.05</td><td>+0.1</td></tr>
<tr><td>E</td><td>0.15</td><td>0.05 (given)</td><td>0.4</td></tr>
</table>
</td></tr>
<tr><td>Step 8: Final answer: put all of the information together into a graph.</td><td>


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

Marks are awarded for:

- the initial concentrations and gradual nature of the initial change (1 mark)
- the direction of movement of all reactants and products after the change is made (i.e. $[N_2]$ and $[O_2]$ decrease while [NO] increases) (1 mark)
- all of the little bits and pieces, including:
  - horizontal lines at equilibrium
  - changes occurring according to the molar ratio
  - change lines reaching equilibrium together
  - change lines having a steeper change at the start and plateauing moving towards equilibrium (as rate is greatest after the change is made).
</td></tr>
</table>

Your turn

Nitrogen and oxygen are in equilibrium with nitrogen monoxide:

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

Initially, their concentrations are 0.2 M, 0.1 M and 0.3 M, respectively. The temperature of the system is decreased and when equilibrium is re-established, the concentration of nitrogen monoxide is found to be 0.25 M.

a **Explain** the effect of this decrease in temperature on the equilibrium system. (2 marks)

b **Construct** a graph of the equilibrium change. (3 marks)

Worked example 2.2E

Graphing temperature changes

Phosphorus trichloride and chlorine gas are in equilibrium with phosphorus pentachloride:

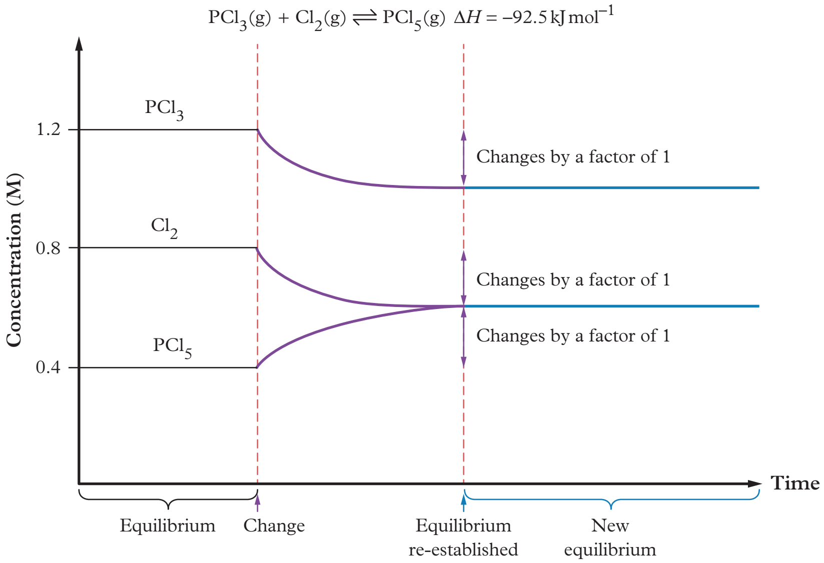
$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \qquad \Delta H = -92.5\,\text{kJ mol}^{-1}$$

Initially, their concentrations are 1.2 M, 0.8 M 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.

a **Explain** the effect of this decrease in temperature on the equilibrium system. (2 marks)

b **Construct** a graph of the equilibrium change. (3 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Explain" means make an idea or situation plain or clear by describing it in more detail or revealing relevant facts. "Construct" means display information in a diagrammatic or logical form. We need to use Le Châtelier's principle and the short-response structure to explain the effect of the change and then represent this diagrammatically in a graph by following the graphing rules.
Step 2: For part **a**, use Le Châtelier's principle to determine what will happen in the system.	**a** If temperature is decreased in an exothermic system, Le Châtelier's principle states that the system will partially oppose this decrease in energy by moving in the direction that will release energy from the molecules. This is the product side because the products have less energy than the reactants. (1 mark) Therefore, a net forward reaction results. (1 mark)
Step 3: For part **b**, initial equilibrium – before the change	**b** At equilibrium, the lines are horizontal, indicating a constant concentration before the change is made.
Step 4: Initial change	There is no initial change because there is no immediate increase or decrease in concentration.
Step 5: Direction of movement after the change is made	The system will move net forward, meaning that the reactants will decrease in concentration as the product increases in concentration.
Step 6: How large are the concentration changes?	The reaction changes by the molar ratio of $1PCl_3:1Cl_2:1PCl_5$.

<table>
<tr><th>Think</th><th>Do</th></tr>
<tr><td>Step 7: Final equilibrium – after the change. Calculations to support this are included in a RICE table.</td><td>When equilibrium is re-established, the lines on the graph must be horizontal again.
<table>
<tr><th>R</th><th>PCl_3</th><th>Cl_2</th><th>PCl_5</th></tr>
<tr><td>I</td><td>1.2</td><td>0.8</td><td>0.4</td></tr>
<tr><td>C</td><td>–0.2</td><td>–0.2</td><td>+0.2</td></tr>
<tr><td>E</td><td>0.10</td><td>0.6</td><td>0.6 (given)</td></tr>
</table></td></tr>
<tr><td>Step 8: Final answer: put all of the information together into a graph.</td><td>


Marks are awarded for:

- the initial concentrations and gradual changes (1 mark)
- the direction of movement of all reactants and products after the change is made (i.e. $[PCl_3]$ and $[Cl_2]$ decrease while $[PCl_5]$ increases) (1 mark)
- all of the little bits and pieces. This includes:
  - horizontal lines at equilibrium
  - changes occurring according to the molar ratio
  - change lines reaching equilibrium together
  - change lines having a steeper change at the start and plateauing moving towards equilibrium (as rate is greatest after the change is made). (1 mark)
</td></tr>
</table>

Your turn

Hydrogen and iodine react to form hydrogen iodide:

$$H_2 + I_2 \rightleftharpoons 2HI \qquad \Delta H = -170\,kJ\ mol^{-1}$$

At equilibrium, their concentrations are measured to be 0.5 M, 1.2 M and 3.5 M, respectively. The temperature of the system is increased. When equilibrium is re-established, the concentration of hydrogen is 1.0 M.

a **Explain** the effect of this increase in temperature on the equilibrium system. (2 marks)

b **Construct** a graph of the equilibrium change. (3 marks)

How does adding a catalyst affect equilibrium?

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

When a **catalyst** is added, it lowers the activation energy of the system. It increase the rates of both the forward reaction and the reverse reaction by the same amounts. 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 reverse 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.

Study tip

When composing written explanations of the effects of changes to systems that were at equilibrium, always refer to Le Châtelier's principle by its name when you describe how the reaction system will partially counteract the changes made.

Challenge

Volume changes in equilibrium

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 reversible reaction between nitrogen and oxygen, where the formation reaction for nitrogen monoxide from the elements has an enthalpy value of +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. (2 marks)

FIGURE 5 Nitrogen monoxide or nitric oxide is a colourless gas that is present in our blood vessels and used to signal when muscles need to relax to increase blood flow.

Real-world chemistry

Wine chemistry

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

Chemical balance in wine

A typical bottle of wine contains about 81% water and 12% alcohol. The remaining 7% consists 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 (thus preventing the alcohol from turning into vinegar), and inhibiting microbial activity.

Sulfites in wine

Glucose in grapes undergoes fermentation to form ethanol and carbon dioxide. The process requires a catalyst; yeasts are 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 hydrogen sulfite ions (formerly known as bisulfite) (HSO_3^-) and H_3O^+. The hydrogen sulfite ion further dissociates to form the sulfite ion (SO_3^{2-}) and a second H^+. The whole process forms the multistep equilibrium reaction:

$$SO_2 + 2H_2O \rightleftharpoons HSO_3^- + H_3O^+$$

$$HSO_3^- \rightleftharpoons SO_3^{2-} + H_3O^+$$

Because this equilibrium involves H_3O^+, 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_3O^+. This results in a net reverse reaction to remove the H_3O^+ and increases the concentration of SO_2 in the process. Sulfites have an optimal pH range of pH 3–4. In this pH range, HSO_3^- is the predominant form, with some free SO_2 present.

The sulfite ion can act as a preservative. SO_3^{2-} reacts with dissolved oxygen within the wine, preventing the oxygen from reacting with the ethanol. The product of this reaction is the hydrogen sulfate ion, 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:

$$2SO_3^{2-} + O_2 + 2H^+ \rightleftharpoons 2HSO_4^-$$

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

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

Apply your understanding

1 **Explain** why SO_2 is an essential molecule in wine making. (1 mark)

2 **Explain** the difference between fermentation and oxidation. (2 marks)

3 **Analyse** the impact of decreasing the pH of a wine on its ability to oxidise and limit microbial growth. (2 marks)

4 Assuming that the wine-making process is an aqueous one, **explain**, with reference to Le Châtelier's principle, a change that could be implemented to decrease the amount of sulfites in wine. (2 marks)

Skill drill

Drawing conclusions from data

Science inquiry skill: Processing and analysing data (Lesson 1.7)

A student investigates the reaction between a blue copper solution and a bromide solution according to the following reaction:

$$[Cu(H_2O)_4]^{2+}(aq) + 4Br^{-}(aq) \rightleftharpoons CuBr_4{}^{2-}(aq) + 6H_2O(l) \quad \Delta H = +ve$$

blue green

The solution is placed in separate test tubes. Initially, the equilibrium mixture is blue-green. Several changes are made to each reaction. The observations shown in Table 7 are recorded.

TABLE 7 Results of copper bromide equilibrium experiment

Change made to reaction	Original colour before change	Colour after change
Temperature is changed	Blue/green	Green
Reaction is diluted	Blue/green	Green
Lead(II) nitrate is added	Blue/green	Blue

Practise your skills

1 **Explain** the effect of adding lead(II) nitrate on the colour change observed in the reaction. (2 marks)

2 The student did not accurately record how the temperature changed. Use the data to **justify** the change that was made to the temperature. (3 marks)

3 **Explain** which of the three changes would result in an increase in equilibrium constant. (2 marks)

Check your learning 2.2

Check your learning 2.2: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** Le Châtelier's principle. (1 mark)

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

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

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

Construct a single graph for the following situations, which occur successively.

- **a** The mixture is at equilibrium for 10 seconds. (1 mark)
- **b** The volume of the system is halved. When equilibrium is re-established 20 seconds later, the concentration of nitrogen is 9.60 M. (3 marks)
- **c** At 20 seconds, the concentration of hydrogen is increased to 8.6 M. When equilibrium is re-established 15 seconds later, the concentration of ammonia is 10 M. (3 marks)
- **d** At 35 seconds, the temperature is increased. When equilibrium is re-established 30 seconds later, the concentration of nitrogen is 9.5 M. (3 marks)
- **e** At 65 seconds, the inert gas argon is added. (2 marks)

4 In the production of ammonia, a problem occurs at high temperatures.

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

- **a** **Explain** the effect that high temperatures have on the rate of a reaction and on the amount of ammonia produced according to Le Châtelier's principle. (3 marks) b **Identify** the problem at high temperatures. (1 mark)

c Based on what you have learnt in this module, **explain** what could be done to overcome this problem, and why it is effective. (1 mark)

Analytical processes

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

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

a The volume is increased. (2 marks)

b The temperature is decreased. (2 marks)

c The concentration of sulfur trioxide is increased. (2 marks)

d The temperature is increased. (2 marks)

Knowledge utilisation

6 NO_2 (a dark brown gas) and N_2O_4 (a colourless and highly toxic gas) are placed in a large sealed 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, **justify** why this happens. (3 marks)

Practical

Lesson 2.3

Investigating the effect of concentration on equilibrium

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Learning intentions and success criteria

Practical

Lesson 2.4

Investigating the effect of volume and pressure on equilibrium

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Learning intentions and success criteria

Practical

Lesson 2.5

Investigating the effect of temperature on equilibrium

Learning intentions and success criteria

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Lesson 2.6

The equilibrium constant (K_c) and solubility product (K_{sp})

Learning intentions and success criteria

Key ideas

→ Equilibrium law represents the ratio between concentrations of reactants and products, raised to appropriate powers, which also represents the position of equilibrium. This can be calculated as K_c (for homogeneous systems) or K_{sp} (for systems involving equilibria between solid compounds and their aqueous ions).

→ Equilibrium law can be used to calculate the amounts or concentrations of chemical species within an equilibrium system.

How do chemical concentrations contribute to equilibrium law?

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. **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:

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

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 (including solvents) and solids are not included in the equilibrium constant expression.

equilibrium law
the law that states that 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), which is a constant value for a particular reaction at a particular temperature.

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

Therefore, the equilibrium law can 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

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

Homogeneous and heterogeneous equilibria

A homogeneous equilibrium system (*homo* meaning "same") is one in which all the reactants and products are in the same state, such as all as gases or all in solution A heterogeneous equilibrium system (*hetero* meaning "different") is one in which the reactants and products are in different states, such as gases and solids.

For example:

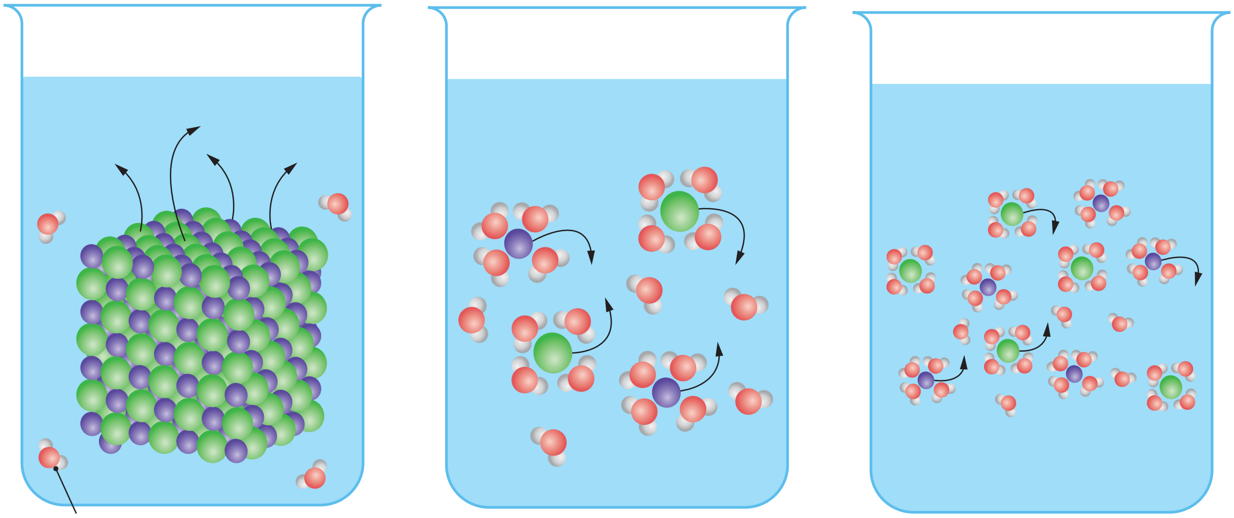
Homogeneous: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

All reactants and products are in the same phase: the gas state.

Heterogeneous: $NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$

NaCl(s) is in the solid state, and the aqueous ions are in the solution phase.

Heterogeneous systems, as in the dissolution of salts into aqueous system, work differently from homogeneous systems because of the difference in states. As seen in Figure 2, solids can only dissolve into water at the surface of the salt. As a result, certain changes imposed on a system at equilibrium may be fully counteracted, rather than partially counteracted. Dilution is an example. When the solid salt and the ions in solution are at equilibrium, adding water lowers the concentration of the ions. Provided there is sufficient solid, it will dissolve until the concentration of the ions is the same as the previous equilibrium.



The polar water molecules interact with salt ions on its surface.

As the salt begins to dissolve, dissolved ions begin to precipitate back out of solution forming a solid salt again.

When the rate of dissolution is equal to the rate of precipitation, equilibrium is achieved.

FIGURE 2 The equilibrium in a heterogeneous equilibrium system where the ions in the solid phase dissolve into the solution as ions in the solution precipitate back out as a solid.

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.

In homogeneous equilibria, all reactants and products exist in the same gaseous, liquid or aqueous state. This maximises the ability of particles to collide successfully, increasing not only the rate but the extent and yield of the reaction.

Calculating K_c in homogeneous systems

Equilibrium constants do not have units, i.e. they are dimensionless numbers. This is because what appears as concentrations in the simplified form of the equilibrium expression are actually each divided by the standard state (e.g. 1.0 M for species in solution). It is a very common misconception that equilibrium constants have units and you may find mistaken information on the internet about this. If you use K_c to calculate a concentration, the concentration unit should be shown with this answer.

Worked example 2.6A

Writing equilibrium expressions

Identify the equilibrium expression for the following equilibrium equation. (1 mark)

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

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Identify" means distinguish; locate, recognise and name; establish or indicate who or what someone or something is. We need to write the K_c expression for the equation given.
Step 2: Put the equation into the K_c expression, remembering that products are on top, and all reactants and products are to the power of their coefficients.	$K_c = \frac{[CO_2]^2}{[CO]^2[O_2]}$ (1 mark)

Your turn

Identify the equilibrium expression for the following equilibrium equation. (1 mark)

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

Worked example 2.6B

Calculating the equilibrium constant K_c

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

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

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to write the equation to determine the equilibrium expression and use the expression to solve the problem.
Step 2: Identify the equilibrium expression.	$K_c = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2}$
Step 3: Substitute the values into the equilibrium expression.	$K_c = \frac{2 \times 2^2}{2^2 \times 2^2}$ $= 0.5$ (1 mark)
Step 4: Finalise your answer to 1 s.f.	$K_c = 0.5$ (1 mark)

Your turn

Calculate the equilibrium constant (K_c) for the following equilibrium equation, where the concentration of all reactants and products is 0.25 M. (2 marks)

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

What does the magnitude of K_c show?

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 $K_c > 10^2$, which is a large number, it contains significantly more product(s) than reactant(s).
- If $K_c < 10^{-2}$, which is a small number, it contains significantly more reactant(s) than product(s).
- Anywhere between these values indicates that there is a significant amount of both reactants and products in the system.

What is the solubility product (K_{sp})?

Equilibrium constants can also apply to solid salts as they dissolve, dissociate or ionise in a solution. This equilibrium constant is called the solubility product, K_{sp}. It reflects the equilibrium position of a saturated solution of slightly soluble ionic compound. This is an equilibrium, because at the same time that the solid is dissolving into the solution, ions are coming out of solution and re-forming solid. The rate of dissolving is the same as the rate of reforming the solid.

- The higher K_{sp} is, the more soluble a salt is because the concentration of product (ions in solution) will increase.

- The lower K_{sp} is, the less soluble a salt is because the concentration of product (ions in solution) will decrease.

For salts with different ionic ratios, it is not as easy to directly compare K_{sp} values, in order to compare solubilities, unless they are very different. Further calculations would need to be used.

You will notice that in neither point above is the solid salt referred to. A general ionic compound, A, dissociates in water according to the reaction:

$$aA(s) \rightleftharpoons cC(aq) + dD(aq)$$

The solubility product seems as though it would be expressed as:

$$K_{sp} = \frac{[C]^c[D]^d}{[A]^a}$$

Pure solids and liquids are never included in equilibrium constant expressions. This is similar to the water in the expression for K_w (Lesson 3.3). If included, it does not change the value of K_{sp}, and therefore it is excluded from the expression. For this reason the expression is simplified to:

$$K_{sp} = [C]^c[D]^d$$

Consider how the expression changes with the formulas of the solid ionic salts:

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

The K_{sp} expression becomes:

$$K_{sp} = [Ca^{2+}][OH^-]^2$$

or

$$FeCl_3(s) \rightleftharpoons Fe^{3+}(aq) + 3Cl^-(aq)$$

The K_{sp} expression becomes:

$$K_{sp} = [Fe^{3+}][Cl^-]^3$$

Worked example 2.6C

Solubility product expressions

Identify the equation and write the expression for the solubility product of sodium sulfate in water. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Identify" means distinguish; locate, recognise and name; establish or indicate who or what someone or something is. We need to find the anion and cation that make the solid salt, write it into a dissociation reaction and write the K_{sp} expression.
Step 2: What is the formula of the solid salt?	The ionic formula for sodium is Na^+ and sulfate is SO_4^{2-}. The salt has the formula $Na_2SO_4(s)$.
Step 3: Write the chemical equation.	$Na_2SO_4(s) \rightleftharpoons 2Na^+(aq) + SO_4^{2-}(aq)$ (1 mark)
Step 4: Write the K_{sp} expression, excluding the solid salt.	$K_{sp} = [Na^+]^2[SO_4^{2-}]$ (1 mark)

Your turn

Identify the equation and write the expression for the solubility product of ammonium carbonate in water. (2 marks)

How is K_{sp} calculated from solution concentrations?

In K_{sp} calculations, it is important to recognise that if the salt is added to pure, deionised water, then the concentrations of ions in solution will follow their molar ratio.

For example, the dissociation of solid silver nitrate ($AgNO_3$) according to the following equation indicates that the silver ions and the nitrate ions will have the same concentrations in solution, as they dissociate in a 1:1 ratio:

$$AgNO_3(s) \rightleftharpoons Ag^+(aq) + NO_3^-(aq)$$

In the K_{sp} expression, the concentration of ions can be simplified from:

$$K_{sp} = [Ag^+][NO_3^-]$$

to

$$K_{sp} = s^2$$

where s represents the molar solubility of silver nitrate, measured in mol L^{-1}.

For 1:1 salts dissolved in water, both ions have the same concentration, which is the solubility of the salt, s, The same number is multiplied by itself, which is the equivalent of squaring the number.

For example, the salt AgCl dissolves and dissociates in very small amounts:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The solubility of AgCl in mol L^{-1} is represented by s. Since the mole ratio in the chemical equation is 1:1:1, $[Ag^+] = [Cl^-] = s$ when AgCl dissolves in pure water.

The K_{sp} expression is:

$$K_{sp} = [Ag^+]\ [Cl^-]$$

And it can be simplified to s^2.

Consider the dissociation of iron(III) sulfide:

$$Fe_2S_3(s) \rightleftharpoons 2Fe^{3+}(aq) + 3S^{2-}(aq)$$

The K_{sp} expression is:

$$K_{sp} = [Fe^{3+}]^2[S^{2-}]^3$$

The solubility of Fe_2S_3 in mol L^{-1} is represented by s, and the mole ratio in the chemical equation is 1:2:3, so $[Fe^{3+}] = 2s$ and $[S^{2-}] = 3s$, and the K_{sp} expression can be simplified to:

$$(2s)^2(3s)^3 = 4s^2 \times 27s^3 = 108s^5$$

The situation in Worked example 2.6E arises when an insoluble salt is in a solution containing another salt with one of the ions in the insoluble salt. The ion is common to both salts. The insoluble salt will be less soluble in this solution than in pure water, due to the presence of this common ion, so this is called the common ion effect. Worked example 2.6F shows this effect.

Study tip

Use the number of moles of each ion in the equation to multiply by s determine the concentration of each ion. Use brackets in working for K_{sp}. Everything inside the brackets also needs to be raised to the appropriate power

Worked example 2.6D

Calculating ion concentration from K_{sp}

The solubility product of lead(II) bromide at 25°C is 6.6×10^{-6}.

a **Identify** the chemical equation. (1 mark)

b **Identify** the equilibrium expression. (1 mark)

c **Calculate** the concentrations of Pb^{2+} ions and Br^- ions in the solution. (4 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	“Identify” means distinguish; locate, recognise and name. “Calculate” means to determine or find a number or answer by using mathematical processes. We need to write the equation to determine the equilibrium expression and use the expression to solve the problem.
Step 2: For part **a**, identify the formula of the solid salt.	**a** The ionic formula for lead(II) is Pb^{2+} and bromide is Br^-. The salt has the formula $PbBr_2$.
Step 3: Write the chemical equation.	$PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$ (1 mark)
Step 4: For part **b**, write the K_{sp} expression, excluding the solid salt.	**b** $K_{sp} = [Pb^{2+}][Br^-]^2$ (1 mark)
Step 5: For part **c**, substitute the value of K_{sp} into the equation.	**c** $6.6 \times 10^{-6} = [Pb^{2+}][Br^-]^2$
Step 6: Recognise that when the salt dissociates, it does it by $1Pb^{2+}$ and $2Br^-$. Therefore, the equation can be simplified.	$[Pb^{2+}] = s$ and $[Br^-] = 2s$ $6.6 \times 10^{-6} = s(2s)^2 = 4s^3$ (1 mark)
Step 7: Solve for s.	$s = \sqrt[3]{\frac{6.6 \times 10^{-6}}{4}} = 0.0118$ (1 mark)
Step 8: Finalise your answer to 2 s.f. and with appropriate units.	$[Pb^{2+}] = s = 0.0118$ mol L^{-1} (1 mark) $[Br^-] = 2s = 0.0236$ mol L^{-1} (1 mark)

Your turn

The solubility product of silver sulfate at SLC is 1.2×10^{-5}.

a **Identify** the chemical equation. (1 mark)

b **Identify** the equilibrium expression. (1 mark)

c **Calculate** the concentrations of Ag^+ and SO_4^{2-} ions in the solution. (4 marks)

Worked example 2.6E

Calculating ion concentration from K_{sp}

The solubility product at 25°C of CaF_2 is $K_{sp} = 3.9 \times 10^{-11}$. The concentration of the fluoride ions is found to be 0.10 M at equilibrium.

a **Identify** the equilibrium reaction. (1 mark)

b **Identify** the equilibrium expression. (1 mark)

c **Calculate** the equilibrium concentration of the calcium ion, stating any assumptions. (2 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	“Identify” means distinguish; locate, recognise and name. “Calculate” means to determine or find a number or answer by using mathematical processes. We need to write the equation to determine the equilibrium expression and use the expression to solve the problem.
Step 2: For part **a**, write the chemical equation.	**a** $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$ (1 mark)

Think	Do
Step 3: For part **b**, write the expression for K_{sp}, excluding the solid salt.	**b** $K_{sp} = [Ca^{2+}][F^-]^2$ (1 mark)
Step 4: For part **c**, substitute the value of K_{sp} and fluoride concentration into the equation.	**c** $3.9 \times 10^{-11} = [Ca^{2+}]\ (0.10)^2$ Assumption: Note that $[Ca^{2+}] = s$, the solubility of CaF_2. $[F^-] = (0.10 + 2s)$. Since K_{sp} is very small, $2s$ is much smaller than 0.1, and $0.1 + 2s$ can be assumed to be 0.1. (1 mark)
Step 5: Solve for $[Ca^{2+}]$.	$[Ca^{2+}] = \frac{3.9 \times 10^{-11}}{0.10^2} = 3.9 \times 10^{-9}$ M
Step 6: Finalise your answer to 2 s.f. and with appropriate units.	$[Ca^{2+}] = 3.9 \times 10^{-9}$ M (1 mark)

Your turn

The solubility product of lead sulfate at SLC is $K_{sp} = 1.8 \times 10^{-8}$. The concentration of the sulfate ions is found to be 0.050 M at equilibrium.

a **Identify** the equilibrium reaction. (1 mark)

b **Identify** the equilibrium expression. (1 mark)

c **Calculate** the equilibrium concentration of the lead ion, stating any assumptions. (2 marks)

Worked example 2.6F

Calculating the concentrations of ions in aqueous solution

Silver chloride has a K_{sp} of 1.8×10^{-10}. **Calculate** the concentration of Ag^+ ions when AgCl reaches solubility equilibrium in a 0.1 M solution of $CaCl_2$. (4 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to do multiple steps. The concentration of Cl^- ions needs to be calculated first. Then we need to write the equation to determine the equilibrium expression and use the expression to solve the problem.
Step 2: Calculate the concentration of Cl^- ions present in the $CaCl_2$ solution. It will be double the concentration of the solution, since the ratio is 1:2.	$[Cl^-] = 2 \times 0.1$ $= 0.2$ M (1 mark)
Step 3: Write the chemical equation.	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ (1 mark)
Step 4: Write the K_{sp} expression.	$K_{sp} = [Ag^+][Cl^-]$
Step 5: Substitute and solve for $[Ag^+]$.	$1.8 \times 10^{-10} = [Ag^+] \times 0.2$ (1 mark) $[Ag^+] = \frac{1.8 \times 10^{-10}}{0.2}$ $= 9 \times 10^{-10}$
Step 6: Finalise your answer to 2 s.f. and with appropriate units.	$[Ag^+] = 9.0 \times 10^{-10}$ M (1 mark)

Your turn

Lead fluoride has a K_{sp} of 3.7×10^{-8}. **Calculate** the concentration of F^- ions when PbF_2 reaches solubility equilibrium in a 0.2 M solution of $PbNO_3$. (4 marks)

Real-world chemistry

Ocean acidification

Atmospheric carbon dioxide (CO_2) is a significant concern to the world's oceans. It dissolves readily in water according to the following equation:

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

Once dissolved in water, carbon dioxide reacts to form carbonic acid (H_2CO_3). As the concentration of CO_2 in the atmosphere increases, the reaction is driven net forward to partially oppose the change, producing more carbonic acid:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \qquad K = 1.7 \times 10^{-3}$$

As the carbonic acid concentration increases, these molecules rapidly decompose into the hydrogencarbonate ions (HCO_3^-) and hydrogen ions (H^+). An increase in the concentration of carbonic acid will drive this reaction net forward, but a decrease in its concentration will drive the reaction net backwards. This increase in the concentration of hydrogen ions increases the acidity, so decreases the pH, of the oceans.

$$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq) \qquad K = 2.5 \times 10^{-4}$$

A further reaction occurs when the hydrogencarbonate ion dissociates into the carbonate ion (CO_3^{2-}) and the hydrogen ion (H^+). This lowers the pH of the oceans further. Figure 4 provides an overall reaction process for ocean acidification.

$$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq) \qquad K = 1.0 \times 10^{-10}$$

Although this implies that the oceans will become acidic, in reality, because of the volume of the oceans and the concentration of the hydrogen ion in them, the pH is still relatively close to 7. However, even a minor change in pH can cause drastic changes to marine and aquatic life. In the eighteenth century, before the Industrial Revolution, the pH of the oceans was 8.18. Currently, the average pH of the oceans is 8.07 and is projected to reach 7.95 by 2050.

As the carbonate ion (CO_3^{2-}) is released into the oceans, it binds to calcium ions (Ca^{2+}), which aquatic organisms use to build and strengthen shells according to the reaction:

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

This results in fewer calcium ions available to build corals and shells. Figure 3 demonstrates the weakening of a shell made of calcium carbonate over a period of days under the acidic conditions of the ocean expected by 2100. After 45 days, the shell has almost completely dissolved.

FIGURE 3 A mollusc shell dissolves under acidic conditions.

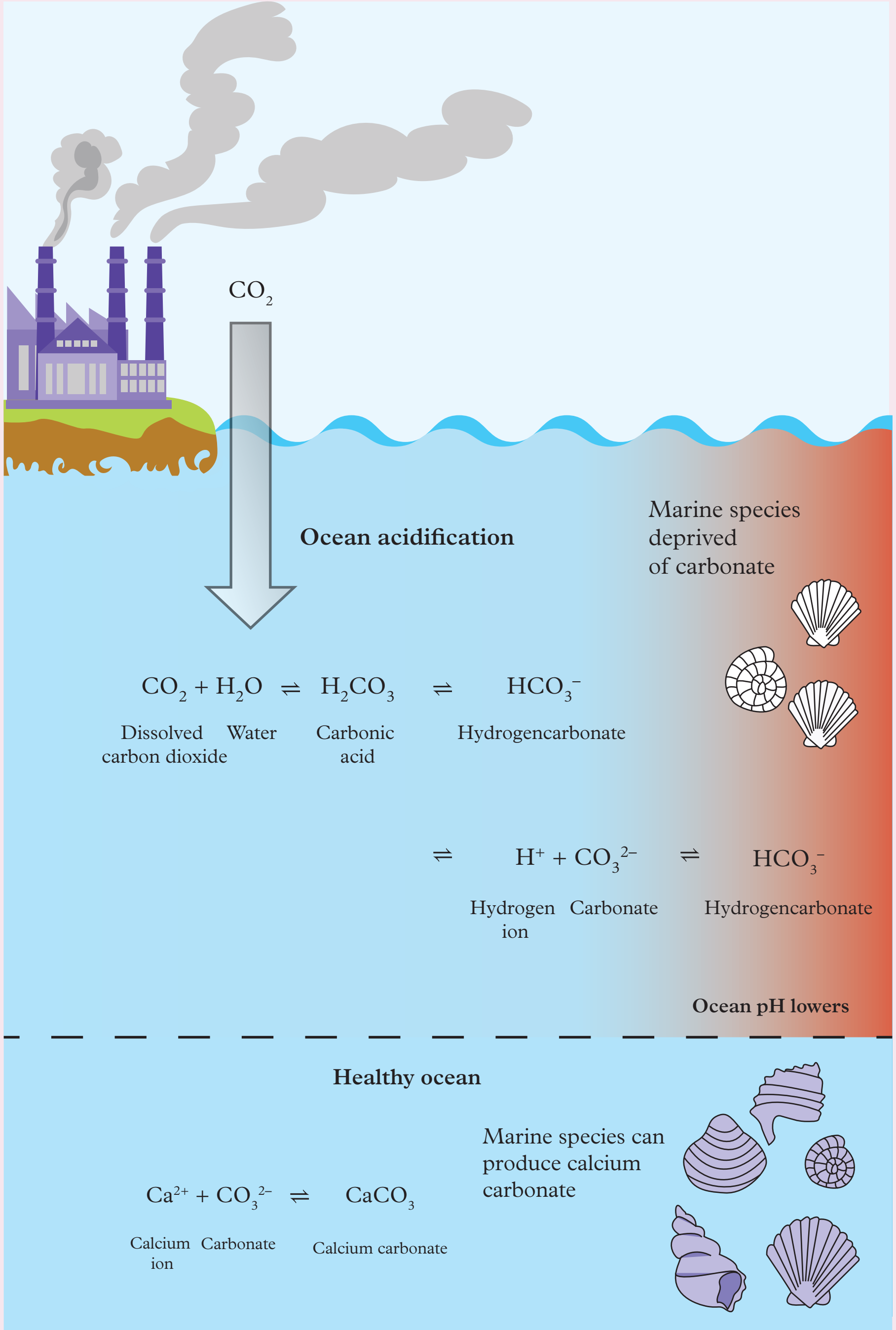


FIGURE 4 The chemical reactions involved in the acidification of the world's oceans

Apply your understanding

1 **Explain** the process of the weakening shells of aquatic life and why this process cannot be reversed. (3 marks)

2 Using Le Châtelier's principle, **explain** the effect of decreasing atmospheric CO_2 on the pH of the oceans. (2 marks)

3 **Compare** the values of *K*. **Explain** what they indicate about the position of equilibrium for the three reactions. (3 marks)

Challenge

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? (3 marks)

Check your learning 2.6

Check your learning 2.6: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** the effect on K_c when the concentrations of reactants in a chemical equation increase. (2 marks)

2 **Describe** the effect on K_c in an exothermic system when the temperature decreases. (2 marks)

3 2 mol of H_2 and 3 mol of I_2 are pumped into a 4 L vessel to form HI. At equilibrium, the concentration of HI is 0.9 M. **Calculate** the equilibrium constant. (3 marks)

4 10.0 mL of a 0.80 M solution of $Fe(NO_3)_3$ and 10.0 mL of a 0.40 M solution of KSCN are added together to make a 20.0 mL solution and dilute each other. The Fe^{3+} ions react with the SCN^- ions, forming $FeSCN^{2+}$ in a reversible reaction. At equilibrium, the concentration of SCN^- is 0.01 M. **Calculate** the equilibrium constant. (3 marks)

5 Use the following solubility products of some salts to **calculate** the concentration of the specified ion in solution.

- **a** $K_{sp}(Ag_2Cr_2O_4) = 1.12 \times 10^{-12}$, calculate $[Ag^+]$ (3 marks)
- **b** $K_{sp}(MgF_2) = 5.16 \times 10^{-11}$, calculate $[F^-]$ (3 marks)

6 Use the concentrations of the following ions in a saturated solution to **calculate** the K_{sp} of the salt.

- **a** $Cr(OH)_3$ salt: $[Cr^{3+}] = 2.9 \times 10^{-8}$ M (3 marks)
- **b** $Zn(CN)_2$ salt: $[CN^-] = 4.0 \times 10^{-8}$ M (3 marks)

Analytical processes

7 **Determine** the equilibrium law expression for the following reactions. (1 mark each)

- **a** $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
- **b** $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$
- **c** $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
- **d** $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

8 **Distinguish** between K_c and K_{sp}. (1 mark)

Knowledge utilisation

9 **Evaluate** the statement "Catalysts have no effect on K_c or K_{sp}". In your response, **justify** whether this is true or false. (3 marks)

10 Many salts are more soluble at higher temperatures. **Determine** the effect that a decrease in temperature has on K_{sp} for these ionic salts. (2 marks)

Practical

Lesson 2.7

Determining the K_{sp} of calcium hydroxide

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Learning intentions and success criteria

Lesson 2.8

The reaction quotient (*Q*)

Key ideas

→ The ratio between reactants and products in systems that are not at equilibrium is called the reaction quotient, *Q*.

→ The comparison of *Q* and the value of K_c or K_{sp} can determine whether an equilibrium reaction is favouring the forward or reverse reaction, and what has to happen to the reaction in order to reach equilibrium.

What effect do changes have on a K_c or K_{sp} value?

Learning intentions and success criteria

K_c values

In Lesson 2.2, you learnt that there are several changes that can be made to an equilibrium system. According to Le Châtelier's principle, these changes are opposed or partially opposed and the system will reach a new equilibrium afterwards.

For any change in concentration (e.g. by changing volume, pressure or dilution, and or adding or removing a reactant or product), the ratio between the concentrations of reactants and products, raised to the appropriate powers, remains the same as the system re-establishes equilibrium after the change is made. For this reason, K_c remains constant. It is the same before and after the change.

However, this is not the case for temperature. Any change to the temperature of a system is not a change in concentration but a change in energy. For this reason, increasing or decreasing temperature will result in a difference in the ratio of reactants to products and a change in K_c after the system re-establishes equilibrium at a new temperature.

K_{sp} values

The solubility product follows the same key understanding as K_c, because both are equilibrium constants. Any change to the equilibrium will have no effect on the value of K_{sp}, other than temperature.

The concentration of a solid salt cannot be increased, and any addition of an aqueous salt with a common ion results in a net reverse reaction until concentrations that achieve the K_{sp} are obtained.

This is an aqueous system, which can only be diluted by adding water, thereby decreasing all concentrations simultaneously. Water cannot be removed quickly to increase all salt concentrations. This continues until the change has been fully opposed and the same concentrations of both ions are obtained. The product is again equal to the K_{sp}.

However, temperature has a different effect, as we have seen in solubility curves in the past (*Chemistry for Queensland Units 1 & 2*, Module 13). Increasing the temperature generally increases the solubility of most salts, resulting in more ions in solution, higher concentrations and larger values of K_{sp}. However, some salts such as calcium hydroxide have decreased solubility as temperature increases.

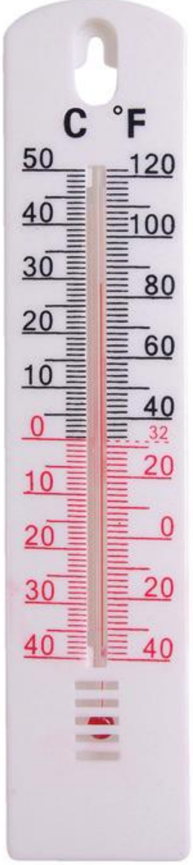


FIGURE 1 Temperature is the only parameter that affects the value of K_c or K_{sp} of a system.

How do you complete calculations when a system is not at equilibrium?

reaction quotient (Q_c)
the ratio of concentration of products to reactants, raised to the appropriate powers in a system when it is not at equilibrium

If a system is not at equilibrium, you can calculate the **reaction quotient (Q_c)**, which has the same form as an equilibrium constant, but does not use equilibrium concentrations. It 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 tables

For systems where you must calculate equilibrium, you can use a RICE table (Table 1). Worked example 2.8A demonstrates this process.

TABLE 1 RICE table

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

Worked example 2.8A

Calculating changes to equilibrium systems

3.0 mol of SO_2 and 2.0 mol of O_2 are pumped into an empty 1.00 L container. At equilibrium, the concentration of the only product (SO_3) is 2.00 M. **Calculate** the value of K_c for the reaction system. (4 marks)

<table>
<tr><th>Think</th><th>Do</th></tr>
<tr><td>Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.</td><td>“Calculate” means to determine or find a number or answer by using mathematical processes. We need to write the equation to determine the equilibrium expression and use the expression to solve the problem.</td></tr>
<tr><td>Step 2: Write a balanced chemical equation.</td><td>$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$</td></tr>
<tr><td>Step 3: Convert all mole amounts to concentrations.</td><td>As $c = \frac{n}{V}$, and the volume of the container is 1 L, divide all mole amounts by 1 to convert to concentrations.
Initial $[SO_2] = 3\,M$
Initial $[O_2] = 2\,M$ (1 mark)</td></tr>
<tr><td>Step 4: Recognise that when SO_2 and O_2 are pumped into the container, it is empty.</td><td>Initially, there is no product, only reactants in the vessel.
Initial $[SO_3] = 0\,M$</td></tr>
<tr><td>Step 5: Recognise that the concentration of SO_3 is measured at equilibrium.</td><td>$[SO_3]$ has increased from 0 M (initially) to 2 M at equilibrium.</td></tr>
<tr><td>Step 6: Use the information to complete a RICE table.</td><td>
<table>
<tr><th>R</th><th>$2SO_2$</th><th>O_2</th><th>$2SO_3$</th></tr>
<tr><td>I</td><td>3</td><td>2</td><td>0</td></tr>
<tr><td>C</td><td></td><td></td><td></td></tr>
<tr><td>E</td><td></td><td></td><td>2</td></tr>
</table>
</td></tr>
<tr><td>Step 7: Determine the change in the product by finding the difference between the initial and equilibrium concentrations.</td><td>
<table>
<tr><th>R</th><th>$2SO_2$</th><th>O_2</th><th>$2SO_3$</th></tr>
<tr><td>I</td><td>3</td><td>2</td><td>0</td></tr>
<tr><td>C</td><td></td><td></td><td>+2</td></tr>
<tr><td>E</td><td></td><td></td><td>2</td></tr>
</table>
(1 mark)</td></tr>
<tr><td>Step 8: 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.</td><td>
<table>
<tr><th>R</th><th>$2SO_2$</th><th>O_2</th><th>$2SO_3$</th></tr>
<tr><td>I</td><td>3</td><td>2</td><td>0</td></tr>
<tr><td>C</td><td>–1 × 2 = –2</td><td>–1 × 1 = –1</td><td>+2</td></tr>
<tr><td>E</td><td>3 – 2 = 1</td><td>2 – 1 = 1</td><td>2</td></tr>
</table>
(1 mark)</td></tr>
<tr><td>Step 9: Determine the equilibrium expression and use the equilibrium values to find the value of K_c.</td><td>$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$
$= \frac{2^2}{1^2 \times 1}$
$= \frac{4}{1}$
$= 4$</td></tr>
<tr><td>Step 10: Express your final answer to 2 s.f. Remember that equilibrium constants do not have units.</td><td>$K_c = 4.0$ (1 mark)</td></tr>
</table>

Your turn

7.0 mol of H_2 and 3.0 mol of I_2 are pumped into an empty 2.00 L container. At equilibrium, the concentration of the only product (HI) is 0.50 M. **Calculate** the value of K_c for the reaction system. (4 marks)

Worked example 2.8B

Calculating changes to equilibrium systems

In a gaseous system, initially, 36 mol of H_2, 16 mol of N_2 and 28 mol of NH_3 are pumped into a 4 L container. For the reaction:

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

K_c is 5×10^{-5} under the conditions in the container.

a **Calculate** the reaction quotient (Q) for the reaction when the chemicals are initially added to the vessel. What can you conclude about this value? (3 marks)

b **Infer** the direction of the reaction to reach equilibrium by using Q and K_c values. (2 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. "Infer" means derive or conclude something from evidence and reasoning, rather than from explicit statements. We need to write the equation to determine the equilibrium expression and use the RICE table to calculate Q then use the Q and K values to infer the direction the reaction must proceed to reach equilibrium.
Step 2: Write a balanced chemical equation.	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
Step 3: For part **a**, calculate the initial concentrations.	**a** $[N_2]$ (initially) $= \frac{n}{V} = \frac{16}{4} = 4$ M $[H_2]$ (initially) $= \frac{n}{V} = \frac{36}{4} = 9$ M $[NH_3]$ (initially) $= \frac{n}{V} = \frac{28}{4} = 7$ M (1 mark)
Step 4: Put the concentration values in the Q expression then solve with correct significant figures.	$Q = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{7^2}{9^3 \times 4} = \frac{49}{2916} = 0.0168$ (1 mark)
Step 5: Explain what you can conclude about the value of Q.	The value is small because there is a larger denominator in the fraction. This means that, initially, there are more reactants present in the system. (1 mark)
Step 6: For part **b**, use the Q and K values in your response and compare them to determine which is larger or smaller.	**b** Q (0.0168) is larger (has more products) than K_c (5×10^{-5}) (has more reactants). (1 mark)
Step 7: Depending on the quantities of reactant and product, infer the direction of equilibrium.	This means that, after the chemicals were initially added to the container, the system moved in a net reverse reaction to reach equilibrium (K_c). (1 mark)

Your turn

At very high temperatures, hydrogen sulfide decomposes to hydrogen and sulfur gases according to the equation below. Initially, 12 mol of H_2S (g), 3 mol of H_2(g) and 3 mol of S_2(g) are pumped into an empty 3.00 L vessel.

$$2H_2S \rightleftharpoons 2H_2 + S_2$$

At equilibrium, the system is found to have a value of K_c of 1.5×10^{-4}.

a **Calculate** the reaction quotient (Q) for the reaction when the chemicals are initially added to the vessel. What can you conclude about this value? (3 marks)

b **Infer** the direction of the reaction to reach equilibrium by using Q and K_c values. (2 marks)

Challenge

Calculating equilibrium constants

Sulfur dioxide undergoes an oxidation reaction to form sulfur trioxide:

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

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% of the oxygen has been converted to product.

Calculate the equilibrium constant for the reaction. (5 marks)

What are the effects of reaction changes on the value of K_c?

Of all of the changes discussed in Lesson 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. If the chemical equation is written differently, the equilibrium constant expression is different and the value of K_c changes for this reason. Reversing a chemical equation results in an inverse of the value of K_c, doubling the coefficients squares the value of K_c and halving the coefficients results in the square root of the value of K_c.

Worked example 2.8C

Effects of reaction changes on the equilibrium constant K_c or K_{sp}

Consider the reaction between nitrogen and hydrogen to form ammonia:

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

Calculate the effect on the equilibrium constant when the

a reaction is reversed (1 mark)

b coefficients are tripled (1 mark)

c coefficients are halved. (1 mark)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. You need to remember that when you: • double coefficients, the value of K_c squares • triple coefficients, the value of K_c cubes • reverse the equation, you get the inverse of K_c ($\frac{1}{K_c}$).
Step 2: For part **a**, reverse = inverse.	**a** $\frac{1}{95.6} = 0.0105$ (1 mark)
Step 3: For part **b**, tripled = cubed.	**b** $95.6^3 = 8.74 \times 10^5$ (1 mark)
Step 4: For part **c**, halved = square root.	**c** $\sqrt{95.6} = 9.78$ (1 mark)

Your turn

Consider the reaction between carbon monoxide and hydrogen to form methanol vapour:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \; K_c = 122.8$$

Calculate the effect on the equilibrium constant when the

a reaction is reversed (1 mark)

b coefficients are tripled (1 mark)

c coefficients are halved. (1 mark)

Skill drill

Analysing equilibrium data

Science inquiry skill: Processing and analysing data (Lesson 1.7)

In laboratory tests, a student performs several tests on the cobalt(IV) chloride reaction:

$$\underset{\text{blue}}{CoCl_4^{2-}(aq)} + 6H_2O(l) \rightleftharpoons \underset{\text{pink}}{Co(H_2O)_6^{2+}(aq)} + 4Cl^-(aq)$$

When both of the coloured compounds are present in an equilibrium mixture, the colour is described as purple.

The results of each test are outlined in Table 2.

TABLE 2 Results of equilibrium tests on the cobalt chloride system

Test	Observation
Addition of $AgNO_3$	Precipitate formed and colour changes from purple to pink
Addition of water	Colour changes from purple to pink in colour
Hot water bath	Colour changes from purple to blue in colour

Practise your skills

1 **Explain** why the results in the silver nitrate test were observed. (3 marks)

2 Use the data in the table to **justify** whether the reaction is exothermic or endothermic. (3 marks)

3 Students are asked to write predictions for each test in advance of conducting the experiment. The student predicts: “For the addition of water, the system will become diluted and partially oppose the change by favouring the side with more particles.”

Analyse the student’s prediction and **discuss** its accuracy. Provide reasons for your answer. (3 marks)

Real-world chemistry

Eunice Foot: A pioneer in climate science

In 1856, Eunice Newton Foote (1819–88), a US scientist and inventor, made a groundbreaking contribution to the understanding of climate science. Her work, presented in a paper titled “Circumstances Affecting the Heat of the Sun’s Rays”, was one of the earliest studies to link carbon dioxide with Earth's temperature – a foundation for modern climate change science.

Foote conducted simple yet innovative experiments using glass cylinders filled with various gases, including carbon dioxide. She exposed the cylinders to sunlight and measured their temperature changes. Foote discovered that carbon dioxide absorbed more heat than regular air and retained that heat for longer periods. She concluded that changes in atmospheric CO_2 levels could significantly influence Earth’s temperature, stating, “An atmosphere of that gas would give to our Earth a high temperature”.

Despite the significance of her findings, Foote's work received little attention, overshadowed by that of her male contemporaries. Her paper was presented at the American Association for the Advancement of Science by a male colleague because women were not allowed to present at such events.

Foote's work predated John Tyndall's more famous studies on greenhouse gases by 3 years, underscoring her pioneering role. Today, Eunice Newton Foote is recognised as a trailblazer whose insights foreshadowed the critical challenges of climate change.

FIGURE 2 Eunice Newton Foote

Apply your understanding

Use the following information to answer questions 1 and 2.

The increase in atmospheric CO_2 concentrations leads to its dissolution in oceans, forming carbonic acid (H_2CO_3). The equilibrium reaction is:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

1 **Determine** how an increase in atmospheric CO_2 would change the position of equilibrium, and what impact this would have on ocean acidity. (2 marks)

2 **Predict** the effects of continued CO_2 emissions on marine ecosystems using Le Châtelier's principle. (2 marks)

3 Methane (CH_4), another greenhouse gas, reacts with oxygen in the atmosphere to form carbon dioxide and water:

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

Determine how increasing CO_2 concentrations in the atmosphere would influence this equilibrium reaction. (2 marks)

Check your learning 2.8

Check your learning 2.8: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain** the difference between Q and K_c or K_{sp}. (2 marks)

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

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ $K_c = 4.20$

Calculate the effect on the equilibrium constant when the

- **a** reaction is reversed (1 mark)
- **b** coefficients are tripled (1 mark)
- **c** coefficients are halved. (1 mark)

Analytical processes

3 10 mol of SO_2, 6 mol of O_2 and 8 mol of SO_3 are added to a 2 L vessel.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $K_c = 2.0 \times 10^{-2}$

Evaluate this information to

- **a** **calculate** Q_c (4 marks)
- **b** **infer** in which direction the reaction must proceed to reach equilibrium. **Explain** your answer, using the values of K_c and Q_c. (2 marks)

4 A closed vessel contains 6 M NO, 8 M O_2 and 10 M NO_2.

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

Evaluate the above information to

- **a** **calculate** Q_c (2 marks)
- **b** **infer** in which direction the reaction must proceed to reach equilibrium. **Explain** your answer, using the values of K_c and Q_c. (2 marks)

5 A reaction has $Q = 5.0$ but $K_c = 0.50$. **Infer** which direction the reaction must proceed to reach equilibrium. (2 marks)

6 A reaction has $Q = 0.20$ but $K_c = 1.50$. **Infer** which direction the reaction must proceed to reach equilibrium. (2 marks)

Practical

Lesson 2.9

Simulating equilibrium systems

Learning intentions and success criteria

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

MODULE 2

Lesson 2.10

Review: Equilibrium

Summary

2.1

- Chemical reactions occur in open systems where particles can escape into the atmosphere or be added and removed during the reaction.
- Chemical reactions occur in closed equilibrium systems where all reactants and products are kept within the same container and cannot escape into the environment.
- Chemical reactions that proceed both forwards and backwards become equilibrium reactions.
- Dynamic equilibrium is reached when the rates of the forward and reverse reactions are equal. At this point, the concentrations of reactants and products are constant.
- The reversibility of a reaction depends on the activation energy of the forward and reverse reactions, which can be identified from an energy profile diagram.

2.2

- The position of equilibrium indicates whether a reaction is favouring the forward or reverse reactions and whether there will be more reactants or more products at equilibrium.
- Le Châtelier laid the foundation for equilibrium understanding in his principle, which states that any change to a system at equilibrium will be partially opposed until equilibrium is re-established.
- Enthalpy changes can be used to determine the effect of temperature changes on an equilibrium system and whether the position of equilibrium will shift forwards or backwards.
- Le Châtelier's principle can be used to predict the effect of changing temperature, concentration and pressure on equilibrium systems and whether the position of equilibrium will shift forwards or backwards.
- Graphs can be used to represent changes to equilibrium systems.

2.3

- Practical: Investigating the effect of concentration on equilibrium

2.4

- Practical: Investigating the effect of volume and pressure on equilibrium

2.5

- Practical: Investigating the effect of temperature on equilibrium

2.6

- Equilibrium law represents the ratio between concentrations of reactants and products, raised to appropriate powers, which also represents the position of equilibrium. This can be calculated as K_c (for homogeneous systems) or K_{sp} (for systems involving equilibria between solid compounds and their aqueous ions).
- Equilibrium law can be used to calculate the amounts or concentrations of chemical species within an equilibrium system.

2.7

- Practical: Determining the K_{sp} of calcium hydroxide

2.8

- The ratio between reactants and products in systems that are not at equilibrium is called the reaction quotient, Q.
- The comparison of Q and the value of K_c or K_{sp} can determine whether an equilibrium reaction is favouring the forward or reverse reaction, and what has to happen to the reaction in order to reach equilibrium.

2.9

- Practical: Simulating equilibrium systems

Key formulas

Concentration	$c = \frac{n}{V}$
Equilibrium constant	$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
Solubility product constant	$K_{sp} = [C]^c[D]^d$
Reaction quotient	$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Review questions 2.10A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

1 In a reaction at equilibrium, when a reactant concentration is increased

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

2 An increase in temperature in a reaction at equilibrium

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

3 The equilibrium constant is calculated by using the concentration of

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

4 The reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ is allowed to reach equilibrium in a sealed container. Initially, the concentrations of CO and H_2 are 0.18398 M and 0.22046 M, respectively, and there is no CH_3OH. The equilibrium concentration of CO is 0.132264 M. The equilibrium concentrations of H_2 and CH_3OH, respectively, are

A 0.168744 M and 0.051716 M.
B 0.117028 M and 0.051716 M.
C 0.168744 M and 0.103432 M.
D 0.117028 M and 0.103432 M.

5 For the reaction:

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

which set of changes would maximise the yield of hydrogen?

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

6 The following statements have been made about dynamic equilibrium.

I Molar amounts of reactants and products are equal.
II Both reactants and products are present in the reaction.
III The rates of the forward and reverse reactions are equal.
IV Reactants and products are breaking down and re-forming in the molar ratio.

Which of the statements about dynamic equilibrium are true?

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

Use the following information to answer questions 7 to 9.

The chromate ion reacts to form the dichromate ion in the reversible reaction shown.

$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$

The chromate ion is yellow and the dichromate ion is orange. The forward reaction is exothermic.

7 What is the equilibrium expression used to represent the equation?

A $K_c = \dfrac{[CrO_4^{2-}]^2[H^+]^2}{[Cr_2O_7^{2-}][H_2O]}$

B $K_c = \dfrac{[CrO_4^{2-}]^2[H^+]^2}{[Cr_2O_7^{2-}]}$

C $K_c = \dfrac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2}$

D $K_c = \dfrac{[Cr_2O_7^{2-}][H_2O]}{[CrO_4^{2-}]^2[H^+]^2}$

8 To maximise the yield of the dichromate ion, a chemist should

A add water.

B increase the concentration of products.

C add some concentrated hydrochloric acid solution.

D add some concentrated sodium hydroxide solution.

9 After the system has reached equilibrium, the temperature is increased. Which of the following will be observed?

A The colour in the solution will fade and disappear.

B The solution will change gradually from more orange to more yellow in colour.

C The volume of the solution will decrease as water is used in the reverse reaction.

D The solution will undergo an instantaneous change to more orange and then change from more orange to more yellow in colour.

10 Consider the following equilibrium for the dissolution of calcium fluoride in water:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

If the solubility product (K_{sp}) is 3.9×10^{-11}, what is the concentration of fluoride ions ($[F^-]$) in a saturated solution of calcium fluoride?

A 6.2×10^{-6} **B** 1.2×10^{-5}

C 4.3×10^{-4} **D** 2.1×10^{-4}

11 The endothermic dissociation of nitrogen tetroxide is represented by the equation.

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

Nitrogen tetroxide is colourless and nitrogen dioxide is brown. An equilibrium mixture of nitrogen tetroxide and nitrogen dioxide in a syringe is compressed by pushing in the plunger to halve the volume. Which alternative describes the observations made?

A The brown colour of the gas will gradually lighten.

B The brown colour of the gas will gradually darken.

C The brown colour will darken suddenly as the plunger is depressed then gradually lighten.

D The brown colour will lighten suddenly as the plunger is depressed then gradually darken.

Review questions 2.10B Short response

Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

12 **Define** "activation energy". (1 mark)

13 **Describe** how the energy profile of a reaction differs from that of its reverse reaction if the first reaction is endothermic. (3 marks)

14 **Define** "Le Châtelier's principle". (2 marks)

15 **Construct** the equilibrium expressions for the following equilibria

a $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ (1 mark)

b $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ (1 mark)

16 **Explain** the effect a catalyst has on an equilibrium system. (2 marks)

17 **Explain** the effect of adding an inert gas into an equilibrium system. (2 marks)

18 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. (4 marks)

19 The solubility product (K_{sp}) for lead(II) chloride ($PbCl_2$) is 1.7×10^{-5} at 25°C.
Calculate the concentrations of both ions in a saturated solution of $PbCl_2$. (3 marks)

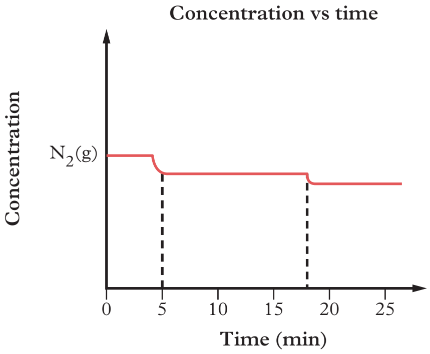
20 The equation for the equilibrium system for the production of nitrogen trichloride is:

$$N_2(g) + 3Cl_2(g) \rightleftharpoons 2NCl_3(g)$$
$$\Delta H = +223 \text{ kJ mol}^{-1}$$

Construct a concentration versus time graph for Cl_2 and NCl_3 on the graph below, incorporating the following changes:

- At 5 minutes, the temperature is increased. (2 marks)
- The system establishes equilibrium again. (1 mark)
- At 18 minutes, the concentration of Cl_2 is increased. (2 marks)
- The system re-establishes equilibrium again at 20 minutes. (1 mark)
- All initial concentrations are 1 M and the temperature of the reaction is 25°C. (2 marks)

(Note: The N_2(g) graph has been provided for you.)



Analytical processes

21 A saturated solution of calcium sulfate ($CaSO_4$) is prepared at 25°C, and the concentration of sulfate ions (SO_4^{2-}) is determined as 7.02×10^{-3} M.

a **Determine** the expression for the solubility product (K_{sp}) for calcium sulfate. (1 mark)

b Using the given concentration of sulfate ions, **calculate** the solubility of Ca^{2+} in mol L^{-1}. (1 mark)

c **Determine** the value of K_{sp} for $CaSO_4$ at 25°C. (2 marks)

22 The equilibrium constant for a certain chemical reaction occurring at a fixed temperature with gaseous reactants and products can be expressed as:

$$K_c = \frac{[C]\,[D]^3}{[A]^2[B]} = 7.46 \times 10^5$$

a **Construct** the balanced chemical equation for the reaction involving gases A, B, C and D. (1 mark)

b **Determine** the value of K for the reverse reaction when this reaction mixture is at equilibrium. (1 mark)

23 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 3.9×10^{-2}.

a **Determine** what can be concluded about the concentrations of reactants and products. (1 mark)

b Use Le Châtelier's principle to **determine** the effect of

i adding methanol to the reaction vessel at a constant temperature (2 marks)

ii decreasing the temperature of the system (2 marks)

iii doubling the volume of the system. (2 marks)

24 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, 0.5 mol of I_2 and 0.8 mol of HI are added to a 2 L vessel.

a **Calculate** Q_c based on the initial concentrations. (2 marks)

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. (2 marks)

Knowledge utilisation

25 The solubility of carbon dioxide in natural systems is affected by a number of competing equilibria:

Equation 1: $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

Equation 2: $2H_2CO_3(aq) + Ca(OH)_2(s) \rightleftharpoons CaCO_3(s) + H_2O(l)$

Equation 3: $3CaCO_3(s) + CO_2(g) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$

a **Identify** one of the sources of the increased concentration of carbon dioxide in the air over the past 200 years. (1 mark)

b **Use** the equation(s) above and your knowledge of Le Châtelier's principle to **discuss** how the oceans can act as a carbon dioxide sink. (3 marks)

26 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 table in the QCAA *Formula and data dook*.

a $AgNO_3(aq)$ is added to the reaction. (3 marks)

b NaF(aq) is added to the reaction mixture. (3 marks)

c The reaction is diluted. (3 marks)

d Solid NaOH is added to the reaction. (3 marks)

Data drill

Interpreting equilibrium graphs

Students at a university outreach excursion used a UV–visible spectrometer to study the equilibrium reaction of iron(III) ions with thiocyanate ions to form iron(III) thiocyanate ions:

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

The temperature is constant up to the time of 30 s.
The reaction is exothermic.
The data collected is shown in Figure 1.

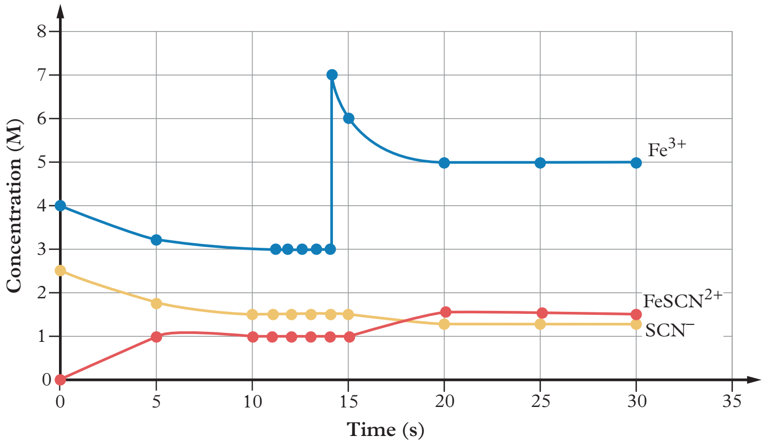


FIGURE 1 Iron(III) ions reacting with thiocyanate ions to form iron(III) thiocyanate ions

Apply understanding

1 Use the graph to **identify** the change made at 14 s. (2 marks)

2 **Calculate** the equilibrium constant between 10 and 14 s and between 20 and 30 s. (4 marks)

Analyse data

3 **Compare** the values from question **2** and **identify** a limitation. (2 marks)

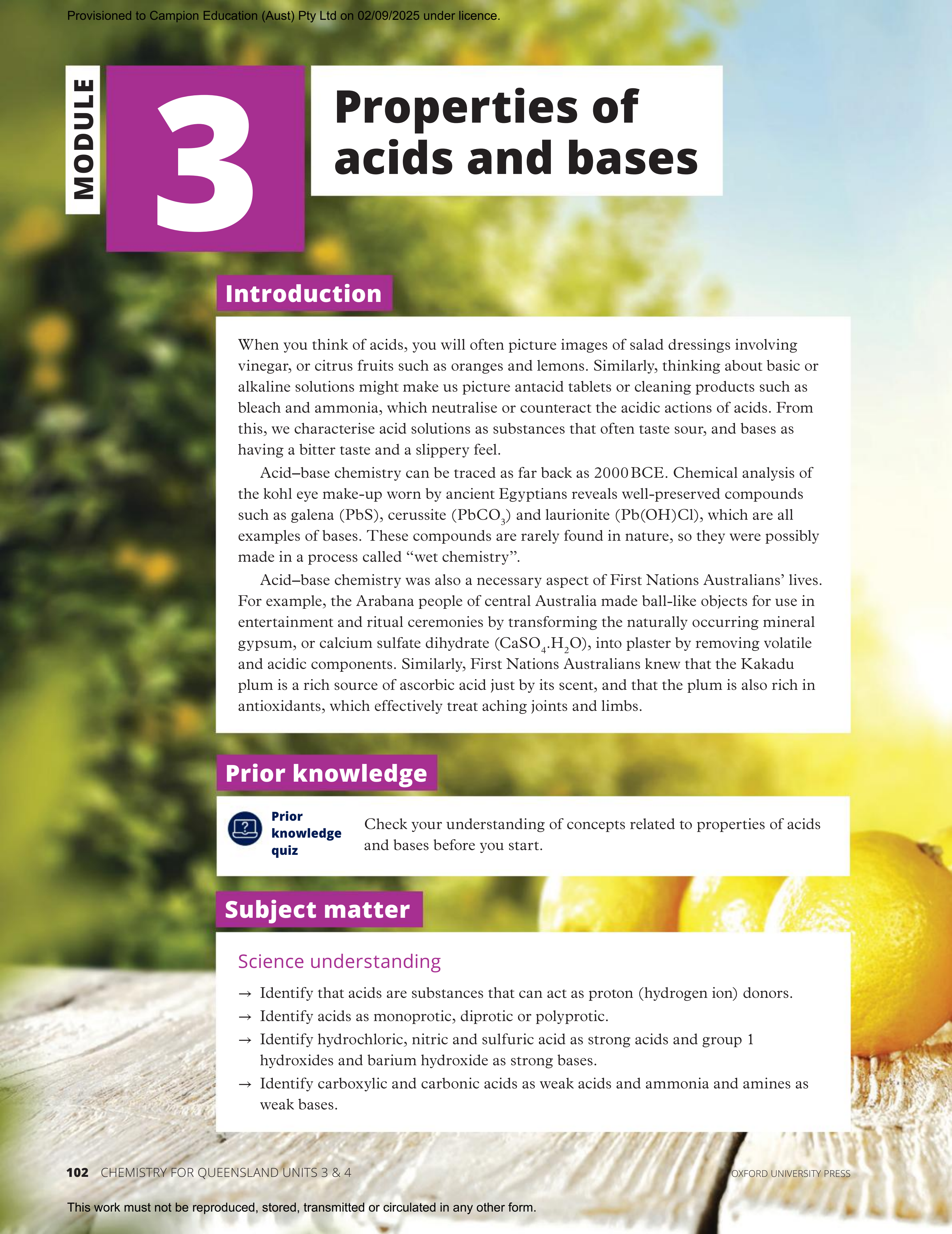
4 Use the graph to **identify** the trends in concentrations following the change made at 14 s. (3 marks)

Interpret evidence

5 **Justify** whether the data is qualitative or quantitative. (2 marks)

6 At 30 s, the temperature of the reaction is increased. **Extrapolate** the graph from 30 to 35 s. (3 marks)

Module 2 checklist: Equilibrium



MODULE 3

Properties of acids and bases

Introduction

When you think of acids, you will often picture images of salad dressings involving vinegar, or citrus fruits such as oranges and lemons. Similarly, thinking about basic or alkaline solutions might make us picture antacid tablets or cleaning products such as bleach and ammonia, which neutralise or counteract the acidic actions of acids. From this, we characterise acid solutions as substances that often taste sour, and bases as having a bitter taste and a slippery feel.

Acid–base chemistry can be traced as far back as 2000 BCE. Chemical analysis of the kohl eye make-up worn by ancient Egyptians reveals well-preserved compounds such as galena (PbS), cerussite ($PbCO_3$) and laurionite ($Pb(OH)Cl$), which are all examples of bases. These compounds are rarely found in nature, so they were possibly made in a process called “wet chemistry”.

Acid–base chemistry was also a necessary aspect of First Nations Australians’ lives. For example, the Arabana people of central Australia made ball-like objects for use in entertainment and ritual ceremonies by transforming the naturally occurring mineral gypsum, or calcium sulfate dihydrate ($CaSO_4.H_2O$), into plaster by removing volatile and acidic components. Similarly, First Nations Australians knew that the Kakadu plum is a rich source of ascorbic acid just by its scent, and that the plum is also rich in antioxidants, which effectively treat aching joints and limbs.

Prior knowledge

Prior knowledge quiz

Check your understanding of concepts related to properties of acids and bases before you start.

Subject matter

Science understanding

→ Identify that acids are substances that can act as proton (hydrogen ion) donors.
→ Identify acids as monoprotic, diprotic or polyprotic.
→ Identify hydrochloric, nitric and sulfuric acid as strong acids and group 1 hydroxides and barium hydroxide as strong bases.
→ Identify carboxylic and carbonic acids as weak acids and ammonia and amines as weak bases.

→ Discriminate between the terms strong, weak, concentrated and dilute for acids and bases.

→ Discriminate between strong and weak acids and bases in terms of the extent of dissociation, rate of reaction, pH and electrical conductivity.

→ Describe acids and bases in equilibrium systems using the Brønsted-Lowry model.

→ Explain the Brønsted-Lowry model using chemical equations that illustrate the transfer of hydrogen ions (protons) between conjugate acid-base pairs.

→ Identify that amphiprotic species can act as Brønsted-Lowry acid (or base).

→ Determine the formula of the conjugate acid (or base) of any Brønsted-Lowry base (or acid).

→ Analyse data to determine the strength, concentration, pH and electrical conductivity of acids and bases.

→ Identify that water is a weak electrolyte and the self-ionisation of water is represented by K_w (Formula: $K_w = [H^+][OH^-]$).

→ Apply K_w to calculate the concentration of hydrogen ions from the concentration of hydroxide ions in a solution.

→ Calculate pH, hydrogen ion concentration $[H^+(aq)]$, pOH and hydroxide ion concentrations $[OH^-(aq)]$ for strong acids and bases. (Formula: $pH = -\log_{10}[H^+]$ and $pOH = -\log_{10}[OH^-]$)

→ Identify 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. (Buffer calculations are not required.)

→ Apply Le Châtelier's principle to explain how buffer solutions respond to the addition of hydrogen ions and hydroxide ions.

Science inquiry

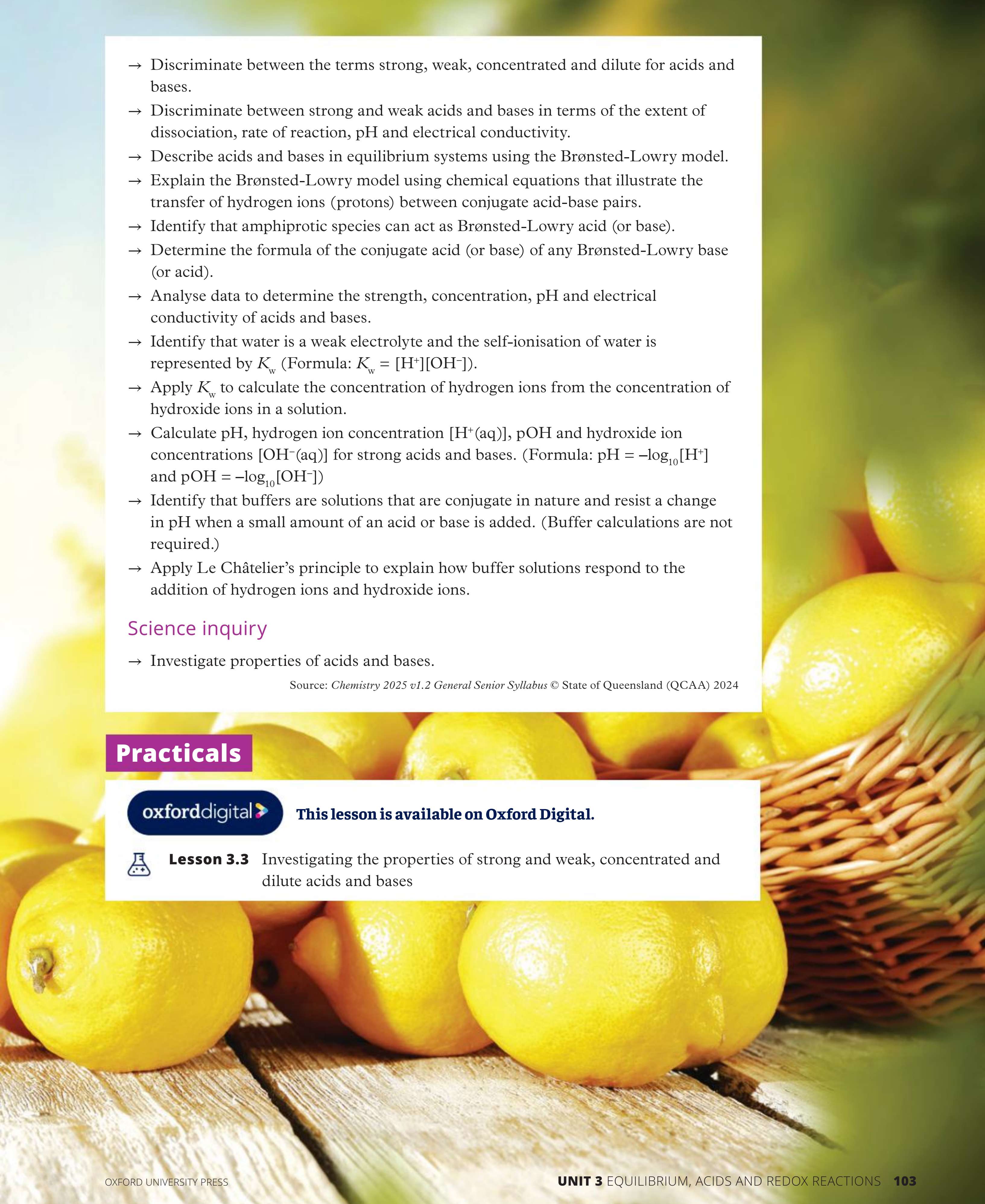
→ Investigate properties of acids and bases.

Source: *Chemistry 2025 v1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

Practicals

oxforddigital **This lesson is available on Oxford Digital.**

Lesson 3.3 Investigating the properties of strong and weak, concentrated and dilute acids and bases



Lesson 3.1
Brønsted–Lowry acids and bases

Key ideas

- → Acids and bases can be defined according to the Arrhenius definition of acids and bases and by the Brønsted–Lowry model.
- → Brønsted–Lowry acids act as proton donors and Brønsted–Lowry bases act as proton acceptors.
- → Acids are proton (H^+) donors. Monoprotic acids can donate one H^+; polyprotic acids can donate more than one H^+.
- → Amphiprotic species can act as Brønsted–Lowry acids or bases depending on the conditions.
- → Conjugate acid and base pairs are the product of acid–base reactions and differ by one hydrogen atom and one charge unit.
- → The relationship between acids and bases in an equilibrium system can be explained by the Brønsted–Lowry model. The transfer of hydrogen ions between conjugate acid–base pairs can be illustrated by using chemical equations.
- → The formulas of conjugate acid and base pairs can be deduced and identified, given the originating Brønsted–Lowry species.

Learning intentions and success criteria

What are Brønsted–Lowry acids and bases?

In the late sixteenth century, Robert Boyle characterised acid and base solutions according to their ability to dissolve many substances and change natural dyes such as litmus from blue to red. He also noticed that acids and bases lose these characteristics when they react with each other. Essential definitions of acids and bases were first developed by Swedish chemist Svante Arrhenius, who proposed two specific classifications of compounds: acids and bases. He defined acids as solutions that produce hydrogen ions in aqueous solutions, and bases as producing hydroxide ions.

However, the Arrhenius concept of acids and bases was limited to aqueous solutions and bases that contain hydroxide ions. It excluded compounds such as the oxidising agent sulfur dioxide gas (SO_2), which when dissolved in water reacts to produce an acidic solution of sulfurous acid. Basic compounds such as ammonia were also not within the Arrhenius definition of bases, because they lacked hydroxide ions, but reacted with water to produce hydroxide ions.

Consequently, the need for a more general definition of acids and bases was required and this led to the Brønsted–Lowry model, which was developed in 1923 by Danish chemist Johannes Brønsted and English chemist Thomas Lowry. In this model, an acid compound (e.g. hydrochloric acid (HCl)) is defined as a **proton** (H^+) **donor** and a base (e.g. sodium hydroxide (NaOH) or ammonia (NH_3)) as a **proton acceptor**.

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

proton acceptor
a substance that can accept H^+ (hydrogen ions)

Challenge

Oxides of nitrogen

Internal combustion engines produce nitric oxide (NO) and then nitrogen dioxide (NO_2). Both of these gases contribute to pollution and the formation of acid rain. Research how NO forms in engines and is then converted to NO_2, and the subsequent reaction that forms nitric acid. (3 marks)

What are proton donors?

If hydrogen chloride gas (HCl) is added to water, the oxygen atom in a water molecule will bond to the hydrogen atom in a HCl molecule and at the same time the H–Cl bond breaks. The products of this reaction are a hydronium ion (H_3O^+) and a chloride ion (Cl^-). H_3O^+(aq) is also often represented as H^+(aq).

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

Different acids can donate different numbers of hydrogen ions depending on their chemical composition. A **monoprotic acid**, such as hydrochloric acid, can donate one (mono = "one") proton per molecule on ionisation, forming a single 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 and present in vinegar). Ethanoic acid has four hydrogens in total per molecule, but only the H attached to an oxygen atom is acidic.

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 are 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 ionise in water in two steps:

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^-(aq)$$

The first reaction goes to completion because H_2SO_4(aq) is a strong acid and HSO_4^-(aq) is a weak acid and does not fully react with water. The second step is reversible, which is why the equilibrium arrow is used.

Triprotic acids such as phosphoric acid (H_3PO_4) ionise 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, so all three steps are reversible. Notice that when acids react with water, the water molecule accepts a proton to form the hydronium ion (H_3O^+).

What are proton acceptors?

A compound such as ammonia (NH_3) is a proton acceptor. Ammonia is a gas but dissolves in water:

$$NH_3(g) \rightleftharpoons NH_3(aq)$$

Because ammonia is quite a polar molecule, the nitrogen atom carries a partial negative charge. It also has a lone pair of electrons.

Protons from water molecules are transferred to ammonia molecules to form ammonium ions and hydroxide ions in a reversible reaction:

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

Ammonia is classed as a weak base because, at equilibrium, only some of the ammonia molecules have reacted with water, forming OH^-.

Another important group of proton acceptors are amines, which are similar to ammonia in structure but one or more of the hydrogen atoms has been replaced by a hydrocarbon group. Methanamine (CH_3NH_2) is the simplest amine. The reaction between methanamine and water is:

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

Notice that in both of these examples, the water molecules donate a proton to the base, and form hydroxide ions (OH^-) in the process.

Bases that dissolve in water are also called alkalis.

What are amphiprotic species?

Some molecules (or ions) can donate or accept a proton and therefore can act as either acids or bases, depending on the acidic or basic characteristics of the other reactant involved. For example, water acts as a base when reacting with an acid such as hydrochloric acid, and acts as an acid when reacting with a weak base such as ammonia:

$$\underset{\text{acid}}{HCl\ (aq)} + \underset{\text{base}}{H_2O\ (l)} \rightarrow H_3O^+(aq) + Cl^-(aq)$$

$$\underset{\text{acid}}{NH_3(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

amphiprotic
a molecule or an ion that can either donate or accept a proton and so therefore can act as an acid or base

Substances that can both accept and donate a proton are called **amphiprotic** substances (from the Greek word for "both"). Common examples are water and amino acids, Many polyprotic species also behave amphiprotically; for example, hydrogencarbonate ions (HCO_3^-) and hydrogen sulfate ions (HSO_4^-):

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$ (acidic property)

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_2SO_4(aq) + OH^-(aq)$ (basic property)

Hydrogencarbonate ions

In aqueous solution, HCO_3^- reacts with water in two 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). 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 because of the presence of a strong base or acid, respectively. Carbonic acid is unstable and readily decomposes to form water and carbon dioxide.

Challenge

Amphiprotic vs amphoteric

The two terms “amphiprotic” and “amphoteric” commonly get confused in acid–base chemistry. Amphoteric describes compounds, especially metal oxides and metal hydroxides, that can react as both a base and an acid. Research the key difference between the two terms and provide an example of both to highlight this difference. (3 marks)

What are conjugate acid–base pairs?

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

$$\text{acid} + \text{base} \rightleftharpoons \text{conjugate base} + \text{conjugate acid}$$

This representation emphasises the significant role of the polar water molecule as a Brønsted–Lowry base in removing the proton from the reacting acid. The conjugate base is the chemical species that is formed by removing the proton from the acid molecule. Similarly, the conjugate acid is the chemical species that is formed when the proton is transferred to the base. The pair of substances that differ by only one proton is called a **conjugate acid–base pair**. This means that the conjugate acid–base pair is not fixed for specific acids and bases but are interchangeable depending on the acid–base reaction occurring.

Consider the acid–base reaction in which ammonium ion (NH_4^+), as the acid, reacts with hydroxide ion (OH^-), as the base:

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

The ammonium ion 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 of ammonia reacting with water, and in this case NH_4^+ is referred to as the conjugate acid of ammonia and OH^- as the conjugate base of water.

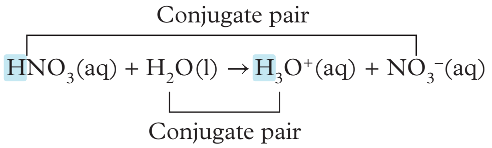
conjugate acid
an acid formed when a base accepts a proton (H^+)

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

conjugate acid–base pair
two chemical species differing only by the presence or absence of a proton

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 H_2O 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. Notice the different number of H atoms and the different charge between each pair

Acid	Conjugate base
HCl	Cl^-
HNO_3	NO_3^-
H_2SO_4	HSO_4^-
CH_3COOH	CH_3COO^-
H_3PO_4	$H_2PO_4^-$
$H_2PO_4^-$	HPO_4^{2-}
HPO_4^{2-}	PO_4^{3-}
H_2O	OH^-
H_3O^+	H_2O
Base	**Conjugate acid**
NH_3	NH_4^+
S^{2-}	HS^-
PO_4^{3-}	HPO_4^{2-}
HPO_4^{2-}	$H_2PO_4^-$
$H_2PO_4^-$	H_3PO_4
OH^-	H_2O
H_2O	H_3O^+

Worked example 3.1A

Explaining the Brønsted–Lowry model using a chemical equation

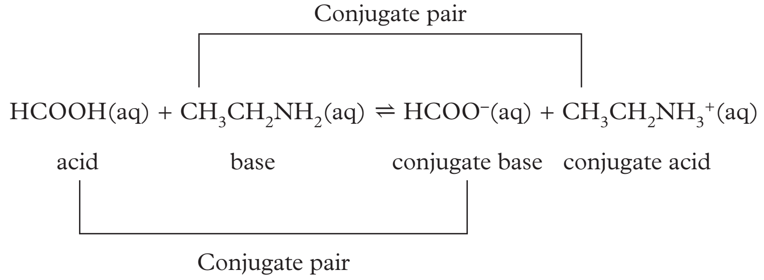
Aqueous solutions of methanoic acid (HCOOH) and ethanamine ($CH_3CH_2NH_2$) react in a reversible reaction and reach equilibrium.

a **Determine** the balanced chemical equation for the reaction. (1 mark)

b **Identify** the conjugate acid–base pairs in the reaction. (3 marks)

c **Explain** the Brønsted–Lowry model of acids and bases, using this reaction as an example. (3 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the questions are asking you to do.	"Determine" means establish, conclude or ascertain after consideration, observation, investigation or calculation. "Identify" means locate, recognise and name. "Explain" means make an idea or situation plain or clear by describing it in more detail or revealing relevant facts. We need to use the reactants given to write and balance the chemical equation. This question is worth 7 marks, so we must express the equation correctly with state symbols. We need to identify the acid and base, the conjugate acid and conjugate base, and indicate the acid–base pairs. We then need to use the example and explain how it shows proton transfer from an acid to a base and from a conjugate acid to a conjugate base, which are the features of the Brønsted–Lowry model.
Step 2: For part **a**, use the two reactants given to write a balanced equation.	**a** $HCOOH(aq) + CH_3CH_2NH_2(aq) \rightleftharpoons HCOO^-(aq) + CH_3CH_2NH_3^+(aq)$ (1 mark)

Think	Do
Step 3: For part **b**, under the equation, label each of the chemical species. Use lines to link each of the two conjugate pairs and label these arrows.	**b**  $HCOOH(aq) + CH_3CH_2NH_2(aq) \rightleftharpoons HCOO^-(aq) + CH_3CH_2NH_3^+(aq)$ Label for acid and conjugate base. (1 mark) Label for base and conjugate acid. (1 mark) Labelled arrows or similar to show both conjugate pairs. (1 mark)
Step 4: For part **c**, finalise your answer by explaining the Brønsted–Lowry model and how this example illustrates it.	**c** The Brønsted–Lowry model of acids and bases states that an acid is a substance that can donate a proton and a base is a substance that can accept a proton. (1 mark) In this reaction, HCOOH is the acid and donates a proton to the base, $CH_3CH_2NH_2$. (1 mark) The products of the reaction are in equilibrium with the reactants. The product of the acid is the conjugate base, $HCOO^-$, which in turn can accept a proton and form HCOOH. The product of the base is the conjugate acid, $CH_3CH_2NH_3^+$, which can donate a proton and form $CH_3CH_2NH_2$. (1 mark)

Your turn

Aqueous solutions of ethanoic acid (CH_3COOH) and ammonia (NH_3) react in a reversible reaction and reach equilibrium.

- **a** **Determine** the balanced chemical equation for the reaction. (1 mark)
- **b** **Identify** the conjugate acid–base pairs in the reaction. (3 marks)
- **c** **Explain** the Brønsted–Lowry model of acids and bases, using this reaction as an example. (3 marks)

Check your learning 3.1

Check your learning 3.1: Complete these questions online or in your workbook.

Retrieval and comprehension

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

2 **Identify** five acidic substances in your home. (5 marks)

3 **Identify** three monoprotic and three polyprotic acids and classify them as strong or weak. (6 marks)

Analytical processes

4 **Determine** the chemical equations of the reactions between the following acids and water.
  - **a** Nitric acid (HNO_3) (1 mark)
  - **b** Carbonic acid (H_2CO_3) (2 marks)
  - **c** Arsenic acid (H_3AsO_4) (3 marks)

5 **Determine** the amphiprotic species and write chemical equations illustrating the amphiprotic character of
  - **a** HSO_3^- (1 mark)
  - **b** S^{2-} (1 mark)

- **c** CO_3^{2-} (1 mark)
- **d** $H_2PO_4^{-}$ (1 mark)
- **e** H_2O. (1 mark)

6 Perchloric acid ($HClO_4$) reacts with water as follows:

$$HClO_4(aq) + H_2O \rightarrow H_3O^+(aq) + ClO_4^-(aq)$$

Determine the two conjugate acid–base pairs in the reaction. (2 marks)

7 Aqueous solutions of sodium hydrogencarbonate ($NaHCO_3$) and ammonia (NH_3) react in a reversible reaction and reach equilibrium.

- **a** **Determine** the balanced chemical equation for the dissociation of $NaHCO_3$ in water. (1 mark)
- **b** **Determine** the balanced chemical equation for the acid–base reaction. (1 mark)
- **c** **Identify** the conjugate acid–base pairs in the reaction in part **b**. (3 marks)

Knowledge utilisation

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

9 **Investigate** three monoprotic and three polyprotic acids and outline for one polyprotic acid the sequential loss of protons in its ionisation steps. (6 marks)

10 **Discuss** how ocean acidity is increasing and **explore** how this affects the Great Barrier Reef. (3 marks)

Lesson 3.2

Properties of acids and bases

Key ideas

→ Acids are often characterised as solutions that taste sour and turn blue litmus paper red, whereas bases often taste bitter and turn red litmus paper blue.

→ Solutions of acids and bases can be described by their strength and concentration.

→ The strength of an acid or a base solution depends on the extent of dissociation: stronger acids and bases dissociate more and therefore have higher rates of reaction and greater electrical conductivity.

→ Weak acids and bases do not dissociate completely but reach an equilibrium with water.

→ Strong acids fully ionise. Strong bases such as sodium hydroxide fully dissociate in water.

What are the properties of acids and bases?

Learning intentions and success criteria

Properties associated with aqueous solutions of acids and bases include the rate at which they react with other substances, pH scale, and level of conductivity. Chemical properties will be discussed in a later lesson.

Concentration of acids and bases has been covered in Units 1 & 2. It is important to distinguish between the reaction rate of 6 M sulfuric acid and 6 M ethanoic acid. Since concentration is a measure of the number of moles of acid or base per litre, it is the type of acid and therefore its **strength** that is largely responsible for the properties of an aqueous solution of the acid, including pH, rate of reaction and conductivity.

strength
the level of dissociation of an acid or a base

What are the properties of strong acids?

The strength of an acid or base depends on the **extent of dissociation** in water. A **strong acid** is one that completely ionises in water, fully donating its proton in solution. You need to know the formulas of the strong acids hydrochloric acid (HCl), nitric acid (HNO_3) and sulfuric acid (H_2SO_4) for the first step of ionisation (Table 1). Because these acids are assumed to almost fully dissociate, we use single forward-facing arrows (→) to show this in the equations.

extent of dissociation
the proportion of the total number of molecules of a substance that dissociate into its constituent ions or molecules

strong acid
an acid that completely ionises in water

TABLE 1 Ionisation reactions of the three most common strong acids: HCl, HNO_3 and H_2SO_4

Strong acid	Ionisation reaction
Hydrochloric acid	$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$
Nitric acid	$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$
Sulfuric acid	$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$

Sulfuric acid is a strong diprotic acid, and its two protons ionise sequentially in separate steps. The first ionisation goes to completion. The second ionisation is considered not to go to completion so equilibrium arrows (⇌) are used for the second ionisation:

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$$

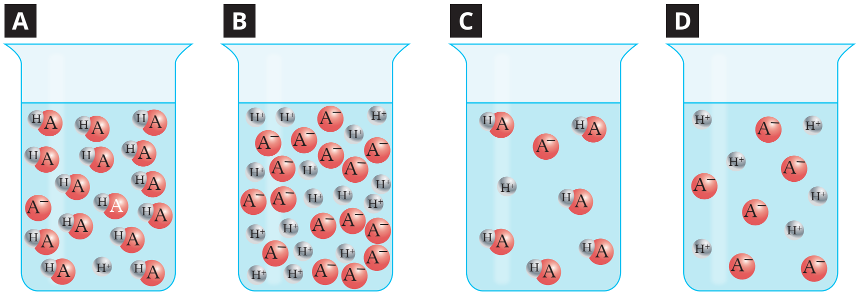
$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

What are the properties of weak acids?

Weak acids only partially ionise in water (Figure 1A,C). A common weak acid is the carboxylic acid ethanoic acid (or acetic acid) (CH_3COOH), which is in vinegar. When ethanoic acid dissolves in water, it donates protons to some of the water molecules, forming hydronium ions (H_3O^+). Eventually, an equilibrium is established with a significant amount of non-ionised ethanoic acid molecules. Only about 0.4% of the ethanoic acid molecules are ionised in a 1 M aqueous solution. The majority of ethanoic acid molecules remain unreacted. The extent of ionisation increases as solutions become less concentrated, or more dilute.

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

weak acid
an acid that only partially ionises in water, with the equilibrium favouring the acid form



Concentrated weak acid

Concentrated strong acid

Dilute weak acid

Dilute strong acid

FIGURE 1 Varying degrees of dissociation in strong, weak, concentrated and dilute acids

Study tip

The terms "ionisation" and "dissociation" may appear to mean similar things when discussing acids and bases. However, ionisation refers to the formation of ions from neutral molecular compounds. Strong acids fully ionise; weak acids and weak bases that are molecules partly ionise. Dissociation refers to the separation of positive and negative ions when an ionic solid such as a metal hydroxide dissolves.

FIGURE 2 Vinegar is made up of the carboxylic acid 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 an acidity constant or acid ionisation constant) (see Module 4).

What are the properties of strong bases?

A **strong base** completely ionises in water. The hydroxide ion is the strongest base that can exist in water. Any base that is stronger than hydroxide ion will react completely with water to immediately form hydroxide ions. All hydroxide salts are strong bases.

$$NaOH(aq) \xrightarrow{Water} Na^+(aq) + OH^-(aq)$$

$$KOH(aq) \xrightarrow{Water} K^+(aq) + OH^-(aq)$$

strong base
a base that completely ionises in water

Hydroxide ions react with hydronium ions in a neutralisation reaction to form water, as shown in Figure 3.

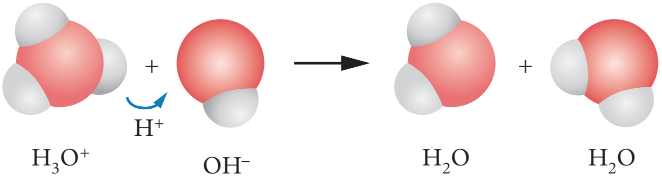
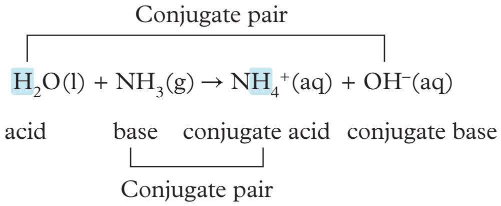


FIGURE 3 The neutralisation reaction involving a hydronium ion (acid) donating a proton to a hydroxide ion (base) to form two water molecules

What are the properties of weak bases?

weak base
a base that does not completely ionise in water

Bases such as ammonia and amines are considered **weak bases** because they do not contain hydroxide ions, but they increase the hydroxide ion concentration when dissolved in solution because of their partial reaction with water. For example, ammonia and many bases like ammonia are Brønsted–Lowry bases because they are polar and have a lone pair of electrons. Their lone pair of electrons can remove a proton from water, producing a hydroxide ion and the conjugate acid of the base. This consequently increases the hydroxide ion concentration to a small extent and yields an overall basic solution. A 1 M aqueous solution of ammonia is only about 0.4% ionised, as most of the ammonia molecules remain unreacted, with the equilibrium favouring the base, rather than the conjugate acid form.



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

Ammonia and amine compounds are weak Brønsted–Lowry bases.

What are the indicators of extent of dissociation?

If given aqueous solutions of several different acids or bases of equal concentration, then there are several techniques for determining the strengths of the acids or bases relative to each other. The degree of dissociation in solution is related to the chemical properties of conductivity, the rate of the reaction taking place with other substances and most obviously the pH of the solutions.

Electrical conductivity

Electrical conductivity is based on a substance's ability to release or dissociate ions in solution that can carry electrical charge. Because all acids and bases dissociate to some degree in water, all aqueous solutions of acids and bases conduct electricity. 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 Module 7). They have variable degrees of dissociation based on their strength.

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

For this reason, solutions of strong acids and bases in water exhibit higher conductivities than solutions of the same concentration of weak acids and bases. For example, comparing 0.1 M aqueous solutions of hydrochloric acid and ethanoic acid reveals that, at 25°C, the HCl solution has a conductivity 87,000 times greater than the ethanoic acid solution (3.9×10^{-2} S cm^{-1} compared to 4.5×10^{-7} S cm^{-1}.) Conductivity also depends on the concentration of the acid or base. So, a very dilute solution of a strong acid or base will have fewer ions and a low conductivity, as exhibited by a weak acid or base. However, it is still considered to be a strong solution due to the degree of dissociation into ions.

It is possible to make a battery from a lemon. The lemon battery cannot produce electricity itself, but it allows two different metals to react with each other and the presence of ions in the citric acid in its juice forms an electrolyte. These kinds of reactions are called redox reactions and are explained in Module 6. One metal is reduced (gains electrons), whereas the other is oxidised (loses electrons).

Rates of reaction

Several reactions can occur between acids and other compounds, including reactions with metals and metal carbonates, which produce gases, such as hydrogen or carbon dioxide. Consequently, the rate at which these reactions take place can be determined experimentally by measuring the rate of gas production. Alternatively, the rate at which reacting mass decreases over time can be measured. Two acid solutions of the same concentration can be compared. The solution of the stronger acid has higher concentrations of protons and so will often yield faster rates of gas production and hence faster reaction rates in general than the weaker acid. The solution of the weaker acid will have lower concentrations of protons in solution (remember that acid solutions of equal concentration are used).

pH

The pH scale provides a convenient way to measure and report the concentration of protons in solution. The pH is a base 10 logarithmic scale, where solutions of $pH < 7$ are acidic and those of $pH > 7$ are basic or alkaline. Solutions with a $pH = 7$ are neutral. Further information about how to quantify the pH of solutions is provided in Lesson 3.3.

Real-world chemistry

Katsuko Saruhashi: The ocean is more than just seawater!

Up until the mid-1950s, the equilibrium levels of the various carbonic acid species and their detection in natural waterways were unclear and unstandardised. It was believed that the oceans were a mitigating factor to global warming because they absorbed much of the atmospheric CO_2 that caused the increase in global warming effects experienced in the last century. However, research conducted by pioneering geochemist Katsuko Saruhashi (1920–2007) revealed that the oceans, particularly

▶

the Pacific Ocean, actually emit more CO_2 than they absorb due to oxidation of organic matter. This is further justification for the persistent monitoring of ocean composition.

Saruhashi's discoveries about oceanic CO_2 levels and pH revolutionised how we view ocean chemistry. Not only did she develop tools to accurately detect concentrations of carbonic substances, temperature, pH and salinity, but her research provided novel insight into the impact of aboveground nuclear testing. Saruhashi's findings provided indisputable evidence that led to the prohibition of aboveground nuclear testing because of its environmental impacts in increasing the concentration of radioactive isotopes ^{137}Cs and ^{90}Sr. Her research concluded that radioactive materials detected in the Atlantic Ocean would be carried in seawater to Japan in 18 months and eventually contaminate the entire Pacific Ocean by 1969 if nuclear testing were to continue. Her research was crucial in forcing the US and the Soviet Union to halt aboveground nuclear blasts.

Not only was Katsuko Saruhashi the first woman elected to the Science Council of Japan, but she is known as a pioneer geochemist and most notably a genius oceanographer.

Apply your understanding

1 **Identify** how Saruhashi's research challenged previous beliefs about the ocean's role in mitigating global warming. (2 marks)

2 **Identify** three oceanic properties that are now monitored by standardised methods of detection based on research tools developed by Saruhashi. (3 marks)

3 **Explain** with the aid of equations how variations in the amount of dissolved CO_2 affects the pH of the oceans. (2 marks)

Skill drill

Investigating the properties of acids and bases

Science inquiry skills: Planning investigations (Lesson 1.4); Processing and analysing data (Lesson 1.7)

Five colourless 0.1 M solutions of methanamine (CH_3NH_2), hydrochloric acid, barium hydroxide, sulfuric acid and butanoic acid have lost their labels. The substances are randomly labelled A, B, C, D and E. Table 2 shows the conductivity of each solution, its effect on blue litmus paper and the rate of reaction as measured by the rate of gas produced upon reaction.

TABLE 2 Properties of five unidentified acids and bases labelled A to E

Solution	Effect on blue litmus paper	Conductivity ($\mu S\ cm^{-1}$)	Relative rate of reaction
A	Turns red	500-800	0.1
B	No change	600-800	No reaction
C	No change	54,000	No reaction
D	Turns red	50,000	9.2
E	Turns red	39,000	8.0

Practise your skills

1 **Identify** the five unknown solutions. **Justify** your responses. (5 marks)

2 **Determine** one additional method to differentiate solutions A, D and E. **Justify** your response. (2 marks)

Check your learning 3.2

Check your learning 3.2: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Recall** whether the following acids are strong or weak.
  a Sulfuric acid (1 mark)
  b Ethanoic acid (1 mark)

2 0.2 L of a 1.0 mol L^{-1} solution of H_3PO_4 and 0.2 L of a 0.5 mol L^{-1} solution of H_2SO_4 were placed into individual circuits, each with a battery and a lamp. **Identify** which of the two solutions will be a better conductor of electricity and cause the lamp to glow brightly. (2 marks)

3 **Construct** a chemical equation for the dissociation of ammonia (NH_3) when it reacts with water (H_2O). (1 mark)

Analytical processes

4 **Distinguish** between weak acids and strong acids. (1 mark)

5 **Distinguish** between concentrated acids and strong acids. (1 mark)

Practical

Lesson 3.3

Investigating the properties of strong and weak, concentrated and dilute acids and bases

Learning intentions and success criteria

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Lesson 3.4

pH and the ionic product constant of water (K_w)

Key ideas

- → 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.
- → The pH scale is logarithmic. This means a solution of pH 3 is 10 times more acidic than a solution of pH 4.
- → Hydrogen and hydroxide ion concentrations can be determined from the equations pH = $-\log_{10}[H^+]$ and pOH = $-\log_{10}[OH^-]$, respectively.
- → K_w increases as temperature increases, changing the pH of pure water as a result.
- → Various mathematical representations can be used for solving problems for hydrogen ion concentrations, pH, hydroxide ion concentrations and pOH.

Learning intentions and success criteria

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

What is the conductivity of water?

Since most acid–base reactions involve ionisation in solution, it is useful to understand the role of water in more detail. Water's ability to weakly conduct electricity is because it ionises partially. Water-containing extinguishers should not be used on electrical fires because the water can create a path for electricity back to the person fighting the fire. For this reason, carbon dioxide-containing fire extinguishers are used instead.

What is the self-ionisation of water?

In water, a very small fraction of H_2O molecules react with themselves to form H_3O^+ and OH^- ions, at normal temperatures and pressures:

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

This **self-ionisation of water** can be written as an equilibrium expression (Figure 2).

self-ionisation of water
the reaction in which a water molecule transfers a hydrogen ion to another water molecule; the first molecule becomes a hydroxide ion (OH^-) and the second water molecule forms a hydronium (H_3O^+)

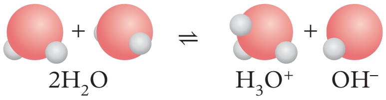


FIGURE 2 The self-ionisation of water

How does the self-ionisation of water contribute to the value of the ionic product constant of water, K_w?

The concentration of water can be considered constant because at normal temperatures and pressures, only very a small fraction ionises and pure liquids do not appear in equilibrium constant expressions. 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

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

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:

$$K_w = [H^+][OH^-] = [H^+]^2 \text{ when } [H^+] = [OH^-]$$

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

To convert to pH:

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

This is why pure water has a pH of 7 at 25°C. It also explains why pure water is a poor electrical conductor compared to aqueous solutions of ionic compounds or electrolytes, because pure water contains very low levels of ions in comparison.

K_w increases as temperature increases. This can be explained by Le Châtelier's principle. Since the dissociation of water is an endothermic reaction, if the temperature of the water is increased by adding energy, the equilibrium moves to use some of the added energy. It does this by absorbing the extra heat and using it to cause further dissociation of water. This means that the forward reaction is favoured and therefore more hydrogen and hydroxide ions are formed:

$$2H_2O(l) + \text{heat} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The effect of this is an increased K_w value due to the increase in H^+ and OH^- ion production. Therefore, it is important to make the distinction that water is not more acidic at higher temperatures despite having a lower pH, because the ionisation of water results in an equal ratio of hydrogen ions to hydroxide ions, still rendering it neutral. It is just that the kinetics of the reaction are altered at higher temperatures so that the equilibrium constant itself is higher. Consequently, pure water at equilibrium is still defined as neutral at any temperature, even when the calculated pH is not equal to 7.

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

TABLE 1 The relationship between temperature, K_w and pH of water

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

How do changes in hydrogen ion concentrations produce the logarithmic pH scale?

FIGURE 1 Søren Sørensen developed the pH scale.

In Lesson 3.1, acidity and alkalinity of solution were shown to depend on the ability to donate or accept a proton (H^+). However, at set temperatures, the concentration of hydrogen ions in various acidic or basic solutions varies quite significantly. For example, at 25°C, some ethanoic acid solutions have extremely low $[H^+]$ and others have significantly higher concentrations. Acidity can be described by the hydrogen ion activity, or concentration. A solution is acidic if the H^+ concentration is above 1×10^{-7} mol L^{-1}. Hydrogen concentrations range over a large order of magnitude and include inconveniently small numbers, as listed in Table 2. This inconvenience motivated Søren Sørensen (1868–1939) (Figure 1) to develop 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 for *potentia hydrogenii* and means the power of hydrogen or the potential of hydrogen. pH values of commonly encountered solutions are generally between 0 and 14. Concentrated strong acids can have negative pH values and concentrated strong bases can have pH values above 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}). Consequently, a solution of pH 5 will be 1,000 times less acidic than a solution of pH 2. Also note that because pH is defined as $-\log[H^+]$, the pH decreases as $[H^+]$ increases.

Study tip

When taking a logarithm (base 10) of a number, the:

- number of decimal places in the logarithm result equals the number of significant figures in the original number
- whole number part (called the characteristic) does not count in this rule – only the decimal part (the mantissa) reflects the significant figures.

TABLE 2 The relationship between pH, $[H^+]$ and $[OH^-]$

pH	$[H^+]$ (mol L^{-1})	$[OH^-]$ (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}

How is $[H^+]$ calculated?

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

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

Some calculators allow you to use 10^{-x}, whereas on other calculators you may need to use the inverse log function: $[H^+] = \log^{-1}(-pH)$

How is pH calculated?

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

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

Worked example 3.4A

Determining the pH of a solution, given acid concentrations

Determine the pH of a 0.0123 M hydrochloric acid (HCl) solution. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Determine" means to establish, conclude or ascertain after consideration, observation, investigation or calculation.
Step 2: The acid is a strong monoprotic acid and therefore is assumed to completely ionise. This would mean that the concentration of un-ionised acid equals the concentration of ionised hydrogen ions.	$[HCl] = [H^+] = [Cl^-]$ because a strong acid completely ionises in aqueous solution.
Step 3: Write the pH equation and substitute the concentration of the acid for $[H^+]$.	$pH = -\log_{10}[H^+]$ $= -\log_{10}0.0123$ (2 marks) $= 1.910094889$
Step 4: Note: The number of significant figures in the log (i.e. the pH or pOH value) is equal to the number of significant figures in the original number. The pH is recorded to 3 s.f. because the concentration had 3 s.f.	pH = 1.91 (1 mark)

Your turn

Determine the pH of a 1.63 M nitric acid (HNO_3) solution. (2 marks)

How is pOH calculated?

pOH is a measure of hydroxide ion concentration and 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:

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

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

Worked example 3.4B

Determining the pOH of a solution, given hydroxide concentrations

Determine the pOH of a solution with a hydroxide ion concentration of 4.2×10^{-5} M at 25°C. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Determine" means to establish, conclude or ascertain after consideration, observation, investigation or calculation.
Step 2: Write the pOH equation and substitute the concentration of the hydroxide.	$\text{pOH} = -\log[\text{OH}^-]$ $= -\log(4.2 \times 10^{-5})$ (1 mark) $= 4.37675071$
Step 3: Note: The number of significant figures in the log (i.e. the pOH value) is 2 and is equal to the number of significant figures in the original OH^- concentration, which was 2.	pOH = 4.4 (1 mark)

Your turn

Determine the pOH of an alkaline solution with a hydroxide ion concentration of 5.2×10^{-3} M. (2 marks)

What is the relationship between pH and pOH?

For an aqueous solution at 25°C, the relationship between pH and pOH is:

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

This relationship follows from the definition and value of K_w:

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

Taking the negative logarithm of both sides of this rule produces the sum pH + pOH on the left and 14 on the right-hand side.

How is [OH⁻] calculated?

Hydroxide ion 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:

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

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

to gain the hydroxide ion concentration.

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

Worked example 3.4D shows how hydrogen ion and hydroxide ion concentrations can be found from pH or pOH. If you know the pH, $[\text{H}^+] = 10^{-\text{pH}}$, pOH = 14 – pH and $[\text{OH}^-] = 10^{-\text{pOH}}$. Similarly, if you know the pOH, pH = 14 – pOH and concentrations can be found. If you have the concentration of either hydrogen or hydroxide ions, you can use pH or pOH to find out information about the other ion. This method is usually simpler than using K_w.

Worked example 3.4C

Calculating the hydroxide ion concentration from pH

Determine the hydroxide ion concentration of a solution of NaOH of pH 13.0 at 25°C. (3 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Determine" means to establish, conclude or ascertain after consideration, observation, investigation or calculation.
Step 2: Recognise that pH is associated with acids and that NaOH is a base. Hence, calculate pOH first. Write the equation that relates pH to pOH.	pH + pOH = 14 Therefore, pOH = 14 – pH
Step 3: Substitute the values in the question to determine the pOH of NaOH.	pOH = 14 – pH = 14 – 13.0 = 1.0 (1 mark)
Step 4: Convert pOH value to OH^- concentration using the formula: $[OH^-] = 10^{-pOH}$	$[OH^-] = 10^{-pOH}$ $= 10^{-1.0}$ (1 mark) = 0.10 M
Step 5: Provide the answer to the correct number of decimal places.	The number of decimal places in the original pH value is equal to the number of significant figures in the OH^- concentration. Hence $[OH^-]$ = 0.1 M (1 mark)

Your turn

Determine the hydroxide ion concentration of a solution of bleach with a pH of 9.3. (3 marks)

Worked example 3.4D

Calculating the concentration of hydrogen and hydroxide ions from either pH or pOH

A well-known cola drink has a pH of 2.6. **Calculate** the concentration of

a hydrogen ions in the drink (2 marks)

b hydroxide ions in the drink. (3 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the questions are asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to select appropriate rules and show working to calculate both concentrations. Part **a** is worth 2 marks and part **b** is worth 3 marks, so we must express each answer to the correct number of significant figures.
Step 2: Select the appropriate formulas and gather the required data. The sum of pH and pOH is 14 and this can be used to find either pH or pOH, when given the other value.	pH = 2.6 $[H^+] = 10^{-pH}$ pH + pOH = 14 $[OH^-] = 10^{-pOH}$
Step 3: For part **a**, because the pH is known, calculate the concentration of hydrogen ions first.	**a** $[H^+] = 10^{-pH}$ $= 10^{-2.6}$ (1 mark) = 0.002511886 (on calculator, you are not expected to write this as working or an answer)

Think	Do
Step 4: For part **b**, use the relationship between pH and pOH to calculate pOH. Keep all the figures in the pOH, even though the final answer will be rounded to 2 s.f.	**b** pOH = 14 – pH = 14 – 2.6 = 11.5 (1 mark)
Step 5: Use the pOH to calculate the concentration of hydroxide ions.	$[OH^-] = 10^{-pOH}$ $= 10^{-11.4}$ (1 mark) $= 3.98107 \times 10^{-12}$ (on calculator, you are not expected to write this as working or an answer)
Step 6: Finalise your answer by rounding the numbers to 2 s.f. and include the units.	**a** $[H^+] = 0.0032\,M$ (or $0.0032\,mol\,L^{-1}$) (1 mark) **b** $[OH^-] = 4.0 \times 10^{-12}\,M$ (or $4.0 \times 10^{-12}\,mol\,L^{-1}$) (1 mark)

Your turn

The pOH of a sample of human blood was measured as 6.43. **Calculate** the concentration of

a hydroxide ions in the sample (2 marks)

b hydrogen ions in the sample. (3 marks)

Check your learning 3.4

Check your learning 3.4: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain** what K_w represents. (2 marks)

2 **Describe** the process of self-ionisation of water. (1 mark)

3 **Identify** the relationship between pH and H^+ concentration of an aqueous solution. (1 mark)

4 **Calculate** the pH of a sodium hydroxide solution at 25°C where the hydroxide ion concentration is 0.0077 M. (2 marks)

5 **Calculate** the pOH of a solution with a hydroxide ion concentration of 3.8×10^{-4} M. (1 mark)

6 **Calculate** the hydroxide ion concentration of a solution of NaOH with pH 11.5. (2 marks)

Analytical processes

7 **Contrast** acidic solutions of pH 3 and pH 5. (1 mark)

8 The hydrogen ion concentration of a sample of human blood was 4.0×10^{-8} M at 25°C. **Determine** the pH and pOH of the blood sample. (2 marks)

Knowledge utilisation

9 The pH of water at 30°C is 6.92. **Justify** the K_w value for water at this temperature. Show all your working. (2 marks)

10 **Justify** with one reason why temperature should always be measured and recorded alongside the dissociation constants of reactions. (2 marks)

11 The K_w of water at 60°C is 9.31×10^{-14}. **Identify** whether water at 60°C will be acidic, basic or neutral. **Justify** your response. (2 marks)

Lesson 3.5

Buffer solutions

Key ideas

→ A buffer is made up of a weak acid and its conjugate base (or a weak base and its conjugate acid) and resists a change in pH.

→ Many systems in the human body involve buffers.

→ It is possible to predict the response of a buffer solution to the addition of hydrogen ions or hydroxide ions.

What is a buffer solution?

Learning intentions and success criteria

A buffer is anything that counteracts the impact of one thing on another. For example, in electronics, buffers are devices that maintain the integrity of a signal despite interferences to the transmission. In acid–base chemistry, buffers act to reduce the impact of added acid or base so that the pH of the chemical system stays constant. This is especially important in biological systems where maintaining a state of homeostasis or balance is vital for the survival of the organism. This is why 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.

The most important example of a solution that is buffered or contains a buffer is blood. Despite absorbing various acids and bases from metabolic processes, blood in an average healthy person maintains a pH within a small range of 7.35–7.45.

If the pH is too low, the body suffers from acidosis; if it is too high, alkalosis occurs. In extreme cases, these conditions can lead to death.

The body maintains a safe pH level through **buffer solutions**. A buffer solution contains appreciable and equal amounts of a weak acid and its conjugate base, or a weak base and equal amounts of its conjugate acid. In some instances, buffer solutions can be said to contain a weak acid and its salt (e.g. HF and NaF), or a weak base and its salt (e.g. ammonia (NH_3) and ammonium chloride (NH_4Cl)). A buffer solution resists change in pH when small amounts of acid or base are added. Table 1 lists some more examples of buffer solutions made from weak acids and their conjugate bases.

buffer solution
a solution that resists changes in pH when small quantities of acids or alkalis are added

TABLE 1 Examples of some buffer solutions

Buffer	Weak acid	Conjugate base
Ethanoic acid/ethanoate	Ethanoic acid	Ethanoate ion (e.g. from sodium ethanoate)
Hydrogencarbonate/carbonic acid	Hydrogencarbonate	Carbonic acid
Citric acid/citrate	Citric acid	Citrate ion (e.g. from potassium citrate)

How do buffer solutions resist a change in pH?

The key to understanding the buffering action of a solution is to focus on the equilibrium system formed by the buffer itself, i.e. the weak acid and its salt. When changes are applied to the system through the addition of H^+ or OH^- ions, we need to identify which of the buffer components are affected by such changes.

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 blood, the acid reacts with the bicarbonate anions. The following reaction occurs, which results in an increase in carbonic acid:

$$H_3O^+ + HCO_3^- \rightleftharpoons H_2CO_3 + H_2O$$

Alternatively, if a small amount of base is added to the blood, the base reacts with carbonic acid, and the following reaction occurs, which results in an increase in bicarbonate ions:

$$OH^- + H_2CO_3 \rightleftharpoons HCO_3^- + H_2O$$

These two reactions control the pH of the blood by removing excess hydronium and hydroxide ions, so that a constant pH level is maintained.

How can Le Châtelier’s principle be applied to 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 a change is made to a system in equilibrium, the reaction proceeds in the direction that partially opposes the applied change.

The chemical reaction describing the equilibrium between carbonic acid and bicarbonate is:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

If a metabolic 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 in equilibrium with carbon dioxide, some of it decomposes to form carbon dioxide and water. If a metabolic process releases base (OH^-) into the blood, then H^+ reacts with the excess OH^- ions. Because this removes some H^+, the system responds by proceeding to the right to produce H^+ and partially counteract this change.

In both these situations, the pH of the system is maintained within the desired range, despite the initial changes (through the addition of acid or base) applied to it.

Study tip

For the exam, you will not need to perform any buffer calculations.

Worked example 3.5A

Deducing the effect of acid–base changes applied to buffered solutions

A phosphate buffer is made of equimolar concentrations of the weak base hydrogen phosphate (HPO_4^{2-}) and its conjugate acid dihydrogen phosphate ($H_2PO_4^-$).

Deduce the effect of adding a

a strong acid to the buffer solution (3 marks)

b strong base to the buffer solution. (3 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocations to determine what the questions are asking you to do.	“Deduce” means to draw a logical conclusion.
Step 2: Write an equilibrium equation of the weak base in water to its conjugate acid and hydroxide ions.	$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$

Think	Do
Step 3: For part **a**, consider the impact on [H⁺] or [OH⁻] that the added acid will have	**a** Added acid will cause [OH⁻] to decrease because it will react with the hydroxide ions present. (1 mark)
Step 4: Use Le Châtelier's principle to identify the response of the buffer to reduce the impact of the added substance and the direction of its reaction to maintain equilibrium.	Decreasing [OH⁻] will cause the forward reaction to be favoured to counteract this and partially replenish the OH⁻ ions. (1 mark)
Step 5: State the impact that the added change will have on the system to maintain pH.	The reaction of the acid with the OH⁻ ions in the buffer followed by the forward reaction occurring prevents the pH from being significantly decreased by the added acid. (1 mark)
Step 6: For part **b**, consider the effect that adding base will have on [H⁺] or [OH⁻].	**b** Added base will cause [OH⁻] to increase. (1 mark)
Step 7: Use Le Châtelier's principle to identify the response of the buffer to reduce the impact of the added substance and the direction of its reaction to maintain equilibrium.	Increasing [OH⁻] will cause the reverse reaction to be favoured to partially counteract the change and decrease the OH⁻ ions. (1 mark)
Step 8: State the impact that the added change will have on the system to maintain pH.	The reverse reaction of the buffer system reduces [OH⁻] from the added base. This prevents the pH from being altered significantly by the added base. (1 mark)

Your turn

A buffer solution is made up of the weak acid ethanoic acid (CH_3COOH) and its salt sodium ethanoate (CH_3COONa), which releases the conjugate base CH_3COO^-.

Deduce the effect of adding a

a strong acid to the buffer solution (4 marks)

b strong base to the buffer solution. (3 marks)

Check your learning 3.5

Check your learning 3.5: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain** what a buffer solution is and give an example. (2 marks)

2 **Describe** the buffer response when a small amount of acid is added to human blood. (2 marks)

3 **Explain**, using Le Châtelier's principle, why it is important to have equimolar concentrations of a weak acid and its conjugate base when preparing a buffer solution. (3 marks)

Knowledge utilisation

4 Consider the following equilibrium equation:

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

  a **Determine** which molecule or ion is an acid, a conjugate base, a base or a conjugate acid and link the acid–base pairs. (2 marks)

  b **Apply** Le Châtelier's principle and **predict** what would happen if a small amount of acid was added. (2 marks)

  c **Discuss** what would happen if a small amount of base was added. (2 marks)

5 The mining industry uses an acid–base buffer of hydrogen sulfate ion (HSO_4^-) and sulfate ion (SO_4^{2-}) to regulate pH of acidic mine drainage.

  a **Determine** the balanced chemical equation showing the equilibrium between these ions, the hydronium ion and water. (1 mark)

  b **Determine** which molecule/ion is an acid, a conjugate base, a base or a conjugate acid and link the acid–base pairs. (2 marks)

  c **Apply** Le Châtelier's principle and **predict** what would happen if a small amount of acid were added. (2 marks)

MODULE 3

Lesson 3.6

Review: Properties of acids and bases

Summary

3.1

- Acids and bases can be defined according to the Arrhenius definition of acids and bases and by the Brønsted–Lowry model.
- Brønsted–Lowry acids act as proton donors and Brønsted–Lowry bases act as proton acceptors
- Acids are proton (H^+) donors. Monoprotic acids can donate one H^+; polyprotic acids can donate more than one H^+
- Amphiprotic species can act as Brønsted–Lowry acids or bases depending on the conditions.
- Conjugate acid and base pairs are the product of acid–base reactions and differ by one hydrogen atom and one charge unit.
- The relationship between acids and bases in an equilibrium system can be explained by the Brønsted–Lowry model. The transfer of hydrogen ions between conjugate acid–base pairs can be illustrated by using chemical equations.
- The formulas of conjugate acid and base pairs can be deduced and identified, given the originating Brønsted–Lowry species.

3.2

- Acids are often characterised as solutions that taste sour and turn blue litmus paper red, whereas bases often taste bitter and turn red litmus paper blue.
- Solutions of acids and bases can be described by their strength and concentration.
- The strength of an acid or a base solution depends on the extent of dissociation: stronger acids dissociate more and therefore have higher rates of reaction and greater electrical conductivity.
- Weak acids and bases do not dissociate completely but reach an equilibrium with water.
- Strong acids fully ionise. Strong bases such as sodium hydroxide fully dissociate in water.

3.3

- Practical: Investigating the properties of strong and weak, concentrated and dilute acids and bases

3.4

- 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.
- The pH scale is logarithmic. This means a solution of pH 3 is 10 times more acidic than a solution of pH 4.
- Hydrogen and hydroxide ion concentrations can be determined from the equations $pH = -\log_{10}[H^+]$ and $pOH = -\log_{10}[OH^-]$, respectively.
- K_w increases as temperature increases, changing the pH of pure water as a result.
- Various mathematical representations can be used for solving problems for hydrogen ion concentrations, pH, hydroxide ion concentrations and pOH.

3.5

- A buffer is made up of a weak acid and its conjugate base (or a weak base and its conjugate acid) and resists a change in pH.
- Many systems in the human body involve buffers.
- It is possible to predict the response of a buffer solution to the addition of hydrogen ions or hydroxide ions.

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

Review questions 3.6A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

1 Monoprotic acids are
- **A** antacids.
- **B** conjugate bases.
- **C** acids that are only used once.
- **D** acids that can donate one hydrogen ion per molecule.

2 The conjugate base of HSO_4^- is
- **A** SO_4^-.
- **B** SO_4^{2-}.
- **C** HSO_4.
- **D** H_2SO_4.

3 pH 6 is less acidic than pH 2 by
- **A** four times.
- **B** 4,000 times.
- **C** 1,000 times.
- **D** 10,000 times.

4 Ammonia and amines are considered to be weak bases. This means that they
- **A** have pH values in the range of 6–8.
- **B** react very slowly to neutralise acids.
- **C** have relatively low solubilities in water.
- **D** partially ionise in aqueous solution.

5 Which of the following is amphiprotic?
- **A** O^-
- **B** NH_4^+
- **C** HCO_3^-
- **D** $Be(OH)_2$

6 Two aqueous solutions of bases, X and Y, both with concentrations of 0.5 M have pH values of 8 and 10, respectively. Which of the following statements is true about the solutions X and Y?
- **A** X is a stronger base than Y.
- **B** X contains 100 times more undissociated molecules than Y.
- **C** The solution of X will conduct electricity better than the solution of Y.
- **D** The solution of Y contains higher concentration of OH^- ions than that of X.

7 If C_2H_5OH is a very weak Brønsted–Lowry acid, what is true about the ion $C_2H_5O^-$?
- **A** It is a good proton donor.
- **B** It is a strong Brønsted–Lowry base.
- **C** It is a stronger Brønsted–Lowry acid than C_2H_5OH.
- **D** In an aqueous solution, it will be present in higher concentrations at equilibrium than C_2H_5OH.

8 A 2.0 M solution of an acid has a pH of 3.5. Which of the following statements is true?
- **A** The acid is weak and dilute.
- **B** The acid is strong and dilute.
- **C** The acid is weak and concentrated.
- **D** The acid is strong and concentrated.

9 A solution is made from CH_3COOH with a concentration of 0.5 M and CH_3COONa with a concentration of 0.1 M. This solution would
- **A** not be able to function as a buffer solution.
- **B** be able to buffer added acid better than added base.
- **C** be able to buffer added base better than added acid.
- **D** be able to buffer added acid and added base equally well.

10 A solution is equimolar in $NaHSO_4$ and Na_2SO_4. Addition of strong acid to this solution will result in

A precipitation of Na_2SO_4.

B precipitation of $NaHSO_4$.

C reaction of SO_4^{2-} to form HSO_4^-.

D reaction of HSO_4^- to form SO_4^{2-}.

Review questions 3.6B Short response

Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

11 **Explain** the difference between strong and weak acids and bases. (2 marks)

12 **Define** "pH" and "pOH". (2 marks)

13 **Define** "amphiprotic". (2 marks)

14 **Explain** how a buffer solution maintains a steady pH. (2 marks)

15 **Calculate** the pOH and $[H^+]$ of aqueous solutions with the following pH values.

a 8.5 (2 marks)

b 3.6 (2 marks)

c 10.2 (2 marks)

16 **Calculate** $[OH^-]$ of an aqueous solution of NaOH with pH 12.0. (2 marks)

17 A buffer is prepared by dissolving hydroxylamine ($HONH_2$) and hydroxylammonium nitrate ($[NH_3OH^+][NO_3^-]$) in water. **Construct** equations to represent how this buffer neutralises added H^+ and OH^-. (3 marks)

Analytical processes

18 **Determine** the pH of a 0.0321 M hydrochloric acid (HCl) solution. (1 mark)

19 **Determine** the conjugate bases of hydrogen sulfate ion (HSO_4^-) and phosphoric acid (H_3PO_4). (2 marks)

Knowledge utilisation

20 Five unlabelled bottles were known to contain 0.5 mol L^{-1} solutions of CH_3COOH, KCl, HNO_3, NaOH and NH_3.

a **Determine** two ways in which the solutions could be identified. (2 marks)

b **Deduce** the order of the solutions from the lowest pH to the highest pH and **justify** your response. (5 marks)

21 **Justify** the claim that polyprotic acids contain species that behave amphiprotically. Provide examples in your response. (2 marks)

22 **Investigate** different buffer solutions in your body, using an appropriate resource, and **evaluate** their role and their importance. (3 marks)

23 It has been shown why pH + pOH = 14 for an aqueous solution at 25°C. **Consider** how this equation may differ with a change in temperature. (2 marks)

Data drill

Changing water temperature affects pH

The ionisation of pure water as represented by:

$$H_2O \rightarrow H^+(aq) + OH^-(aq)$$

was studied at a variety of different temperatures and the resulting pH values were recorded in Figure 1.

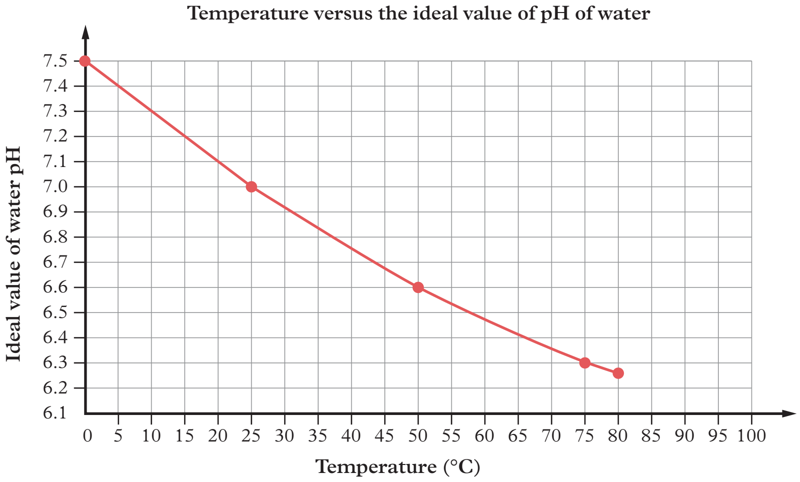


FIGURE 1 The effect of increasing temperature on the ideal value of pH of water

Apply understanding

1 **Determine** the difference in the pH of water between 50°C and 65°C. (2 marks)
2 **Identify** the trend in pH as the temperature of the water increases. (1 mark)
3 **Calculate** the equilibrium constant of water at 75°C. (3 marks)

Analyse data

4 Use your result from Question **3** to **contrast** the equilibrium constant for the self-ionisation of water at 75°C to that at 25°C. (1 mark)
5 **Categorise** the self-ionisation of water as exothermic or endothermic. **Justify** your reasoning. (2 marks)

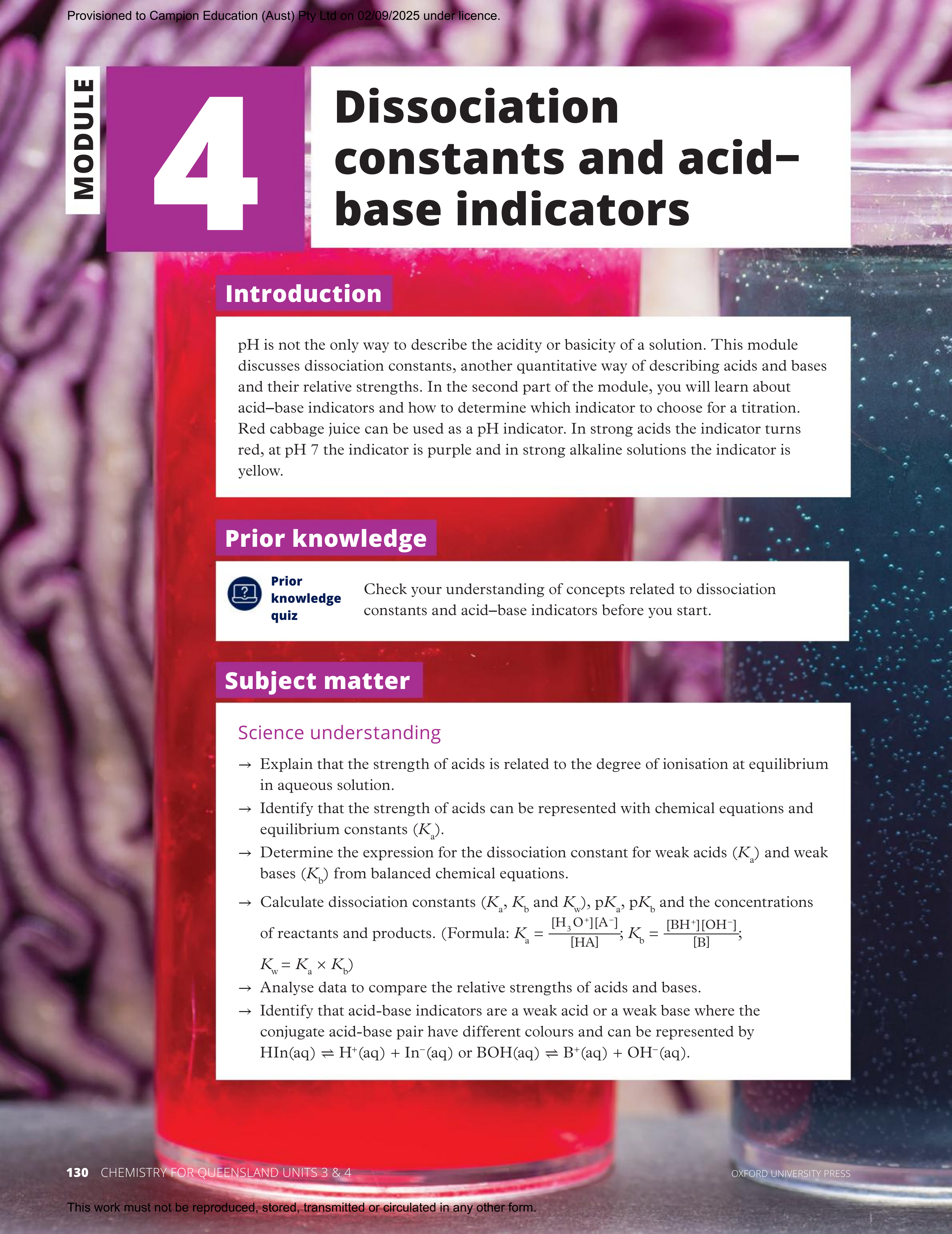
Interpret evidence

6 **Extrapolate** the graph to find the expected pH of water at 90°C. (1 mark)
7 **Justify** why the statement "water is more acidic at higher temperatures" is not theoretically accurate? (2 marks)

Module 3 checklist: Properties of acids and bases

MODULE 4

Dissociation constants and acid–base indicators



Introduction

pH is not the only way to describe the acidity or basicity of a solution. This module discusses dissociation constants, another quantitative way of describing acids and bases and their relative strengths. In the second part of the module, 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.

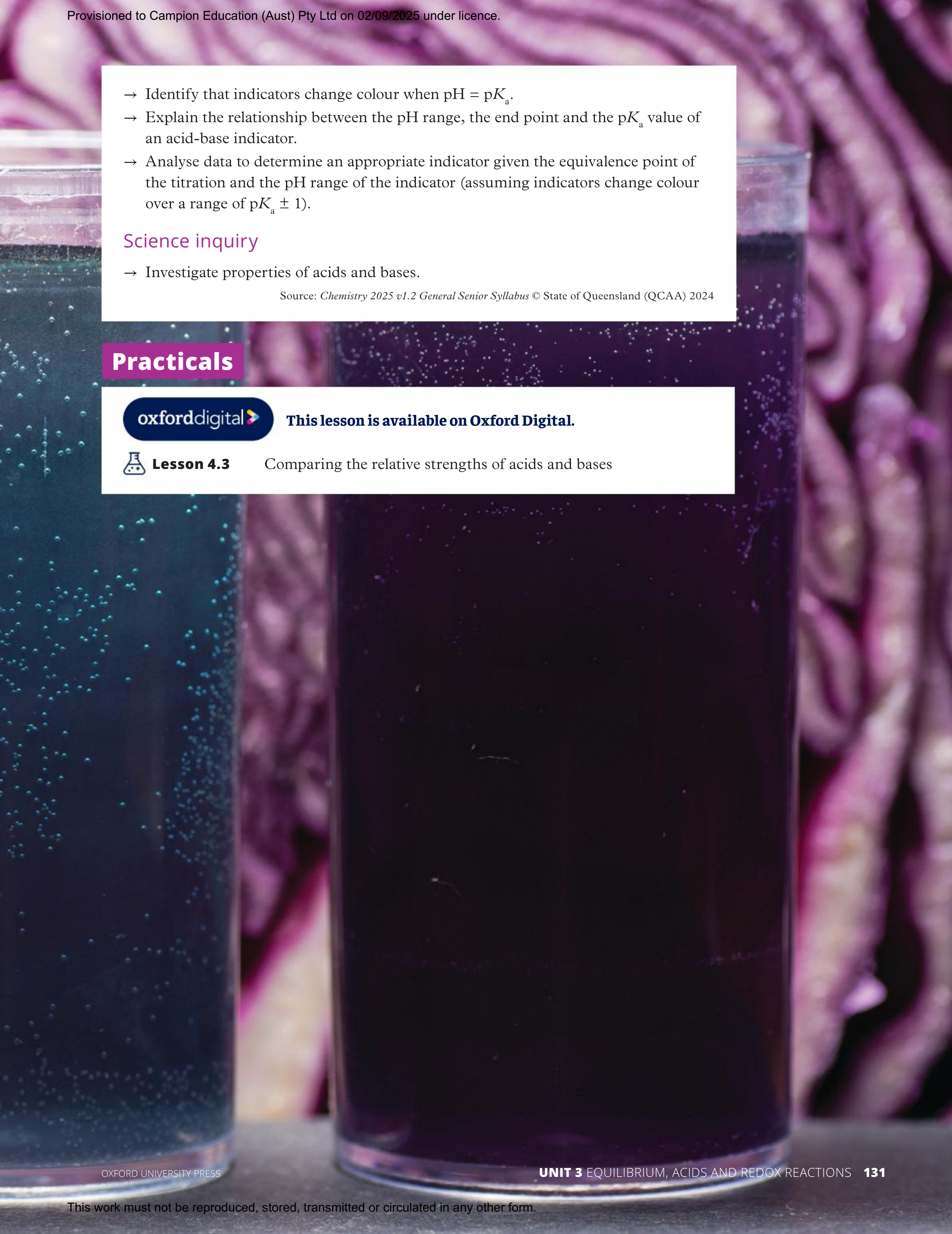
Prior knowledge

Prior knowledge quiz Check your understanding of concepts related to dissociation constants and acid–base indicators before you start.

Subject matter

Science understanding

- → Explain that the strength of acids is related to the degree of ionisation at equilibrium in aqueous solution.
- → Identify that the strength of acids 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.
- → Calculate dissociation constants (K_a, K_b and K_w), pK_a, pK_b and the concentrations of reactants and products. (Formula: $K_a = \frac{[H_3O^+][A^-]}{[HA]}$; $K_b = \frac{[BH^+][OH^-]}{[B]}$; $K_w = K_a \times K_b$)
- → Analyse data to compare the relative strengths of acids and bases.
- → Identify that acid-base indicators are a weak acid or a weak base where the conjugate acid-base pair have different colours and can be represented by $HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$ or $BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$.



- → Identify that indicators change colour when pH = pK_a.
- → Explain the relationship between the pH range, the end point and the pK_a value of an acid-base indicator.
- → Analyse data to determine an appropriate indicator given the equivalence point of the titration and the pH range of the indicator (assuming indicators change colour over a range of pK_a ± 1).

Science inquiry

- → Investigate properties of acids and bases.

Source: *Chemistry 2025 v1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

Practicals

This lesson is available on Oxford Digital.

Lesson 4.3 Comparing the relative strengths of acids and bases

Lesson 4.1
Dissociation constants

Key ideas

- → The strength of an acid or a 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 in the form of pK_a and pK_b, where $pK_a = -\log_{10}K_a$ and $pK_b = -\log_{10}K_b$.

Learning intentions and success criteria

What are the dissociation constants for acids?

The proverb "What you don't know cannot hurt you" might not be applicable to chemistry. If you handle acids or bases, strength and concentration are both important factors to consider. Acids and bases are both corrosive and can also cause severe chemical burns like the one in Figure 1. As explained in Module 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 reacts with water to form the conjugate base A^- and a hydronium ion (H_3O^+). For weak acids, a double arrow should be used, while for the first ionisation of a strong acid, a single arrow indicates that the ionisation is complete.

FIGURE 1 Both acids and bases can cause severe burns to the skin.

The chemical species in this reaction are considered to be in equilibrium when their concentrations do not change over time. The equilibrium constant (also known as acid ionisation constant or **acid dissociation constant (K_a)**) can be written for the acid ionisation equation above as:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

acid dissociation constant (K_a) the equilibrium constant for the dissociation of an acid in aqueous solution

In this reaction, because the concentration of liquid water is considered a constant, it can be removed from the equation and hence also removed from the expression. The concentration of water is very large, more than 55 M, and so does not change significantly when there are solutes in it.

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 $K_a > 1$.

Carboxylic acids (RCOOH), such as ethanoic acid and methanoic acid, are weak acids. Carbonic acid is also a weak acid – it is in soft drinks (Figure 2).

Study tip

The chemical equation for dissociation is often written as $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ and the K_a expression is often written as $K_a = \frac{[H^+][A^-]}{[HA]}$. It is understood that when H^+ is written, it is actually H_3O^+.

Because pH is related to the concentration of H_3O^+ ions, pH can be thought of as a function of K_a and the concentration of the acid. It is important to realise that for two different acids at the same concentration, the acid with the lower pH will have a larger K_a due to being more fully ionised and having a larger $[H_3O^+]$.

Study tip

The conjugate base of a strong acid is a very weak base. Consequently, salts containing the conjugate base do not affect pH when dissolved in water.

FIGURE 2 Carbon dioxide is added to soft drinks. When it dissolves in water, it forms carbonic acid, H_2CO_3.

Real-world chemistry

Unleashing the power of superacids

Superacids are so corrosive that they can eat straight through the glass vial they are contained in! Carborane acids (e.g. $H(CHB_{11}Cl_{11})$) can be considered the first superacids. They are made from a combination of strong acids and are a million times more potent than concentrated sulfuric acid, but surprisingly less corrosive. Carborane acids have the general formula $H(HCB_{11}X_{11})$, with $H(CHB_{11}Cl_{11})$ being the best-studied example. Carborane acids act as Brønsted–Lowry acids and hence donate a proton to form a very stable anionic conjugate base. For example:

$$H(CHB_{11}Cl_{11}) \rightleftharpoons CHB_{11}Cl_{11}^- + H^+$$

The conjugate base is perhaps the most stable group of atoms to exist. Its cluster of 11 boron atoms, 11 chlorine atoms and one carbon atom and one hydrogen atom is arranged into an icosahedron shape. The conjugate base formed from carborane's proton donation is a mechanism that is useful in applications such as catalysts in fuel chemistry of manufacturing pharmaceuticals.

Apply your understanding

1 **Identify** one feature of carborane acids that characterises them as a Brønsted–Lowry acid. (1 mark)

2 **Identify** two practical applications of superacids. (2 marks)

What are the dissociation constants for bases?

As explained in Module 3, weak acids and weak bases only partially ionise in aqueous solution and therefore do not fully dissociate. To quantify the relative strengths of weak acids and bases, you can look at their dissociation constants.

The general equilibrium equation for bases is:

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

where B represents a base, and BH^+ and OH^- are the products. Note that B can be neutral, or positively or negatively charged, but must have the ability to accept a proton from an acid, as shown by the formation of BH^+. Similarly, in writing BH^+, this species does not necessarily carry a 1+ charge. For example, the hydrogen phosphate ion (2– charge) is a base in the equation below due to accepting a proton to form the dihydrogen phosphate ion.

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

base dissociation constant (K_b) the equilibrium constant for the dissociation of a base in aqueous solution

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 side with 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.

What is the relationship between K_a and K_b?

Methanoic acid is a well-known weak acid. Its reaction with water is:

$$CHOOH(aq) + H_2O(l) \rightleftharpoons CHOO^-(aq) + H_3O^+(aq)$$

The equilibrium constant expression for the ionisation of CHOOH is:

$$K_a = \frac{[CHOO^-][H_3O^+]}{[CHOOH]}$$

The methanoate ion ($CHOO^-$) is a weak base. The reaction for $CHOO^-$ reacting with water is:

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

and the corresponding equilibrium constant expression for the reaction of $CHOO^-$ with water is:

$$K_b = \frac{[CHOOH][OH^-]}{[CHOO^-]}$$

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).

$$\begin{aligned} K_a \times K_b &= \left(\frac{[CHOO^-][H_3O^+]}{[CHOOH]}\right)\left(\frac{[CHOOH][OH^-]}{[CHOO^-]}\right) \\ &= \left(\frac{\cancel{[CHOO^-]}[H_3O^+]}{\cancel{[CHOOH]}}\right)\left(\frac{\cancel{[CHOOH]}[OH^-]}{\cancel{[CHOO^-]}}\right) \\ &= [H_3O^+]\times[OH^-] \\ &= K_w \end{aligned}$$

The dissociation constant of water has a value of 1.0×10^{-14} at 25°C. K_w represents the equilibrium constant for the self-ionisation of two water molecules to produce one hydronium ion and one hydroxide ion:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Worked example 4.1A demonstrates how to express equilibrium constants, given a chemical reaction.

Worked example 4.1A

Determining the equilibrium expression for acid–base reactions

Determine the expression for the dissociation constants for the following reactions.

a $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$ (1 mark)

b $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ (1 mark)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Determine" means to establish, conclude or ascertain after consideration, observation, investigation or calculation. In this case, you need to use K_a and K_b dissociation constant expressions. Parts **a** and **b** are worth 1 mark each, so you will need write the dissociation constant expression for each part to get both marks.
Step 2: For part **a**, consider the forward reaction to identify whether the reaction is that of an acid or base. This will determine whether your expression is for K_a or K_b.	**a** CH_3COOH donates a proton to produce CH_3COO^-. So the expression is for K_a because it is acting as an acid.
Step 3: Write the expression so that it is expressed as a ratio of product concentration to reactant concentration. Ensure that water as a liquid is not included in the expression and concentrations of species are raised to their molar coefficients.	$K_a = \frac{[H_3O^+][A^-]}{[HA]}$ $= \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$ (1 mark)
Step 4: For part **b**, consider the forward reaction to identify whether the reaction is that of an acid or base. This will determine whether your expression is for K_a or K_b.	**b** NH_3 accepts a proton to produce NH_4^+. So the expression is for K_b because it is acting as a base.
Step 5: Write the expression so that it is expressed as a ratio of product concentration to reactant concentration. Ensure that water as a liquid is not included in the expression and concentrations of species are raised to their molar coefficients.	$K_b = \frac{[BH^+][OH^-]}{[B]}$ $= \frac{[NH_4^+][OH^-]}{[NH_3]}$ (1 mark)

Your turn

Determine the expression for the dissociation constants for the following reactions.

a $C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$ (1 mark)

b $H_3C_6H_5O_7 + H_2O \rightleftharpoons H_2C_6H_5O_7^- + H_3O^+$ (1 mark)

Challenge

The danger of acids

Research the effects of a strong acid such as the acid in a car battery (sulfuric acid) when it comes in contact with skin. Why does it cause burns? How might its effects differ from other strong acids such as hydrochloric acid or nitric acid? Hint: Consider the impact of both strength and concentration of an acid in contributing to its ability to act as either an oxidising or a dehydrating agent. (5 marks)

What are pK_a and pK_b?

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

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 show some selected acids and bases and their strengths.

TABLE 1 Selected acids and their conjugate base with their K_a, pK_a, K_b and pK_b values (numbers in brackets refer to the ionisation step of the polyprotic acids)

Acid	Formula	K_a	pK_a		Conjugate base	K_b	pK_b	
Carbonic acid (first ionisation)	H_2CO_3	4.4×10^{-7}	6.4	← Relative acid strength increasing	HCO_3^-	4.4×10^{7}	7.7	Relative base strength increasing →
Carbonic acid (second ionisation)	HCO_3^-	4.7×10^{-11}	10.3		CO_3^{2-}	4.7×10^{3}	3.7	
Ethanoic acid (acetic acid)	CH_3COOH	1.8×10^{-5}	4.7		$CH_3CO_2^-$	5.8×10^{-10}	9.2	
Methanoic acid (formic acid)	HCO_2H	1.8×10^{-4}	3.8		HCO_2^-	5.6×10^{-11}	10.3	
Hydronium ion	H_3O^+	1.0	0.0		H_2O	1.0×10^{-14}	14.0	
Nitric acid	HNO_3	2.3×10^{1}	–1.4		NO_3^-	4.3×10^{-16}	15.4	
Sulfuric acid (first ionisation)	H_2SO_4	1.0×10^{2}	–2		HSO_4^-	1.0×10^{-16}	16.0	
Sulfuric acid (second ionisation)	HSO_4^-	1.0×10^{-2}	19.9		SO_4^{2-}	9.8×10^{-13}	12.0	
Hydrochloric acid	HCl	1.0×10^{6}	–5.9		Cl^-	1.0×10^{-13}	23.3	
Hydroiodic acid	HI	2.0×10^{9}	–9.3		I^-	5.0×10^{-24}	2.0	

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 →
Methanamine*	CH_3NH_2	4.4×10^{-4}	3.34	
Ethanamine	$C_2H_5NH_2N$	4.5×10^{-4}	3.35	
Sodium acetate	CH_3COONa	5.6×10^{-10}	9.25	
Sodium carbonate	Na_2CO_3	2.1×10^{-4}	3.68	
Aniline	$C_6H_5NH_2$	3.8×10^{-10}	9.42	

*All amines are weak bases.

Skill drill

Identify trends patterns and relationships between the type of acid, degree of dissociation and conductivity

Science inquiry skills: Processing and analysing data (Lesson 1.7); Evaluating evidence (Lesson 1.8)

HCl is a strong acid that almost completely dissociates; lactic acid is a weak acid that only partially dissociates in solution. It has a K_a of 1.38×10^{-4}. Analyse the graph in Figure 3 to determine the effect diluting weak acids has on conductivity.

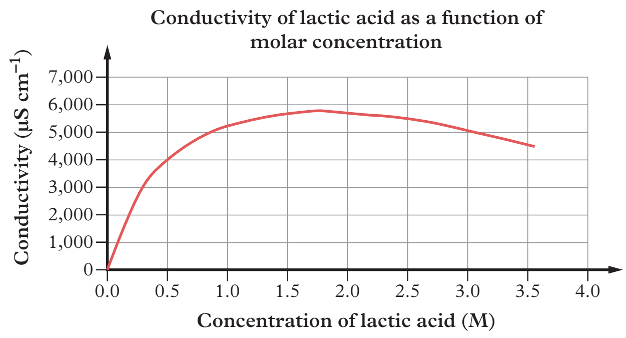


FIGURE 3 The effect of dilution on conductivity of a weak lactic acid solution.

Practise your skills

1 **Analyse** the relationship between the concentration of weak acid in solution to draw a conclusion about the level of dissociation at various concentrations. **Justify** your answer with data from the stimulus. (4 marks)

2 Formic acid has a dissociation of $K_a = 1.8 \times 10^{-4}$. **Predict** how its conductivity would compare to a solution of lactic acid at concentration of 0.5 M. (2 marks)

3 **Identify** any limitations in drawing conclusions about the conductivity of formic acid, given the data above for lactic acid. Use the data to **justify** your response. (2 marks)

Check your learning 4.1

Check your learning 4.1: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** what a dissociation constant is. (1 mark)

2 **Construct** the general chemical equation of an ionisation process at equilibrium for an acid and **explain** the process. (2 marks)

Analytical processes

3 **Determine** the expression for K_a for the following reactions.

- **a** $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$ (1 mark)
- **b** $HCO_2H(aq) + H_2O(l) \rightleftharpoons HCO_2^-(aq) + H_3O^+(aq)$ (1 mark)

4 **Determine** the expression for K_b for the following reactions.

- **a** $NH_2^-(aq) + H_2O(aq) \rightleftharpoons NH_3(aq) + OH^-(aq)$ (1 mark)
- **b** $HS^-(aq) + H_2O(l) \rightleftharpoons H_2S(aq) + OH^-(aq)$ (1 mark)

Lesson 4.2

Calculating dissociation constants and concentrations

Key ideas

- → 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.

Learning intentions and success criteria

How do we calculate the K_a of a weak acid?

For strong acids, we can assume that the concentration of hydrogen ions $[H^+]$ will be equal to the concentration of acid [HA]. We can also calculate the pH of the acid solution from the formula pH = $-\log[H^+]$. However, a weak acid only partially dissociates in water, so we cannot make the same assumptions for weak acids such as nitrous (HNO_2) or ethanoic 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. Likewise, the K_b of a weak base can be calculated, given the concentration and the pH or the pOH.

If K_a of the acid is less than or equal to 10^{-4}, then that acid is considered weak.

Consider 0.029 mol of ethanoic (acetic) acid (CH_3COOH) dissolved in 1 litre of aqueous solution. 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:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

The initial concentration $[CH_3COOH]$ is known (before any has dissociated or reacted with water), so we need to determine the concentration of $[H_3O^+]$ and $[CH_3COO^-]$. Given a pH of 3.15 at 25°C, we can assume that the $[H^+]$ was almost entirely sourced from the dissociation of $[CH_3COOH]$ because the dissociation of water at the same temperature is much lower. Thus, we can use the pH of the solution to find $[H^+]$. Use the equation for pH to find $[H_3O^+]$ (i.e. $[H^+]$):

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

Therefore:

$$pH = -\log[H_3O^+]$$
$$3.15 = -\log[H_3O^+]$$
$$[H_3O^+] = 10^{-3.15}$$
$$= 7.08 \times 10^{-4}\ \text{mol L}^{-1}$$

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
- equilibrium concentration of ethanoic acid.

TABLE 1 Using ICE to determine $[CH_3COO^-]$

Stage of ICE method	CH_3COOH	H_2O	H_3O^+	CH_3COO^-
Initial concentration (mol L^{-1})	0.029	H_2O has a very large concentration that does not change (approx. 55 M)	0	0
Change in concentration (mol L^{-1})	$-x$		$+x$	$+x$
Equilibrium concentration (mol L^{-1})	$0.029 - x$		x	x

Since the balanced dissociation equation of ethanoic acid states that there are equal numbers of moles of CH_3COO^- and H_3O^+ formed, then, from Table 1, you can see that:

$$[CH_3COO^-] = [H_3O^+]$$
$$= 7.08 \times 10^{-4}\,\text{mol L}^{-1}$$

From Table 1, at equilibrium:

$$[CH_3COOH] = 0.029 - x$$
$$\text{Given that } x = 7.08 \times 10^{-4}$$
$$[CH_3COOH] = 0.029 - (7.08 \times 10^{-4})$$
$$\approx 0.028\ \text{mol L}^{-1}$$

It is important to note that because the dissociation of weak acids is often so small compared to the initial concentration of the acid, it is often valid to make the approximation that the equilibrium concentration of acid equates the initial concentration. For example:

$$[CH_3COOH]_{\text{initial}} \approx [CH_3COOH]_{\text{equilibrium}}$$

which means that in the above example $[CH_3COOH] = 0.029 - x \approx 0.029$. Therefore, substituting these concentrations into the equilibrium expression gives you:

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$
$$= \frac{(7.08 \times 10^{-4})^2}{0.029}$$
$$= 1.7 \times 10^{-5}$$
$$[CH_3COOH] = 0.029\,\text{mol L}^{-1} - 7.08 \times 10^{-4}\,\text{mol L}^{-1}$$
$$= 0.028\,\text{mol L}^{-1}$$

Now you can substitute the values into the equilibrium equation:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$
$$= \frac{(7.08 \times 10^{-4})^2}{0.028}$$
$$= 1.8 \times 10^{-5}$$

So, K_a of ethanoic acid is calculated to a value of 1.8×10^{-5} (which you can confirm is correct in Table 1 from Lesson 4.1).

Study tip

RICE and ICE tables are used interchangeably in chemistry to determine concentrations. The reaction (R) is only required when there are different coefficients on either side of a reaction.

Study tip

You may choose to omit the ICE table from calculations using K_a and K_b for weak acids and bases. Ensure that you clearly state the equilibrium concentrations of all species in terms of x. Also, clearly state the assumption and reasoning for why the equilibrium concentration of the acid or base can be considered equal to the initial concentration.

How do we calculate concentrations and pH or pOH from K_a or K_b?

You can calculate the concentrations of all species, as well as the pH and pOH of a solution of a weak acid or base, if you know the acid or base dissociation constant (K_a or K_b). Worked example 4.2A shows calculations for a weak acid.

Note: In these questions, the terms "hydronium ions" and "hydrogen ions" are used interchangeably. Any assumptions need to be clearly stated.

Worked example 4.2B shows how to use K_b for a weak base to calculate concentrations, pOH and pH.

Worked example 4.2A

Calculating concentrations and pH from K_a

The K_a of hypochlorous acid (HClO) is 3.7×10^{-8}. For a 0.10 M solution of the acid, **calculate** the

a concentration of hydronium ions (5 marks)

b pH. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the questions are asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to show all of the logical steps and reasoning including a chemical equation, a RICE table, and state assumptions made. Part **a** of this question is worth 5 marks, so we must express the concentration with the correct units. Part **b** is worth 2 marks, so the working and answer for pH must be shown.
Step 2: Select the appropriate formulas and gather the required data.	$K_a = 3.7 \times 10^{-8}$ $K_a = \frac{[H_3O^+][A^-]}{[HA]}$ $pH = -\log[H^+]$
Step 3: For part **a**, write a balanced equation for the ionisation of the acid.	**a** $HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$ (1 mark)
Step 4: Draw up a RICE table for the initial, change and equilibrium concentrations of the three chemical species. Water can be omitted as the concentration of water is very large (approx. 55 M) and so essentially constant. State assumptions.	See RICE table below. (1 mark) Assume that the initial concentration of H_3O^+ is 0 because the change in concentration will be much greater than the concentration in water, and that the final concentrations of H_3O^+ and ClO^- are the same. Assume that the equilibrium concentration of HClO is 0.10 M because x is very small since K_a is very small. (1 mark)
Step 5: Write the K_a expression, substitute equilibrium values, and solve for x. The first line of substitution is awarded a mark for working. The next line of working is not marked but it is useful to write it out. There is no requirement to write out the calculated answer with all the digits shown – simply round it appropriately to record your final answer for the concentration.	$K_a = \frac{[H_3O^+][ClO^-]}{[HClO]}$ $3.7 \times 10^{-8} = \frac{x^2}{0.10}$ (1 mark) $x = \sqrt{3.7 \times 10^{-8} \times 0.10}$ $= 6.08276 \times 10^{-5}$

R	[HClO]	$[H_3O^+]$	$[ClO^-]$
I	0.10 M	0	0
C	$-x$	$+x$	$+x$
E	$0.10 - x$ ≈ 0.10 M	x	x

Think	Do
Step 6: Finalise your answer to part **a** by rounding the numbers to an appropriate number of significant figures and include the units. Check that your assumption about [HClO] was valid.	$[H_3O^+] = 6.1\times10^{-5}$ M (1 mark) x is very small and the assumption about [HClO] is valid.
Step 7: For part **b**, write the rule to find the pH and substitute. It can be useful to use the digits saved in your calculator from the answer to part **a**, to avoid rounding errors.	**b** $pH = -\log[H_3O^+]$ $= -\log(6.1\times10^{-5})$ (1 mark)
Step 8: Finalise your answer to part **b** by rounding the numbers to an appropriate number of significant figures. pH does not have units.	pH = 4.2 (1 mark)

Your turn

The K_a of hydrocyanic acid (HCN) is 4.9×10^{-10}. For a 0.050 M solution of the acid, **calculate** the

a concentration of hydronium ions (5 marks)

b pH. (2 marks)

Worked example 4.2B

Calculating concentrations, pOH and pH from K_b

Consider a 0.15 mol L^{-1} solution of ammonia (NH_3) ($K_b = 1.8 \times 10^{-5}$). **Calculate** the

a concentration of hydroxide ions (5 marks)

b pOH (2 marks)

c pH. (1 mark)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the questions are asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to show all of the logical steps and reasoning including a chemical equation, a RICE table, and state assumptions made. Part **a** of this question is worth 5 marks, so we must express the concentration with the correct units. Part **b** is worth 2 marks, so the working and answer for pOH must be shown. Part **c** is worth 1 mark, so pOH must be used to find pH.
Step 2: For part **a**, select the appropriate formulas and gather the required data.	**a** $K_b = 1.8 \times 10^{-5}$ $= \frac{[OH^-][B^+]}{[B]}$ $pOH = -\log[OH^-]$ $pH = 14 - pOH$
Step 3: Write a balanced equation for the ionisation of the base.	$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ (1 mark)

<table>
<tr><th>Think</th><th>Do</th></tr>
<tr><td>Step 4: Draw up a RICE table for the initial, change and equilibrium concentrations of the three chemical species. Water can be omitted as the concentration of water is very large (approx. 55 M) and so essentially constant. State assumptions.</td><td>
<table>
<tr><th>R</th><th>$[NH_3]$</th><th>$[NH_4^+]$</th><th>$[OH^-]$</th></tr>
<tr><td>I</td><td>0.15 M</td><td>0</td><td>0</td></tr>
<tr><td>C</td><td>$-x$</td><td>$+x$</td><td>$+x$</td></tr>
<tr><td>E</td><td>$0.15 - x$
≈ 0.15 M</td><td>x</td><td>x</td></tr>
</table>
(1 mark)
Assume that the initial concentration of OH^- is 0 because the change in concentration will be much greater than the concentration present in water and that the final concentrations of NH_4^+ and OH^- are the same.
Assume that the equilibrium concentration of NH_3 is 0.15 M because x is very small since K_b is very small.
(1 mark)</td></tr>
<tr><td>Step 5: Write the K_b expression, substitute equilibrium values, and solve for x.
The first line of substitution is awarded a mark for working. The next line of working is not marked but it is useful to write it out. There is no requirement to write out the calculated answer with all the digits shown – simply round it appropriately to record your final answer for the concentration.</td><td>$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$
$1.8 \times 10^{-5} = \frac{x^2}{0.15}$ (1 mark)
$x = \sqrt{1.8 \times 10^{-5} \times 0.15}$
$x = 1.6432 \times 10^{-3}$</td></tr>
<tr><td>Step 6: Finalise your answer to part a by rounding the numbers to an appropriate number of significant figures and include the units. Note that mol L^{-1} and M are the same units.
Check that your assumption about $[NH_3]$ was valid.</td><td>$[OH^-] = 1.6 \times 10^{-3}$ mol L^{-1} (1 mark)
x is very small and the assumption about $[NH_3]$ is valid.</td></tr>
<tr><td>Step 7: Write the rule to find the pOH and substitute. It can be useful to use the digits saved in your calculator from the answer to part a, to avoid rounding errors.</td><td>b $pOH = -\log[OH^-]$
$= -\log(1.6 \times 10^{-3})$ (1 mark)</td></tr>
<tr><td>Step 8: Finalise your answer to part b by rounding the numbers to an appropriate number of significant figures. pOH does not have units.</td><td>pOH = 2.8 (1 mark)</td></tr>
<tr><td>Step 9: For part c, calculate pH by subtracting pOH from 14. Finalise your answer by rounding the numbers to an appropriate number of significant figures. In this case a third figure is included as pOH was to 1 decimal place. pH does not have units.</td><td>c pH = 14 – pOH
= 14 – 2.8
= 11.2 (1 mark)</td></tr>
</table>

Your turn

Consider a 0.50 mol L^{-1} solution of pyridine (C_5H_5N), which accepts one proton to form $C_5H_5NH^+$ ($K_b = 1.7 \times 10^{-9}$). **Calculate** the

- **a** concentration of hydroxide ions (5 marks)
- **b** pOH (2 marks)
- **c** pH. (1 mark)

Check your learning 4.2

Check your learning 4.2: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain** the steps involved in determining the acid dissociation constant K_a from pH. (2 marks)

2 **Describe** how to calculate pOH, given pH. (1 mark)

3 Benzoic acid (C_6H_5COOH) has a K_a value of 6.3×10^{-5}. For a 0.50 M solution of benzoic acid, **calculate** the pH and the pOH. (8 marks)

4 **Calculate** the pH of 0.10 mol L^{-1} sodium acetate (CH_3COONa) ($K_b = 5.6 \times 10^{-10}$). Start by writing the equilibrium equation. The acetate ion of this salt acts as a proton acceptor. State any assumptions you have made. (6 marks)

Analytical processes

5 **Deduce** the equation for the reaction of the weak base aniline ($C_6H_5NH_2$) with water. (1 mark)

6 A 0.1 M solution of an acid has pH 4.0. **Determine** its K_a value. (2 marks)

7 A 0.01 M solution of a base has pH 8.0. **Determine** its K_b value. (2 marks)

Practical

Lesson 4.3

Comparing the relative strengths of acids and bases

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Learning intentions and success criteria

Lesson 4.4

Acid–base indicators

Key ideas

- → Acid–base indicators are weak acids or bases, which dissociate slightly in water and form ions.
- → The acid or base form and the ionic form have different colours so the colour of an indicator is pH-dependent. Each indicator has a characteristic pH at which the two forms are equimolar, and the colour change occurs across a range of pH values close to that pH.
- → Indicators can be used in titrations. It is important to select an indicator that suits the class of titration.

Learning intentions and success criteria

indicator
a chemical substance that changes colour at different pH values

What are some common acid-base indicators?

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 lesson discusses some of the most common indicators, their properties and applications.

Solutions that change colour depending on pH are called pH indicators. Natural indicators include turmeric and red cabbage. Even some flowers such as camellias can change the colour of their petals depending on the pH of the soil and therefore act as pH natural indicators.

The most common acid–base indicators (e.g. phenolphthalein and methyl red) are complex molecules that are weak acids or bases. They can be represented by the general formula Hin (In = indicator). Indicators exhibit one colour in the protonated form (HIn) and a different colour when unprotonated – or when the proton is absent (i.e. its In^- or conjugate base form).

Consider the hypothetical indicator HIn, which appears red in its undissociated form and blue in its dissociated form. Its dissociation constant at equilibrium is $K_a = 1 \times 10^{-5}$.

$$\underset{\text{red}}{HIn} \rightleftharpoons \underset{\text{blue}}{In^-} + H^+$$

The K_a expression for HIn is:

$$K_{a(In)} = \frac{[H^+][In^-]}{[HIn]}$$

The notation $K_{a(In)}$ is used here to distinguish the K_a of the indicator. This equation can be rearranged to demonstrate the effect of pH changes on the ratio of acid indicator and its conjugate base:

$$\frac{K_{a(In)}}{[H^+]} = \frac{[In^-]}{[HIn]}$$

Consequently, if a small volume of a solution containing the indicator HIn at equilibrium was added to a solution of an acid with a pH of 1.0 ($[H^+] = 1 \times 10^{-1}$), then:

$$\frac{K_a}{[H^+]} = \frac{[10^{-5}]}{[10^{-1}]} = \frac{[In^-]}{[HIn]}$$

$$= 10^{-4} = \frac{1}{10{,}000} = \frac{[In^-]}{[HIn]}$$

This indicates that the amount of the red form of the indicator (HIn) far exceeds the amount of the blue form of In^-, so the solution is red.

If OH^- was added to the solution, $[H^+]$ would decrease. This would cause the reaction to proceed to the right to restore equilibrium in favour of the blue form, which is the In^- ion. In practice, the human eye can usually distinguish colour changes in the ratio of 10:1 for indicators, which means that the colour change is observed within 1 pH unit of the pK_a of the indicator.

What are examples of weak acid indicators?

Most indicators are weak acids (HIn). In solution, for an indicator to effectively change colour during pH changes, it must be in equilibrium with its conjugate base (In^-):

$$\underset{\text{colour A}}{HIn(aq)} + H_2O(l) \rightleftharpoons \underset{\text{colour B}}{In^-(aq)} + H_3O^+(aq)$$

Given that the acid indicator and its conjugate base are different colours, the general rule can be made that 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 acidic solution, 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 less acidic/more alkaline conditions, the equilibrium shifts to the right and the solution becomes pink because of the higher concentration of the anions. Phenolphthalein has a K_a of 5.0×10^{-10} and a pK_a of 9.3, so the colour change occurs in the range from about pH = 8 to pH = 10, becoming a more intense pink at the higher end of this range.

$$\underset{\text{colourless}}{HPhph(aq)} + H_2O(l) \rightleftharpoons \underset{\text{pink}}{Phph^-(aq)} + H_3O^+(aq)$$

What are examples of weak base indicators?

Weak bases (B) can also be used as indicators. If the weak base indicator is added to an alkaline solution, the indicator is in its base B form and therefore displays colour C. If the weak base indicator is added to a more acidic solution, the indicator dissociates to form BH^+, its conjugate acid, and colour D is displayed, according to the equilibrium:

$$\underset{\text{colour C}}{B} + H_3O^+ \rightleftharpoons \underset{\text{colour D}}{BH^+} + H_2O$$

What is the significance of the pK_a or pK_b of an indicator? Indicators change colour over a small pH range when the solution contains roughly 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 at the point where $[In^-] = [HIn]$, the following is true:

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

Since $[In^-] = [HIn]$ at the point of colour change, you can cancel them from the above equation:

$$K_a = \frac{[H^+]\cancel{[In^-]}}{\cancel{[HIn]}}$$
$$= [H^+]$$

which leads to:

$$K_a = [H^+]$$

$$pK_a = pH$$

This means that the colour of the indicator changes in the region when pK_a of the indicator is equal to the pH of the solution. The same sort of reasoning applies to indicators that are weak bases.

Different indicators change colour over different pH ranges. Most indicators change colour over a range of $pK_a \pm 1$ (Table 1) because this is enough of a change in the ratio of the two forms for the human eye to detect.

titration
the addition of a solution of known concentration to a known volume of a solution of unknown concentration until the reaction reaches neutralisation

equivalence point
the point in a titration when the reactants have reacted in the stoichiometric molar ratio of the balanced chemical equation

end point
the point in a titration when the indicator changes colour

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
Bromophenol 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

What indicators are used in titration?

Indicators are used in titrations as a visual way of seeing when stoichiometric amounts of reagents have been added (see Module 5). **Titration** is a method for determining the concentration of an unknown acid or base by neutralising it with a known base or acid (there are also other types of titrations besides acid and base titrations, but we will discuss just acid–base titrations in this section). The **equivalence point** in a titration is when just enough titrant (known solution) has been added to completely react with all of the analyte (unknown solution) solution for an acid–base pair. At this equivalence point, the acid and base have been added in stoichiometric quantities to both react fully and neither is in excess. This is why it is also called the stoichiometric point of equivalence.

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, and the analytical process of titration is stopped or ended. 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 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, which can be measured with a pH meter and an electrode. On neutralisation, the pH rapidly increases from pH 3 to 11. The equivalence point is at pH 7, which is neutral. In this case, it is an easy task to choose an indicator because all common indicators change colour within the range of pH 3 to 11 (see Table 1). Phenolphthalein is frequently used when the acid is titrated with the base, as the colour change is easy to detect.

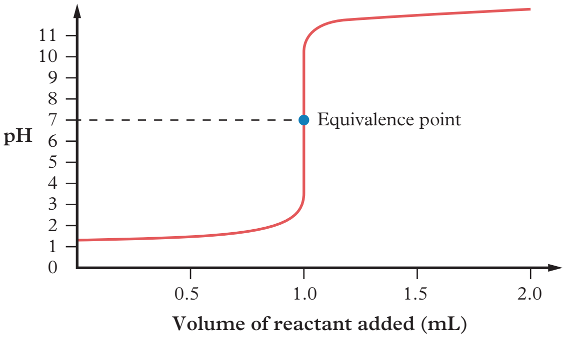


FIGURE 2 The titration curve for a strong acid with a strong base. As the equivalence point is reached and passed, the pH rapidly changes from 3 to 11.

titration curve
a graph of pH against volume of reactant added

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. At equivalence point, the solution is not neutral, due to the effect on pH of the conjugate base of the weak acid. The change in pH near the equivalence point is less than that for a strong acid–strong base and occurs at pH 7–11. A suitable indicator from Table 1 is phenolphthalein, which changes colour in the middle of the rapid pH change.

Other recognisable features of this titration curve are that the:

- initial pH is higher than in the curve for a strong acid
- pH rises more rapidly to start with, but then changes very gradually, due to the reaction mixture being a buffer solution. This region of very gradual pH change is called the buffer region
- half-equivalence point is when the volume of reactant added is half that of the volume at equivalence point
- pH at half-equivalence point is the pK_a of the weak acid being titrated.

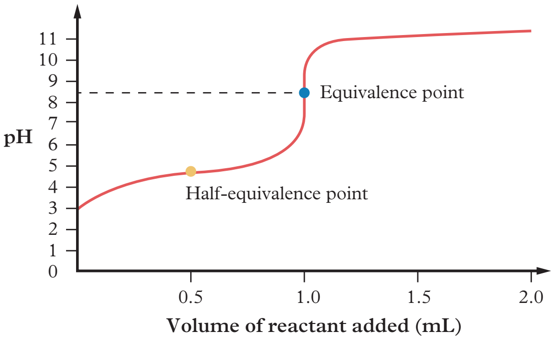


FIGURE 3 The titration curve for a weak acid with a strong base

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 rather than neutral. This is due to the presence of the conjugate acid of the weak base. The change in pH near the equivalence point 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.

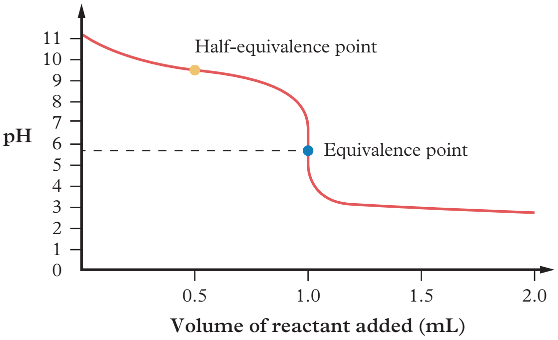


FIGURE 4 The titration curve for a weak base with a strong acid

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 trend in conductivity changes in gradient.

Worked example 4.4A

Analysing the effectiveness of indicators in different solutions

Consider the titration curve in Figure 5. Oxalic acid is diprotic and the end of the titration in the steepest part of the titration curve corresponds to the completion of the reaction with the second proton.

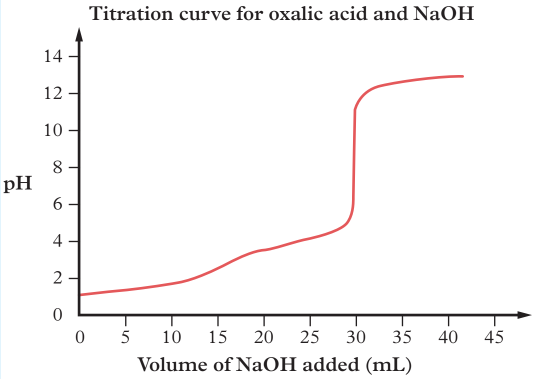


FIGURE 5 The titration curve for oxalic acid and NaOH

a **Determine** an appropriate indicator for the complete neutralisation reaction between oxalic acid and sodium hydroxide as shown in the curve. (1 mark)

b **Identify** the colour change at the end point of the titration. (1 mark)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	“Determine” means to establish, conclude or ascertain after consideration, observation, investigation or calculation. In this case you will need to analyse the titration curve and use information on indicators provided to you in the data booklet to determine the appropriate indicator. Part **a** is worth 1 mark for providing an appropriate indicator. “Identify” means to locate, recognise and name. You will need to use the colour change associated with your indicator from part **a** to work this out. Part **b** is worth 1 mark so a concise description of the colour change will suffice.
Step 2: For part **a**, identify the equivalence point on the titration curve by where a rapid change in pH occurs.	**a** The titration curve for oxalic acid shows two distinct sudden rises in pH, at about a volume of 15 mL of NaOH and again at about 30 mL of added NaOH. This shows that oxalic acid is diprotic. The equivalence point for the first proton does not produce a rapid enough change in pH, and thus is difficult to detect with an indicator. The second equivalence point produces a rapid change in pH from about 5.5 to about 11.5. The equivalence point will be at the steepest point of this rapid change approximately pH = 9. An appropriate indicator would change colour between pH 8 and 10.

<table>
<tr><th>Think</th><th>Do</th></tr>
<tr><td>Step 3: Check the acid–base indicators table in the QCAA <i>Formula and data book</i> to identify an indicator with a pK_a value that aligns closely to the identified equivalence point.</td><td>Ensure that the identified pH value at equivalence point aligns with the steepest part of the titration curve.
<table>
<tr><th>Name</th><th>pK_a</th><th>pH range of colour change</th><th>Colour change (acidic to basic)</th></tr>
<tr><td>Methyl orange</td><td>3.7</td><td>3.1–4.4</td><td>Red to yellow</td></tr>
<tr><td>Bromophenol blue</td><td>4.2</td><td>3.0–4.6</td><td>Yellow to blue</td></tr>
<tr><td>Bromocresol green</td><td>4.7</td><td>3.8–5.4</td><td>Yellow to blue</td></tr>
<tr><td>Methyl red</td><td>5.1</td><td>4.4–6.2</td><td>Pink to yellow</td></tr>
<tr><td>Bromothymol blue</td><td>7.0</td><td>6.0–7.6</td><td>Yellow to blue</td></tr>
<tr><td>Phenol red</td><td>7.9</td><td>6.8–8.4</td><td>Yellow to red</td></tr>
<tr><td>Phenolphthalein</td><td>9.6</td><td>8.3–10.0</td><td>Colourless to pink</td></tr>
</table>
Phenolphthalein has a pK_a of 9.6, which is the closest to the identified equivalence point and hence is the most suitable indicator for this titration. (1 mark)</td></tr>
<tr><td>Step 4: For part b, use the indicator from part a to describe the colour change when the endpoint is reached.</td><td>b The end point of the titration will occur when the solution changes from colourless to pink. The point at which the first pale pink appears is approximately indicative of the equivalence point. (1 mark)</td></tr>
</table>

Your turn

Consider the titration curve in Figure 6.

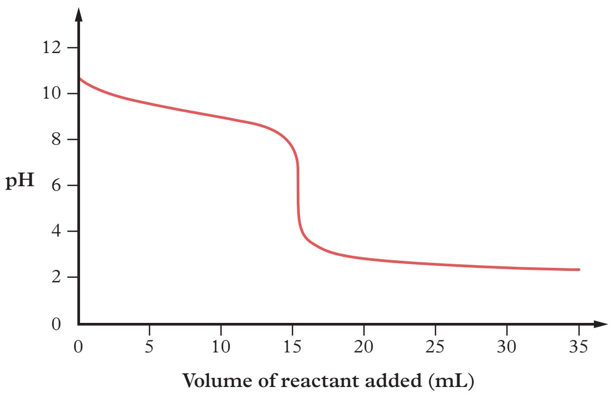


FIGURE 6 A titration curve

a **Determine** an appropriate indicator for the neutralisation reaction. (1 mark)

b **Identify** the colour change at the end point of the titration. (1 mark)

Check your learning 4.4

Check your learning 4.4: Complete these questions online or in your workbook.

Retrieval and Comprehension

1 **Explain** the relationship between pH and pK_a. (2 marks)

2 **Explain** how to choose an appropriate pH indicator for a titration. (1 mark)

3 **Explain** what the equivalence point represents in a titration. (1 mark)

4 **Explain** what the end point represents in a titration. (1 mark)

Analytical processes

5 **Determine** the types of titration (e.g. strong acid–strong base) for which the following indicators are suitable.

  a Thymolphthalein, pH range 9.4–10.6, colour change from red to yellow (1 mark)

  b Alizarin yellow, pH range 10.1–12.0, colour change from yellow to red (1 mark)

6 The following table includes some suitable indicators for different titrations.

  a Bromophenol blue has a pH range of 3.0–4.6 and changes from yellow to blue as the pH increases. **Determine** an approximate value for the pK_a of this indicator. (1 mark)

  b **Determine** the colour this indicator will be at pH 3.3. (1 mark)

  c Using the acid–base indicator table in the QCAA *Formula and data book*, **deduce** the approximate pH of a solution in which bromocresol green is blue and bromothymol blue is yellow. (1 mark)

Reactants	pH range at predicted equivalence point	Suitable indicators	pK_a
Strong acid + strong base	3–11	Methyl orange	3.7
Weak acid + strong base	7–11	Phenol red	7.9
Strong acid + weak base	3–7	Bromocresol green	4.7
Weak acid + weak base	Because both reagents are weak, a significant change in pH is not detectable so there is no suitable indicator.		

MODULE 4

Lesson 4.5

Review: Dissociation constants and acid–base indicators

Summary

4.1
- The strength of an acid or a 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 $\mathrm{p}K_a = -\log_{10}K_a$ and $\mathrm{p}K_b = -\log_{10}K_b$.

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
- Practical: Comparing the relative strengths of acids and bases

4.4
- Acid–base indicators are weak acids or bases, which dissociate slightly in water and form ions.
- The acid or base form and the ionic form have different colours so the colour of an indicator is pH-dependent. Each indicator has a characteristic pH at which the two forms are equimolar, and the colour change occurs across a range of pH values close to that pH.
- Indicators can be used in titrations. It is important to select an indicator that suits the class of titration.

Key formulas

Acid dissociation constant	$K_a = \frac{[H^+][A^-]}{[HA]}$
Base dissociation constant	$K_b = \frac{[BH^+][OH^-]}{[B]}$
Dissociation constant of water, for an acid or base and its conjugate	$K_w = K_a \times K_b$
pK_a	$\mathrm{p}K_a = -\log_{10}K_a$
pK_b	$\mathrm{p}K_b = -\log_{10}K_b$
At 25°C for an aqueous solution	pH + pOH = 14

Review questions 4.5A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

1 K_a stands for

A potassium acid.

B acid dissociation constant.

C equilibrium constant of air.

D correlation constant for acids.

2 What is the relationship between K_a, K_b and K_w?

A $K_w = \frac{K_a}{K_b}$

B $K_w = K_a \times K_b$

C $K_a = K_w \times K_b$

D $K_w = -\log_{10}K_a + -\log_{10}K_b$

3 What is the relationship between pK_b and K_b?

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.

5 Consider the following acid–base indicator solution. The pH of the solution the indicator is in is initially at the pK_a of the indicator.

$HInd \rightleftharpoons H^+ + Ind^-$

colour A   colour B

What is the effect on this indicator when a small amount is added to hydrochloric acid?

A The equilibrium shifts to the left and more colour B is seen.

B The equilibrium shifts to the left and more colour A is seen.

C The equilibrium shifts to the right and more colour A is seen.

D The equilibrium shifts to the right and more colour B is seen.

6 A 20 mL concentrated solution of a weak acid and a 20 mL dilute solution of a strong acid are compared. Which of the following will definitely be true?

A The pH of the strong acid will be lower than the pH of the weak acid.

B The conductivity of the weak acid will be greater than the conductivity of the strong acid.

C The reaction rate with calcium carbonate will be greater for the strong acid than the weak acid.

D The weak acid will require a greater amount of base to neutralise it than the strong acid will require.

Review questions 4.5B Short response

Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

7 **Calculate** the pH of a 0.50 M solution of hypochlorous acid (HOCl, $K_a = 3.5 \times 10^{-8}$). (7 marks)

8 **Calculate** the pH of a 1.0 M aqueous solution of ammonia (NH_3, $K_b = 1.8 \times 10^{-5}$). (8 marks)

9 **Explain** how to find an appropriate acid–base indicator for a titration of a

a strong acid with a strong base (2 marks)

b weak acid with a strong base (2 marks)

c weak base with a strong acid. (2 marks)

10 **Explain** why the conjugate base of the weak acid ethanoic acid (CH_3COOH) is a weak base, given that in general, as acid strength increases, conjugate base strength decreases. (2 marks)

11 The base $Sr(OH)_2$ is not very soluble in water and a saturated solution of the base has a concentration of 0.10 M. **Calculate** the pH of this saturated solution. (3 marks)

Analytical processes

12 A 0.200 M solution of an acid has a pH of 3.0. **Determine** its K_a value. (2 marks)

13 Methyl orange has a pH range of 3.1–4.4. **Determine** the titration types that methyl orange is suitable for. (2 marks)

14 **Categorise** the following from weakest to strongest based on their K_a and K_b values. (2 marks)

a Ethanoic acid (CH_3COOH, $K_a = 1.8 \times 10^{-5}$)

b Carbonate ion (CO_3^{2-}, $K_b = 2.1 \times 10^{-4}$)

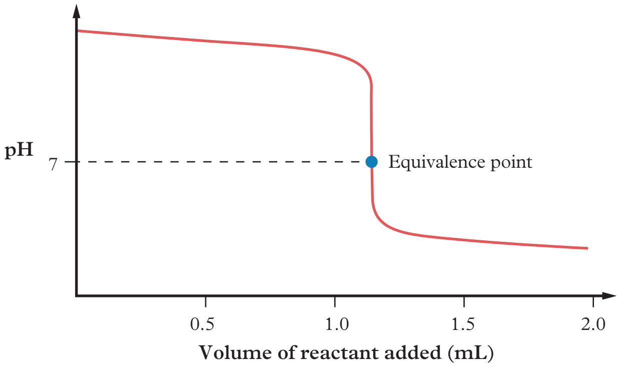
c Ammonium ion (NH_4^+, K_b of $NH_3 = 1.8 \times 10^{-5}$)

d Phenol (C_6H_5OH, $K_a = 1.0 \times 10^{-10}$)

Knowledge utilisation

15 **Determine** the most suitable indicator for a titration between aqueous methylamine, (CH_3NH_2) with nitric acid (HNO_3). **Justify** your answer. (2 marks)

16 Consider the titration curve shown and **justify** the type of titration it represents. (1 mark)



17 The table 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. (4 marks)

Indicator	A	B	C
Methyl orange	Yellow		Yellow
Bromothymol blue		Green	
Phenolphthalein	Colourless	Colourless	
Litmus			Blue

18 A 50.0 mL solution of 0.10 M lactic acid ($K_a = 1.4 \times 10^{-4}$) is mixed with 25.0 mL of 0.10 M NaOH. **Calculate** the resulting concentration of lactic acid and the concentration of the conjugate base of lactic acid in the solution and **justify** why small amounts of 0.10 M HCl will not appreciably alter the pH of the solution. Lactic acid is a monoprotic acid. (5 marks)

Data drill

Acid strength versus concentration

A titration reaction with 0.1 M NaOH was used to identify two unlabelled vials of monoprotic acids Acid 1 and Acid 2, which are known to contain either hydrochloric acid or ethanoic acid. The graph below shows changes in pH for the respective titrations of 25 mL of the two acids.

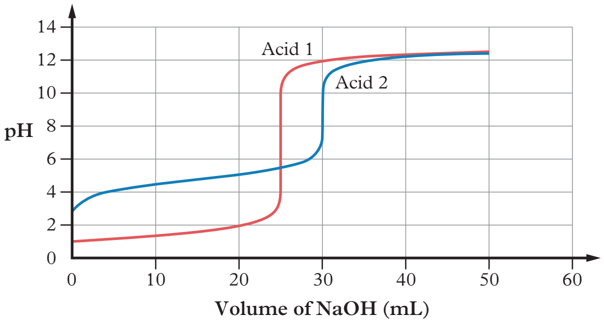


FIGURE 1 Titration curve of two monoprotic acids with 0.1 M NaOH

Apply understanding

1 **Identify** the volume of NaOH required to reach the equivalence point of Acid 1. (1 mark)

2 **Determine** the pK_a for Acid 2. (1 mark)

3 **Calculate** the concentration of the bottle containing ethanoic acid. Show all working. (3 marks)

Analyse data

4 **Contrast** the pH and volume of NaOH at the equivalence point and half-equivalence point. (4 marks)

5 **Compare** the differences between Acid 1 and Acid 2 with respect to strength and concentration and therefore **identify** which acid vial contains hydrochloric acid. (3 marks)

Interpret evidence

6 Use the acid–base indicators table from the QCAA *Formula and data book* to **determine** the indicator most suitable for identifying the end point of both titrations. **Justify** your response. (2 marks)

Module 4 checklist: Dissociation constants and acid–base indicators

MODULE 5

Volumetric analysis

Introduction

Volumetric analysis is an essential wet chemistry technique that is used to determine the concentration or amount of a solute in a larger volume of solvent. It is a quantitative technique that produces accurate and reliable results.

Volumetric analysis was first developed in the late 1700s and has been highly effective and useful ever since. It is often used in food chemistry to determine the amounts of nutrients in a food sample, in the development of biodiesels as fuels, in mining to analyse minerals, and in environmental chemistry to analyse nutrients in seawater.

Prior knowledge

Prior knowledge quiz

Check your understanding of concepts related to volumetric analysis before you start.

Subject matter

Science understanding

→ Discriminate between the terms *end point* and *equivalence point*.

→ Sketch the general shapes of conductometric and acid-base titration curves involving strong and weak acids and bases. (Titration of weak acids to weak bases is not required.)

→ Interpret acid-base titration curves to determine the intercept with pH axis, equivalence point, buffer region and points where $pK_a = pH$ or $pK_b = pOH$.

→ Interpret conductometric titration curves to determine the intercept with conductivity axis, equivalence point and volume of titrant

→ Analyse volumetric data, including solubility, conductometric and acid-base titration curves, to determine moles, mass, volume and concentration.

→ Analyse titration curves to calculate the concentration of a solution with reference to a standard solution.

Science inquiry

→ Investigate acid-base or conductometric titrations.

Source: *Chemistry 2025 v1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

Practicals

These lessons are available on Oxford Digital.

Lesson 5.3	Determining the concentration of ethanoic acid in white vinegar
Lesson 5.5	Conductometric titration

Lesson 5.1

Principles of volumetric analysis

Key ideas

→ Volumetric analysis uses titration to determine the volume of chemicals when they react in a known molar ratio. The reaction occurs at the equivalence point. An indicator that changes colour when the reaction has reached this point can be used as well for the analysis. The colour change is referred to as the end point.

→ A standard solution is a solution whose concentration is known to a high degree of accuracy. Such solutions are used in titration to determine the concentration of a second reactant.

→ The equivalence point of a titration is reached when amounts of both reactants are in the stoichiometric ratio and no reactant remains. The end point of a titration is a chemical observation that scientists use to determine when to end the titration. The end point can be found by observing a suitable indicator or changes in conductivity and should be close to the equivalence point.

Learning intentions and success criteria

volumetric analysis
a quantitative analytical technique for determining the concentration of a solution by titrating it against a solution of known concentration

stoichiometry
the calculation of the amount of reactants and products in chemical reactions by using a balanced equation

solution
a homogeneous mixture of a solute dissolved in a solvent, where the concentration is the same throughout the solution

mole ratio
the actual ratio of amounts in moles of reactants (or products) in a given reaction mixture or sample

stoichiometric ratio
the coefficient ratio in a chemical equation

standard solution
a solution of accurately known concentration

volumetric flask
a piece of laboratory glassware that can measure highly accurate volumes

Study tip

When completing stoichiometry problems, always calculate the number of moles of the chemical with known values first.

What do I need to know before I perform a titration?

Volumetric analysis uses **stoichiometry** to determine the concentration of a **solution** of accurately known volume, by titrating it against another solution of known concentration.

Equivalence point

The equivalence point of a titration is reached when chemicals have completely reacted. The **mole ratio** of the two reactants added to the mixture is the same as their molar **stoichiometric ratio** and no reactant is in excess. At the equivalence point, there are no reactants remaining. Consider the reaction between sodium hydroxide and hydrochloric acid:

$$\mathrm{NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)}$$

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.

Standard solutions

To perform a titration, you need to prepare a **standard solution**. A standard solution is a solution of a highly accurate concentration. To make a standard solution, you require a piece of specialised equipment, called a **volumetric flask** (Figure 1), which helps in preparing 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 make the standard solution with a very accurate concentration.

A primary standard must have several important qualities. It must:

- be a solid that is soluble in water so it can dissolve and make a standard solution
- be very pure

- have a known chemical formula
- have a high molar mass 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. For example, NaOH is not an appropriate primary standard because it absorbs water from the air, and the damp solid also reacts with carbon dioxide.
- be anhydrous. For example, $MgSO_4.7H_2O$ (hydrated magnesium sulfate or Epsom salts) is not an appropriate standard because the seven water molecules can evaporate, changing the chemical formula and molar mass
- be reasonably priced.

At times, the solution used in a titration is not made from a primary standard. For instance, sodium hydroxide readily absorbs moisture and carbon dioxide from air, making it difficult to accurately measure its mass when preparing a solution.

When a solution cannot be prepared directly from a primary standard, it must first be **standardised** by titration. After its concentration is accurately determined, it is referred to as a **secondary standard**. To do this, a suitable primary standard – one that reacts with the substance of unknown concentration – is chosen and used to prepare a standard solution. By titrating this against the solution of unknown concentration, the exact concentration can be calculated. The new secondary standard can then be standardised future titrations.

Worked examples 5.1A and 5.1B demonstrate the calculations required for preparing standard solutions.

FIGURE 1 A volumetric flask is calibrated to measure highly accurate volumes.

primary standard
a substance that is readily available in a highly pure form that can be 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

standardise
the process of determining the exact concentration of a solution, typically by titration against a solution of known concentration

secondary standard
a solution whose concentration has been accurately determined by titration with a primary standard, allowing it to be used in further titrations

Worked example 5.1A

Calculating the mass required to make a standard solution

Students are to make a 0.20 M standard solution of aqueous sodium carbonate (Na_2CO_3) in a 250 mL volumetric flask. **Calculate** the mass of sodium carbonate that they should use. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to calculate the final answer to the correct number of significant figures, showing all working throughout the process. The question is worth 2 marks, 1 mark for obtaining the correct answer and another mark for showing the correct working.
Step 2: Using concentration and volume, calculate the number moles of sodium carbonate.	$n(Na_2CO_3) = c \times V$ $= 0.20\,mol\,L^{-1} \times 0.250\,L$ $= 0.050\,mol$ (1 mark)

Think	Do
Step 3: Using the number of moles and molar mass, calculate the mass of sodium carbonate and express your answer to an appropriate number of significant figures (in this case, 2 s.f.)	$m(\mathrm{Na_2CO_3}) = n \times M$ $= 0.050\,\mathrm{mol} \times 105.99\ \mathrm{g\ mol^{-1}}$ $= 5.3\ \mathrm{g}$ Therefore, the student must use 5.3 g of sodium carbonate. (1 mark)

Your turn

Students need to make a 0.150 M standard solution of aqueous potassium hydrogen phthalate ($C_8H_5KO_4$) in a 200 mL volumetric flask. **Calculate** the mass of potassium hydrogen phthalate that they should use. (2 marks)

Study tip

Never round off your answers in intermediate steps in a calculation. Always keep values in your calculator, and round at the final step. If not, your final answers might be incorrect.

Study tip

In stoichiometry problems, volumes must be expressed in litres when using $c = \frac{n}{V}$.

Challenge

Not enough primary standard?

A student wishes to synthesise a standard solution of 0.300 M sodium chloride (NaCl). In the chemical storeroom, there is only 0.200 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. (6 marks)

Worked example 5.1B

Calculating the concentration of a standard solution

A standard solution is made from 1.25 g of sodium carbonate (Na_2CO_3) in water in a 20.00 mL volumetric flask. **Calculate** the concentration of the solution. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to calculate the final answer to the correct number of significant figures, showing all working throughout the process.
Step 2: Calculate the number of moles of sodium carbonate, using mass and molar mass.	$n(\mathrm{NaOH}) = \frac{m}{M}$ $= \frac{1.25\ \mathrm{g}}{105.99\ \mathrm{g\ mol^{-1}}}$ $= 0.0118\ \mathrm{mol}$ (1 mark)
Step 3: Use the number of moles and volume to calculate the concentration of sodium carbonate. Avoid rounding the number of moles from step 1 to get a precise value. Use the value stored in your calculator instead.	$c(\mathrm{NaOH}) = \frac{n}{V}$ $= \frac{0.0118\ \mathrm{mol}}{0.02000\ \mathrm{L}}$ $= 0.590\ \mathrm{mol}$
Step 4: Express your answer to an appropriate number of significant figures, in this case 3 s.f.	Therefore, the concentration of sodium hydroxide is 0.590 M (3 s.f.). (1 mark)

Your turn

A standard solution is made from 0.50 g of potassium hydrogen phthalate ($C_8H_5KO_4$) in water in a 150.00 mL volumetric flask. **Calculate** the concentration of the solution. (2 marks)

How do you prepare a standard solution?

A common method for preparing a standard solution is as follows.

1 Rinse the volumetric flask with the desired solvent, which is usually water in high school chemistry. 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 clean beaker, being sure to transfer all of the solid. The solid may be washed into the beaker with a small amount of solvent. Add the solvent (e.g. distilled water) to the beaker and use a glass rod to help dissolve the solid. Do not splash or spill any of the solution.

4 Transfer the solution quantitatively from the beaker to the volumetric flask using a funnel. “Quantitatively” here means completely. You will need to rinse the beaker, glass rod and funnel into the volumetric flask.

5 Use a wash bottle to bring the solution up to a few centimetres below the mark on the flask. Place the stopper on the flask and mix thoroughly by inverting the flask at least 10 times. Some solutions have a different density from water, so must be well-mixed before being made up to the line. Then, use a Pasteur pipette or dropping pipette to bring the level of the liquid up to the line. The bottom of the **meniscus** must sit on this line (for liquids like water where the meniscus curves down) (Figure 2D). Place the volumetric flask on the bench and crouch down so that the meniscus is at eye level to minimise errors.

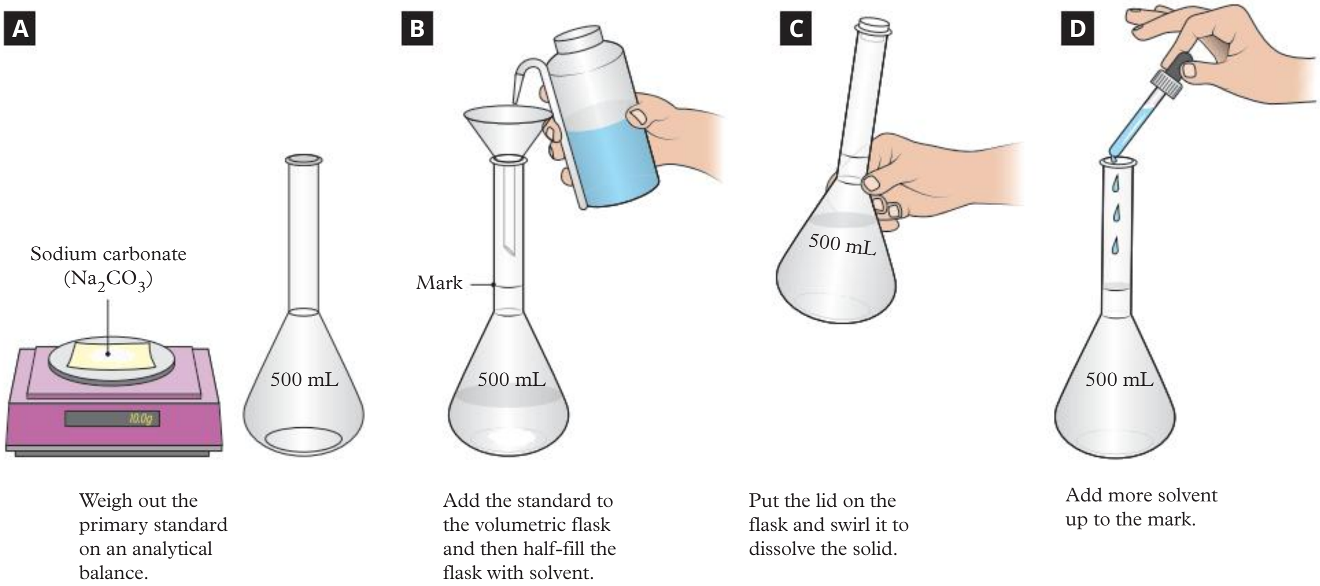
6 Place the lid back on the flask and hold it firmly in place while you tip the flask upside down and then upright again at least 10 times. This will ensure that the solution has an evenly distributed concentration.

Worked examples 5.1B and 5.1C demonstrate the calculations required for preparing standard solutions.

Study tip

To revise your understanding of how to calculate molar mass, review Unit 1 Topic 3.

meniscus
the curved upper surface of a liquid in a piece of measurement glassware



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

What is titration?

Titration is a technique in which the concentration of a solution is determined by adding an accurate volume of a solution of known concentration, the standard solution, to reach the equivalence point. In some titrations, the solution with the unknown concentration is titrated into a sample of the standard solution, whose volume and concentration are known.

Titration uses equipment that dispenses very accurate volumes of solutions. If the volumes of both reactants are known accurately, and the standard solution concentration is also known, you can calculate the concentration of the second reactant, provided you can recognise when the reaction has reached the equivalence point.

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 the phosphoric acid has a known concentration, it is the standard solution. If a known volume is used in the reaction, you can calculate the number of moles of phosphoric acid using the formula:

$$n = c\ (\text{mol L}^{-1}) \times V\ (\text{L})$$

Sodium hydroxide is then added until the equivalence point has been reached (we will talk about how you can determine this later in the module). 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 required to reach the equivalence point is also accurately known, you can determine the concentration of this solution. Worked example 5.1C demonstrates this process.

End point

To determine when the equivalence point has been reached in a chemical reaction, several experimental methods can be used. These are primarily based on a colour change but can also be based on a change in a solution's conductivity. Colour changes are typically caused by the addition of an indicator. Conductivity changes are caused by a change in ions or ion concentration and can be measured using a conductivity meter and electrode.

An end point is experimentally measurable and observable, whereas an equivalence point is purely theoretical. It is essential that the method chosen to observe an end point ensures that the colour change or conductivity or other change occurs as close to the equivalence point as possible.

Worked example 5.1C

Using stoichiometry to calculate unknown quantities

In a titration, 10.00 mL of 0.2000 M phosphoric acid reacts with 15.00 mL of sodium hydroxide of unknown concentration. **Calculate** the concentration of the sodium hydroxide solution. (6 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to calculate the final answer to the correct number of significant figures, showing all working throughout the process.

Think	Do
Step 2: Write a balanced chemical equation for the reaction.	$H_3PO_4(aq) + 3NaOH(aq) \rightarrow Na_3PO_4(aq) + 3H_2O(l)$ (1 mark)
Step 3: Calculate the amount (in moles) of the "known" chemical phosphoric acid.	$n(H_3PO_4) = c \times V$ $= 0.2000\ \text{mol L}^{-1} \times 0.01000\ \text{L}$ (1 mark) $= 0.002000\ \text{mol}$ (1 mark)
Step 4: Use the stoichiometric ratio (H_3PO_4:NaOH is 1:3) to calculate the number of moles of the "unknown" chemical sodium hydroxide.	$n(NaOH) = n(H_3PO_4) \times 3$ $= 0.002000\ \text{mol} \times 3$ $= 0.006000\ \text{mol}$ (1 mark)
Step 5: 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.	$c(NaOH) = \frac{n}{V}$ $= \frac{0.006000\ \text{mol}}{0.01500\ \text{L}}$ $= 0.4000\ \text{mol L}^{-1}$ (1 mark)
Step 6: Express your answer to 2 s.f.	0.40 M (1 mark)

Your turn

In a titration, 15.50 mL of 0.1500 M phosphoric acid reacts with 27.30 mL of sodium hydroxide of unknown concentration. **Calculate** the concentration of the sodium hydroxide solution. (6 marks)

Challenge

Titration involving dilution

Some students were set the task of determining the concentration of ethanoic (acetic) acid in a particular brand of vinegar. A 10.00 mL sample of vinegar was diluted by a factor of 10 in a 100.00 mL volumetric flask and a pipette was used to transfer 20.00 mL of diluted vinegar to a conical flask. The vinegar was titrated with a 0.1000 M NaOH standardised 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. (6 marks)

Study tip

Concentration is usually expressed in mol L^{-1} (M), g L^{-1} and ppm, and other units include ppb (μg L^{-1}), %w/v (g in 100 mL), %w/w (g in 100 g) and %v/v (mL in 100 mL).

What specific terminology do I need to know to perform a titration?

To perform a titration, you need specialised equipment – a **burette** and a **pipette**. Burettes and pipettes dispense very precise volumes of a solution and can deliver volumes to within 0.01 mL, increasing the accuracy of the analytical technique.

burette
a graduated glass cylinder with a stopcock (tap) that dispenses very precise volumes of a solution

pipette
a glass tube that dispenses very precise 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 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 solution dispensed from a burette that differ by only 0.1 mL between the highest and the lowest

precision
the consistency of a series of measurements

The general method to perform a titration is as follows.

1. Fill the burette with the standard solution. This is called the **titrant**. The volume of solution dispensed from the burette 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 to the nearest 0.02 mL. 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 titrant 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. Note that some colours fade with time; for example, for the phenolphthalein indicator, the pink colour will slowly fade.
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 usually differ by 0.1 mL from lowest to highest, although the precise level of expected reproducibility will depend on the titration of equipment used. These concordant titres must be averaged to use in calculations. This increases the **precision** of the results.

Note: if the titrant is not a primary standard, it may need to be standardised first. It is titrated into a known volume of a primary standard, and calculations then enable you to find the concentration of the titrant. It is then known as a secondary standard.

Worked examples 5.1D to F demonstrate some titration calculations.

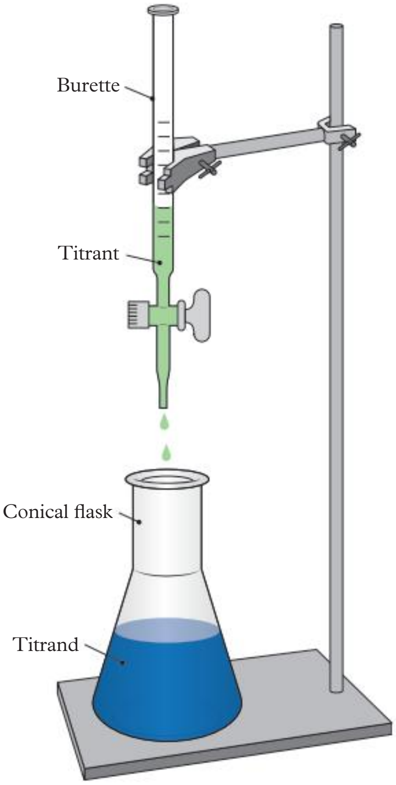


FIGURE 3 Titration apparatus

Study tip

Concordant titres must usually only differ by 0.1 mL or less from the highest to the lowest readings.

Worked example 5.1D

Analysing titre volumes

A student performs the same titration five times. They obtain titres with the following volumes: 21.16, 21.21, 21.08, 21.04 and 21.00 mL.

a Analyse the data and **justify** whether the titres are concordant. Which titres can be used? (2 marks)

b **Calculate** the volume the student should use in their calculations. (1 mark)

c **Explain** what the student must do if the titres are not concordant. (1 mark)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Justify" means give reasons or evidence to support an answer. "Calculate" means to determine or find a number or answer by using mathematical processes. "Explain" means make an idea or situation plain or clear by describing it in more detail or revealing relevant facts. We need to examine the titres obtained in the experiment to determine which can be used in the calculation, and why some are different to others.
Step 2: For part **a**, recall that concordant titres are three titres that are within a 0.1 mL range, ±0.05 mL.	**a** The titres of 21.08, 21.04 and 21.00 mL are within 0.1 mL of one another, so they are concordant. (1 mark for the titres and 1 mark for the justification of the 0.1 mL range)
Step 3: For part **b**, determine the volume to be used in the calculations by calculating the average of the concordant titres.	**b** $\text{volume} = \frac{(21.08 + 21.04 + 21.00)\ \text{mL}}{3}$ $= 21.04\ \text{mL}$ (1 mark)
Step 4: For part **c**, consider that a titration cannot stop until titres are concordant.	**c** If the titres are not concordant, the data is not sufficiently precise, and the student must continue to repeat the titration until concordant titres are obtained. (1 mark)

Your turn

A student performs the same titration six times. They obtain the following titres: 37.23, 35.27, 34.26, 34.33, 34.41 and 34.29 mL.

a Analyse the data and **justify** whether the titres are concordant. Which titres can be used? (2 marks)

b **Calculate** the volume that the student should use in their calculations. (1 mark)

c **Explain** what may have resulted in the initial two titres being larger than the remaining four. (2 marks)

Worked example 5.1E

Applying titration calculations

A student performs a titration using a 0.1200 M standardised solution of HCl. They 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. (5 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to calculate the final answer to the correct number of significant figures, showing all working throughout the process.
Step 2: Write a balanced chemical equation.	$HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$ (1 mark)
Step 3: Calculate the average titre of HCl solution. The concordant titres are 14.95, 15.05 and 15.02 mL.	$V(HCl) = \frac{(14.95 + 15.05 + 15.02)\ \text{mL}}{3}$ $= 15.01\ \text{mL}$ (1 mark)
Step 4: 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.	$n(HCl) = c \times V$ $= 0.1200\ \text{mol L}^{-1} \times 0.01501\ \text{L}$ $= 0.0018012\ \text{mol}$ (1 mark)
Step 5: Use the stoichiometric ratio to calculate the number of moles of the "unknown" chemical.	The mole ratio for the reactants HCl:KOH is 1:1, so the number of moles of KOH equals the number of moles of NaCl. $n(KOH) = n(HCl)$ $= 0.0018012\ \text{mol}$ (1 mark)

Think	Do
Step 6: Use the number of moles of the "unknown" to solve the problem. Express your answer to 2 s.f.	$c(\text{KOH}) = \frac{n}{V}$ $= \frac{0.0018012\,\text{mol}}{0.02000\,\text{L}}$ $= 0.09006$ M (1 mark)

Your turn

A student performs a titration using a 0.100 M standardised solution of HNO_3. They used 15.00 mL aliquots of calcium hydroxide and obtained the following titres: 25.01, 24.26, 24.60, 24.35 and 24.28 mL. **Calculate** the concentration of the calcium hydroxide solution. (5 marks)

Worked example 5.1F

Combining solution and titration calculations

1.32 g of lithium hydroxide (LiOH) is dissolved in water and made up to the mark in a 250.0 mL volumetric flask. An average titre of 12.13 mL of this solution was obtained when titrating against 15.00 mL aliquots of a nitric acid (HNO_3) solution.

a **Calculate** the concentration of the LiOH solution. (2 marks)

b **Calculate** the concentration of the nitric acid. (4 marks)

Note: Lithium hydroxide is not a primary standard but has been used in this example to illustrate combined calculations.

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the questions are asking you to do.	"Calculate" means to obtain a numerical answer showing the relevant stages in the working. We need to calculate the final answer to the correct number of significant figures, showing all working throughout the process.
Step 2: For part **a**, calculate the number of moles of LiOH in the standard solution.	**a** $n(\text{LiOH}) = \frac{m}{M}$ $= \frac{1.32\,\text{g}}{23.95\,\text{g mol}^{-1}}$ $= 0.05511$ mol (1 mark)
Step 3: Calculate the concentration of the standard solution.	$c(\text{LiOH}) = \frac{n}{V}$ $= \frac{0.05511\,\text{mol}}{0.2500\,\text{L}}$ $= 0.2205$ M (1 mark)
Step 4: For part **b**, write a balanced chemical equation for the reaction.	**b** $\text{LiOH(aq)} + \text{HNO}_3\text{(aq)} \rightarrow \text{LiNO}_3\text{(aq)} + \text{H}_2\text{O(l)}$ (1 mark)
Step 5: Calculate the number of moles of the standard solution in the average titre.	$n(\text{LiOH}) = c \times V$ $= 0.2205\ \text{mol L}^{-1} \times 0.01213\,\text{L}$ $= 0.002674$ mol (1 mark)
Step 6: Use the mole ratio from the balanced chemical equation to determine the number of moles of HNO_3 in the aliquot.	$n(\text{HNO}_3) = n(\text{LiOH})$ $= 0.002674$ mol (1 mark)

Think	Do
Step 7: Use the aliquot volume to determine the concentration of HNO_3 and express your answer to 3 s.f.	$c(HNO_3) = \frac{n}{V}$ $= \frac{0.002674\,\text{mol}}{0.01500\,\text{L}}$ $= 0.178\ \text{mol L}^{-1}$ (1 mark)

Your turn

An amount of 0.550 g of sodium hydroxide (NaOH) is dissolved in water in a 250.0 mL volumetric flask, which is then brought up to the mark. An average titre of 17.56 mL of this solution was obtained when titrating with 20.00 mL aliquots of a sulfuric acid (H_2SO_4) solution.

a **Calculate** the concentration of the NaOH solution. (2 marks)

b **Calculate** the concentration of the sulfuric acid. (4 marks)

Where can errors occur in a titration?

Titration is an inherently precise technique because titres must be concordant (within a 0.10 mL range, or ±0.05 mL). Errors may occur in the technique, if the methodology is not followed precisely.

Systematic errors occur when equipment has not been calibrated, or the standard solution is not accurate (it is not the concentration it was intended to be). In these cases, performing repeats will result in the same titre volumes and precise results are possible.

Random errors may occur when glassware is not washed properly. Water may remain in the glassware, diluting the aliquot or titre. As the titration is repeated multiple times, and new solutions are added to the glassware, this type of error can be eliminated by repeats.

Study tip

When performing multistep calculations, use the answer saved in your calculator for the following step, rather than a rounded-off version you have written down. It avoids rounding errors as well as transcription errors. In the final step, record the answer to the correct number of significant figures, to agree with the least number of significant figures in the data provided.

Burette

A burette dispenses an accurate volume of 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, empty and then rinse 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 interior 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 carefully pour 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 left in the burette, it will lower the concentration of the titre solution.
Burettes should always be filled below eye level, to avoid spills getting into eyes.

2 Fill the burette after washing. Remove the funnel to prevent any suspended drips falling into the burette during the titration and changing the volume.

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 4). Remove any bubbles before you start the experiment. If the bubble washes into the conical flask during the titration, you will record the titre volume as higher than it actually is. Remove the funnel from the burette after filling to prevent any drops from the funnel falling into the burette giving a false initial or final volume.

3 Avoid parallax error.

Always read the burette at eye level. Figure 5 shows how the volume reads differently when you look at the meniscus from three different angles: from above, at eye level and from below.

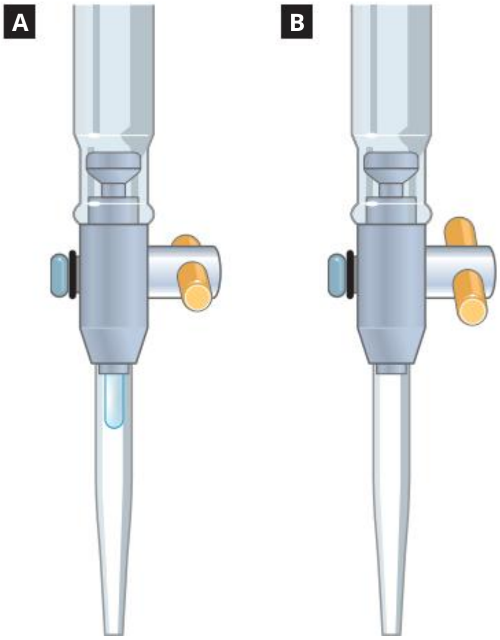


FIGURE 4 (A) A bubble formed in the tip of the burette introduces errors in the titre volume. (B) A burette without a bubble

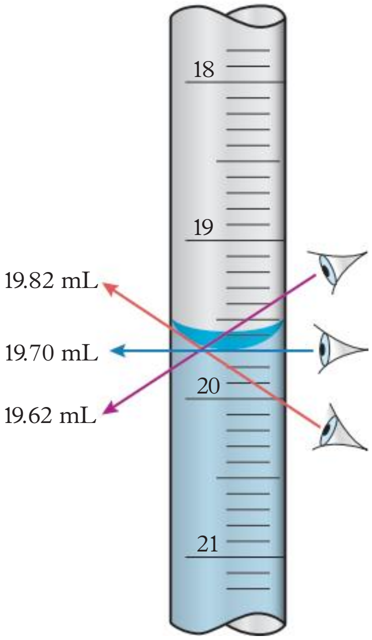


FIGURE 5 The changes in measurement when not viewed at eye level. From above to below: a measurement of 19.62 mL, the correct measurement of 19.70 mL and a measurement of 19.82 mL

Pipette

A pipette also dispenses very accurate volumes. In a titration, a pipette is used to measure and dispense the initial solution into the conical flask.

The following points will help you to use a pipette effectively.

1 Wash the pipette.

As with the burette, you must wash the pipette with water and then with the aliquot solution, 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 aliquot solution in a clean

bulb
a piece of equipment responsible for drawing solutions into the pipette

beaker and fill the pipette. Dispose of the chemical into a waste beaker. Fill the pipette with aliquot solution for a second time and dispense it into the conical flask by holding the tip of the pipette against the side of the conical flask. This is the analyte or sample.

2 Leave the drop of solution that remains in the pipette tip. The volume of the pipette has been calculated to allow for this small amount of solution remaining in the pipette.

When you have dispensed the aliquot 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.

Check your learning 5.1

Check your learning 5.1: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** the difference between a primary standard and a standard solution. (2 marks)

2 **Describe** the difference between an end point and an equivalence point. (2 marks)

3 **Calculate** to the correct number of significant figures the

  a approximate concentration of a solution of sodium hydroxide (NaOH) when 0.80 g is dissolved in water in a 100.0 mL volumetric flask (2 marks)

  b mass required to produce an aqueous 0.500 M standard solution of sodium carbonate (Na_2CO_3) in a 250.0 mL volumetric flask. (2 marks)

4 An amount of 1.20 g of potassium hydroxide (KOH) is dissolved in water in a 250.0 mL volumetric flask. Of this solution, 10.00 mL aliquots are titrated with sulfuric acid. An average titre of 31.36 mL is found.

  a **Calculate** the concentration of the sulfuric acid. Express your answer to the correct number of significant figures. (6 marks)

  b **Identify** a major limitation with the process described above. (1 mark)

Knowledge utilisation

5 A student performs a titration and forgets to rinse the burette with a standard solution before filling it. **Evaluate** the effect on the concentration determined for the unknown solution. (2 marks)

6 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. **Justify** the effect of this error on the

  a concentration of the standard (2 marks)

  b number of moles of the standard that reacts with the analyte (2 marks)

  c concentration of the analyte. (2 marks)

Lesson 5.2

Acid–base titrations

Key ideas

→ The equivalence point of an acid–base reaction can be determined from a pH–volume titration curve.

→ The equivalence point is in the middle of the steepest part of the titration curve. An indicator can be used to determine the equivalence point if its colour change also occurs in this steep section. The equivalence point can be used to accurately determine the concentration of the species being titrated.

→ Weak acids and bases, when titrated against a strong base or acid, demonstrate a buffer region, an almost flat portion of the titration curve, where there are smaller changes in pH as the titrant is added.

→ The midpoint (pK_a) of the buffer region is the pH at which there are equal amounts of an acid and its conjugate base. It is the pH at a volume halfway to the equivalence point. This pK_a value can be used to accurately determine the K_a of a weak acid.

What are the principles of acid–base titration?

Learning intentions and success criteria

Acid–base titrations are widely used in the food industry to determine the amounts of salt, sugar or vitamins in a food product and then compare the results to the manufacturer's claims. It was formerly used to determine the amount of sulfuric acid in past acid rain and the amounts 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.

In an acid–base titration, an acid is reacted with a base to form products that have a different pH from the reactants. The starting pH of the reactants depends upon the strength and concentration of the acid and the base. There are three different types of acid–base reactions you need to learn (see also Module 4):

- strong acid and strong base
- weak acid and strong base
- strong acid and weak base.

When a strong acid reacts with a strong base, a salt and water are formed. The aqueous salt solution present at the equivalence point is neutral (pH 7). The pH of the solution in the bottom flask or beaker can be measured at various points during the titration, using a pH meter. The initial pH can be used to give a rough indication of the concentration of the strong acid, as it dissociates completely. As a strong base is added from the burette, the pH gradually increases at first. As the equivalence point approaches, the pH increases sharply. When the pH of the conical flask reaches 7, the equivalence point has been reached. If an indicator is selected that changes colour at pH 7, the indicator will change colour at the equivalence point. After the equivalence point, the addition of extra base continues to increase the pH, but there is no more acid remaining to react with the base.

How do we interpret titration curves?

A titration curve can be developed; this is a graph with pH of the solution graphed against volume of the titrant added. The titration is set up and a pH electrode connected to a pH meter is placed into 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 addition of titrant, the pH of the solution is recorded in a results table. The pH initially changes very gradually and then more rapidly as more titrant is added. When the pH starts to change more rapidly, the titrant is added in smaller volumes. Smaller volumes should be added close to the equivalence point, where the change in pH is steepest, down to a single drop at a time. The pH should change rapidly and then increase again more slowly.

The resulting data is plotted as a titration curve – a graph with 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.

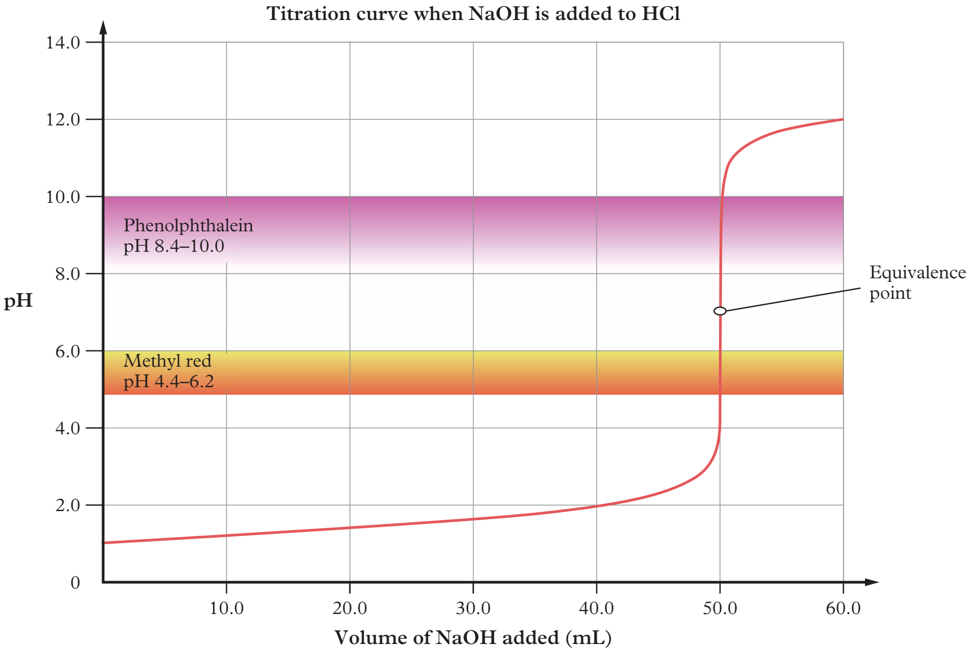


FIGURE 1 The titration curve generated when a sodium hydroxide (NaOH) titrant is added to a hydrochloric acid (HCl) analyte. Both methyl red and phenolphthalein are suitable indicators for this titration.

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 low pH, below 7. Therefore, the solution in the conical flask is an acid.

2 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. For the titration of a strong acid with a strong base, the equivalence point will have a pH of 7, because the ions present at the equivalence point do not affect the pH of the solution.

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 lists some relevant acid–base indicators, and Figure 2 shows the colours of various indicators.

Study tip

The QCAA *Formula and data book* has seven pH indicators that you will need for your external examination. These can be found in Module 4. Figure 2 shows many more pH indicators.

TABLE 1 Acid–base indicator pH ranges and colour changes

Name	pK_a range	pH range	Colour change from lower pH to higher pH in range
Methyl orange	3.7	3.1–4.4	Red to yellow
Bromophenol blue	4.2	3.0–4.6	Yellow to blue
Bromocresol green	4.7	3.8–5.4	Yellow to blue
Methyl red	5.1	4.4–6.2	Pink to yellow
Bromothymol blue	7.0	6.0–7.6	Yellow to blue
Phenol red	7.9	6.8–8.4	Yellow to red
Phenolphthalein	9.6	8.3–10.0	Colourless to pink

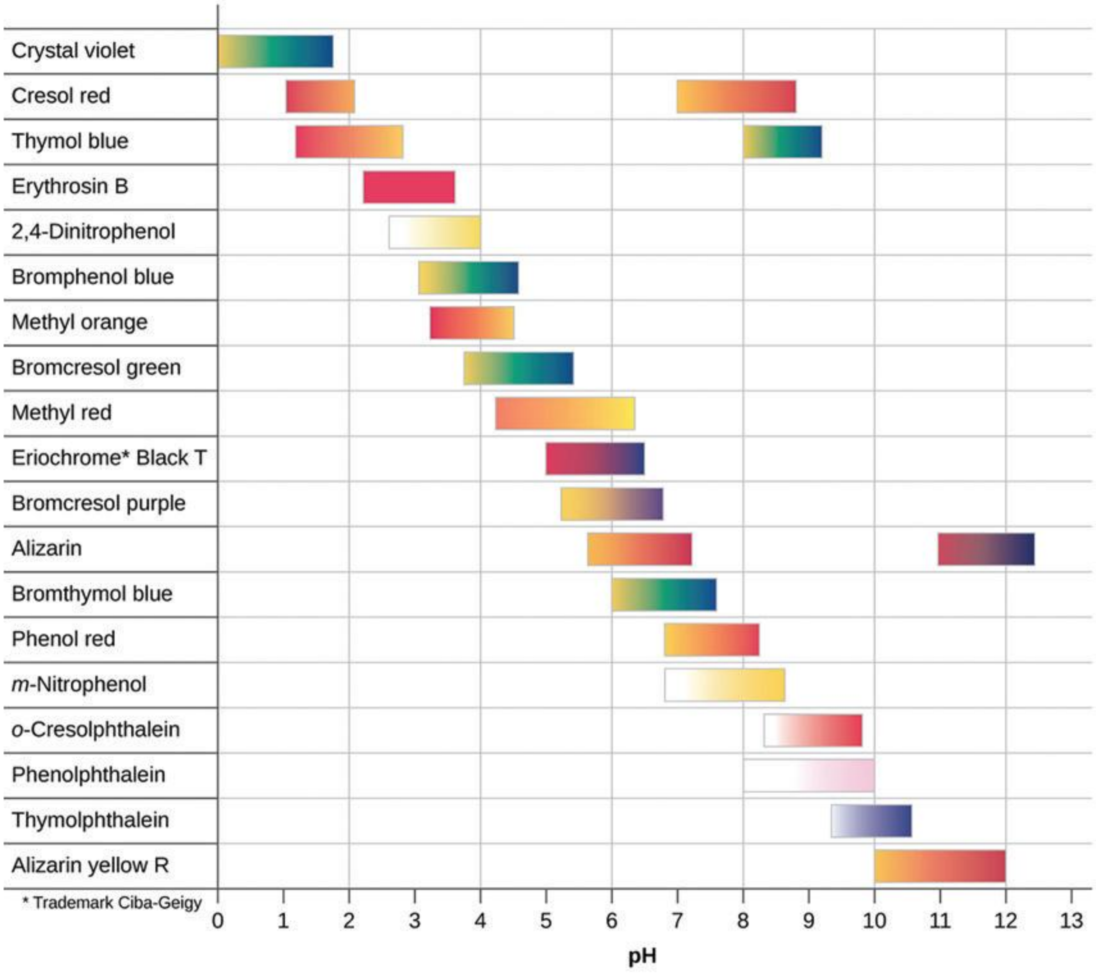


FIGURE 2 The colour changes of some acid–base indicators and the pH at which these changes occur

Weak acid and strong base

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 below 7, so there must have been an acid in the conical flask at the start of the titration. The initial pH of the solution is not sufficient to say that it is a weak acid. A dilute solution of a strong acid can have a higher pH than a concentrated solution of a weak acid.

2 The pH displays a rapid change initially. This is followed by a very gradual change. This region of very gradual change in pH is called the **buffer region**. After the buffer region, the pH again changes more rapidly as the equivalence point is approached.

3 The equivalence point is in the middle of the steepest part of the gradient, pH 8.73 in this case. Note that the pH of the equivalence point is higher than 7. This is because at the equivalence point, we have a solution of the conjugate base of the weak acid, which is itself a weak base. For example, in the titration of acetic acid with sodium hydroxide, at the equivalence point there is a solution of sodium acetate, a weak base, and hence the pH is higher than 7.

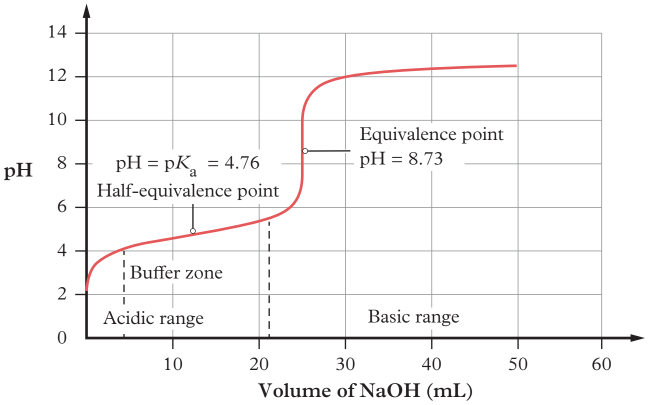


FIGURE 3 The titration of a 0.1 M solution of a weak acid (e.g. ethanoic acid (CH_3COOH)) with a strong base (0.1 M NaOH)

4 The **half-equivalence point** is the point in the buffer region at which half of the original analyte has been reacted with the titrant. It is also called the midpoint of the titration. The volume of titrant at the half-equivalence point is half the volume of the titrant required to reach the equivalence point. In Figure 3, 25 mL of the titrant is added to reach the equivalence point, and 12.5 mL of the titrant is added to reach the half-equivalence point.

5 At the half-equivalence point, pH = pK_a (see Module 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.)

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 half of the original analyte has reacted with the titrant; also called the midpoint

Strong acid and weak base

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. It is not possible to say at this point whether it is a strong or weak base, as the initial pH depends on both the concentration of the base solution and strength of the base. It is entirely possible for a dilute solution of a strong base to have a lower pH than a concentrated solution of a weak base.

2 The pH decreases at first then remains relatively unchanged until the equivalence point is reached. The region where the pH changes very little 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. Note that the equivalence point pH is lower than 7. This is because at the equivalence point all of the base has reacted and we are left with a solution of the conjugate acid, which is itself a weak acid. For example, in the titration of an aqueous ammonia solution with hydrochloric acid solution at the equivalence point we have an aqueous solution of ammonium chloride, a weak acid. A pH less than 7 at the equivalence point indicates that a weak base was titrated.

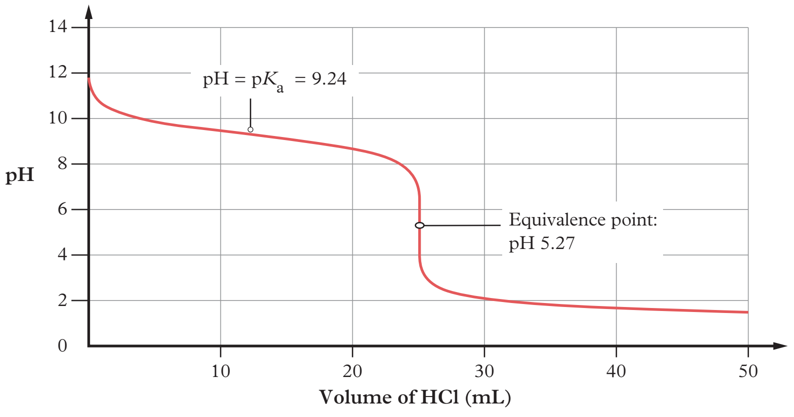


FIGURE 4 The titration of a strong acid (0.1 M HCl) and weak base (25 mL of 0.1 M NH_3)

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 of the conjugate acid of the base. 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. In the example in Figure 4, the pH at the half-equivalence point is equal to the pK_a of NH_4^+. Mathematically, since pH + pOH = 14, pOH = pK_b = 14 – pH (at half equivalence point). In Figure 4, $pK_b = 14 - 9.24 = 4.76$. $K_b = 10^{-4.76}$.

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.

$$pK_a = -\log_{10} K_a$$

$$K_a = 10^{-pK_a}$$

$$K_a \text{ monoprotic acid} = \frac{[H_3O^+][A^-]}{[HA]}$$

$$= \frac{[H_3O^+]^2}{[HA]}$$

Study tip

Ensure you always use log to base 10 rather than natural log when doing pH calculations. The reverse applies when finding concentrations from pH. To use the inverse function, 10^x should be used, and not e^x.

Since the acid is weak, the assumption that the equilibrium concentration of the weak acid is approximately the same as the original concentration of the acid can be made. This assumption should be stated in working.

Taking logs of both sides and simplifying:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

Worked example 5.2A

Analysing titration curves

Analyse the following titration curves.

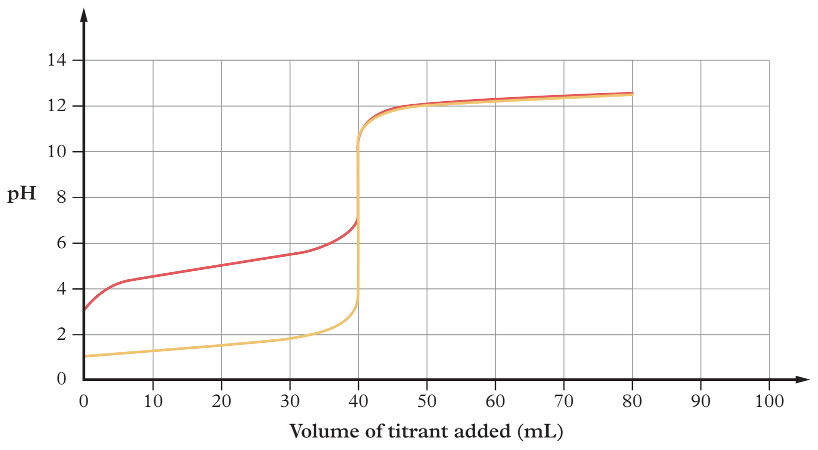


FIGURE 5 Titration curves

For Figure 5

- **a** **identify** whether the titrand and titrant are strong or weak, acids or bases (2 marks)
- **b** **identify** the pH and volume of the equivalence point (2 marks)
- **c** **identify** the volume of the half-equivalence points for the red curve (1 mark)
- **d** **identify** the range of any buffer regions present (1 mark)
- **e** **identify** a suitable indicator for the titrations (2 marks)

f **identify** whether the titrand and titrant are strong or weak, acids or bases (2 marks)

g **determine** the pK_a of the weak acid titrated. (1 mark)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Identify" means to recognise and name. We need to analyse the titration curve and apply the terminology from the questions. "Determine" means to establish, conclude or ascertain after consideration, observation, investigation or calculation.
Step 2: For part **a**, identify whether the initial reactant and final is a strong/weak, acid/base based on their pH values at equivalence point.	**a** Red curve: The pH at the equivalence point is higher than 7, hence this is a weak acid. (1 mark) Yellow curve: The pH at the equivalence point is equal to 7, hence this is a strong acid. (1 mark)
Step 3: For part **b**, identify the equivalence point (which is the middle of the vertical portion of the curve).	**b** Red curve: The equivalence point has a pH of 8.5–9. The volume is 40.0 mL (1 mark) Yellow curve: The equivalence point has a pH of 7. The volume is 40.0 mL (1 mark)
Step 4: For part **c**, identify the half-equivalence point (which is halfway from 0 on the *x*-axis to the equivalence point volume of 40.0mL).	**c** Half-equivalence point volume is 20 mL. (1 mark)
Step 5: For part **d**, identify the buffer region, which is the relatively constant pH region just after the initial rapid rise and just before the steep vertical drop, around the half-equivalence point.	**d** The red curve has a buffer region. pH 4–6 (1 mark)
Step 6: For part **e**, identify a suitable indicator, which is one that changes colour in the region of the titration where the curve is closest to vertical. Several choices are listed, but one answer for each curve is sufficient.	**e** Red curve: The steepest part of the curve is between 7 and 10, so suitable indicators are bromothymol blue (6.0–7.6), phenol red (6.8–8.4) or phenolphthalein (8.3–10.0) (1 mark) Yellow curve: The steepest part of the curve is between 4 and 10, so suitable indicators are methyl red (4.4–6.2), bromothymol blue (6.0–7.6), phenol red (6.8–8.4) or phenolphthalein (8.3–10.0) (1 mark)
Step 7: For part **f**, identify whether the initial reactant and final is a strong/weak, acid/base based on their pH values at equivalence point.	**f** Red curve: Initial pH is 3, indicating that an acid is being titrated. The pH at the equivalence point is higher than 7; therefore, this is a weak acid being titrated with a strong base. (1 mark) Yellow curve: Initial pH is 1, indicating that an acid is being titrated. The pH at the equivalence point is 7; therefore, this is a strong acid being titrated with a strong base. (1 mark)
Step 8: For part **g**, determine the pK_a (remembering that at the half-equivalence point, pH = pK_a).	**g** pK_a = 5 (1 mark)

Your turn

Analyse the following titration curves.

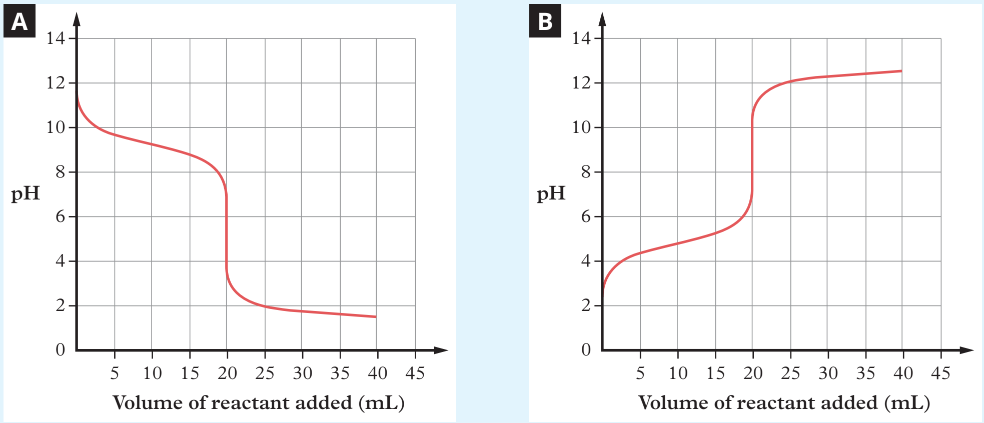


FIGURE 6 Two titration curves

For Figure 6A

- **a** **identify** whether the reactants are strong or weak, acids or bases (2 marks)
- **b** **identify** the pH and volume of the equivalence point (1 mark)
- **c** **identify** the half-equivalence point (1 mark)
- **d** **identify** the range of the buffer region (1 mark)
- **e** **identify** a suitable indicator for the reaction (1 mark)
- **f** **determine** the pOH at the half-equivalence point. (1 mark)

For Figure 6B

- **a** **identify** whether the reactants are strong or weak, acids or bases (2 marks)
- **b** **identify** the pH and volume of the equivalence point (1 mark)
- **c** **identify** a suitable indicator for the reaction. (1 mark)

Challenge

Diprotic and triprotic acids

Diprotic acids, such as carbonic acid (H_2CO_3), 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. Research such curves to check your predictions

Although sulfuric acid is diprotic, the shape of its titration curve does not resemble that of other diprotic acids. **Explain** why. (5 marks)

Skill drill

Constructing and analysing titration curves

Science inquiry skill: Processing and analysing data (Lesson 1.7)

In an acid–base titration, 50.0 mL of a hydrochloric acid (HCl) solution of unknown concentration was titrated with a 0.100 M sodium hydroxide (NaOH) solution. The data in Table 2 was recorded for the volume of NaOH added and the pH at each point:

TABLE 2 Titration data

Volume of NaOH added (mL)	pH
0.00	1.10
5.00	1.19
10.00	1.30
15.00	1.41
20.00	1.54
25.00	1.69
30.00	1.90
35.00	2.23
37.00	2.48
38.00	2.65
39.00	2.95
39.50	3.26
39.90	3.96
40.00	7.00
40.10	10.04
40.50	10.73
41.00	11.04
42.00	11.33
43.00	11.51
45.00	11.72
50.00	12.00
55.00	12.15
60.00	12.25

Practise your skills

1 **Construct** a graph of pH versus volume of NaOH added. (2 marks)

2 **Identify** the equivalence point from the titration curve. (1 mark)

3 **Explain** why the pH increases more sharply just before and just after the equivalence point. (2 marks)

4 **Calculate** the concentration of the hydrochloric acid solution based on the volume of NaOH required to reach the equivalence point. (4 marks)

5 **Explain** how the curve would differ if a weak acid of the same concentration was titrated with the same concentration of NaOH. (2 marks)

Check your learning 5.2

Check your learning 5.2: Complete these questions online or in your workbook.

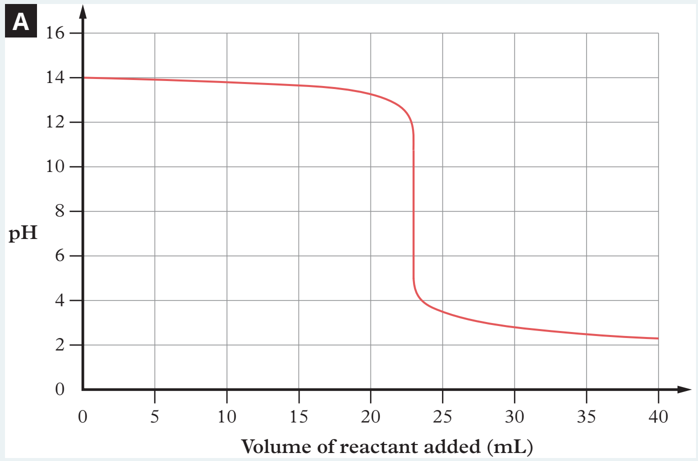
Retrieval and comprehension

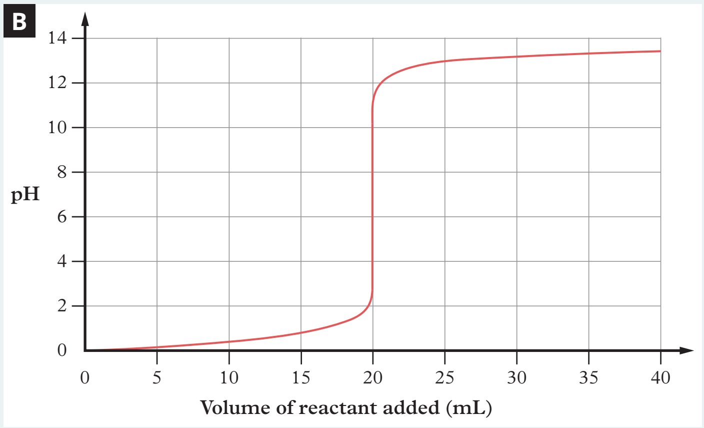
1 **Explain** the purpose of a titration curve. (2 marks)

2 Consider the following titration curves. For each curve

 a **identify** whether the titrands and titrants are strong or weak acids or bases (2 marks)

 b **identify** a suitable indicator for titration. (2 marks)





Analytical processes

3 A student standardises a solution of sodium hydroxide using 20.00 mL aliquots. 0.1100 M standardised hydrochloric acid is used as the titrant 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. (1 mark)
- **b** **Calculate** the molarity of the sodium hydroxide solution. (4 marks)
- **c** **Determine** why methyl orange was chosen as the indicator. (2 marks)
- **d** Once its concentration is determined, can the sodium hydroxide solution be called a standard solution? **Explain**. (2 marks)

4 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 standardised solution of 0.02140 mol L^{-1} hydrochloric acid. Using phenolphthalein as the indicator, he obtained an average titre of 19.65 mL. **Determine** the concentration of ammonia in the bucket (in g L^{-1}). (5 marks)

Knowledge utilisation

5 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. **Evaluate** the impact on the

- **a** titre (2 marks)
- **b** apparent number of moles in the aliquot (2 marks)
- **c** apparent concentration of the aliquot. (2 marks)

Practical

Lesson 5.3

Determining the concentration of ethanoic acid in white vinegar

Learning intentions and success criteria

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Lesson 5.4

Conductometric titrations and solubility titrations

Key ideas

- → The equivalence point of a conductometric titration can be determined from a graph of conductivity vs. volume of titrant.
- → The equivalence point is identified by where the two linear regions of the graph intersect.
- → A conductivity electrode or probe together with a conductometer or multimeter, on a resistance setting, can be used to measure conductivity to generate a graph and determine the equivalence point.
- → Strong acids and bases completely ionise in water and therefore have high ion concentrations and high conductivity. Weak acids and based only partially ionise in water and therefore have low ion concentrations and low conductivity.
- → The K_{sp} of an insoluble salt can be determined using a solubility titration.
- → Insoluble salts have very low solubilities and form very dilute solutions. A solubility titration can titrate a solution of known concentration until a precipitate appears. Alternatively, a solubility titration can be used to titrate a saturated solution of an insoluble salt, to determine the concentration of one of the ions.

How can conductivity determine an end point?

Learning intentions and success criteria

conductivity a measure of the ability of a solution to conduct an electrical current

Conductivity is the measure of a solution's ability to conduct an electric current due to the presence of charged ions in the solution. It can be measured on a multimeter, using the resistance setting or, alternatively, a conductometer can be used. Conductivity is the reciprocal of resistance.

The basic unit of conductivity is the mho or siemens per distance. Conductivity is measured in micromhos per centimetre (μmho cm^{-1}) or microsiemens per centimetre (μS cm^{-1}). The conductivity of a titration depends on the concentration of ions present as well as the identity of those ions, as some ions, such as hydronium ions and hydroxide ions are more conducting than others. Conductivity changes are caused by the changing number and types of ions during the course of the titration.

What happens when strong acids and strong bases react?

Strong acids and bases completely ionise in water, resulting in a high ion concentration relative to the concentration of the strong acid or base. Consider the example of a strong base, sodium hydroxide, reacting with a strong acid, hydrochloric acid:

$$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$$

Using this representation of a chemical reaction, it is difficult to see the ions. Remember that ionic salts dissociate in water so the same equation can be represented as their ions:

$$\text{H}^+\text{(aq)} + \text{Cl}^-\text{(aq)} + \text{Na}^+\text{(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{Na}^+\text{(aq)} + \text{Cl}^-\text{(aq)} + \text{H}_2\text{O(l)}$$

This allows us to more easily observe that the reactants will have a higher conductivity than the products.

During the titration, aqueous sodium hydroxide is in the beaker under the burette and has a high conductivity. As the hydrochloric acid is added, some of the sodium hydroxide reacts to form sodium chloride in the form of ions and water. At the same time, the volume is increasing. Therefore, even though the actual number of ions is constant, their concentration is decreasing. Additionally, small OH^- ions are more mobile and conductive than the larger Cl^- ions in the product solution. A drop in conductivity is due to both factors: an increase in volume causing a decrease in ion concentration and the formation of less conductive products.

The conductivity continues to decrease in a linear fashion on the graph with the addition of hydrochloric acid until the equivalence point is reached and there is no more sodium hydroxide or hydrochloric acid in solution; only sodium chloride and water remains. At this point, the solution still conducts electricity, due to the presence of sodium and chloride ions, but the conductivity is at its lowest.

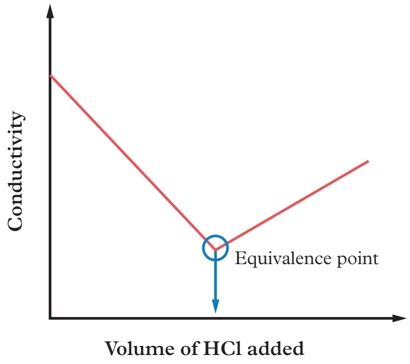


FIGURE 1 The conductometric titration curve of a strong acid being added to a strong base

After this point, any addition of hydrochloric acid results in the acid being in excess as there is no more sodium hydroxide to react with. This increases the ion concentration and therefore increases the conductivity again, forming a straight line with a positive gradient on the graph.

The equivalence point is represented as the intersection of the two straight lines in Figure 1.

If the volume of HCl where the two lines meet is read from the *x*-axis (see the arrow), the volume of HCl added to reach the equivalence point can be determined (see the arrow in Figure 1).

What happens when a strong base and a weak acid react?

The equivalence point has a different appearance on the graph depending on the strength of acid and base used. Weak acids are proton donors but will only partially dissociate in water. This means that only a small amount of the reactant is dissociated at the start of the titration and minimal protons (H^+) are donated, decreasing the ion concentration and the conductivity. Consider the dissociation equation of ethanoic acid:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

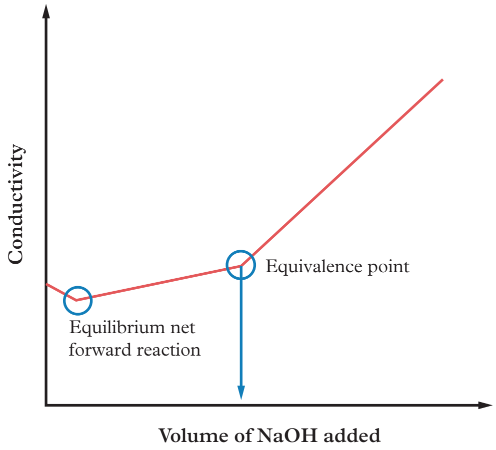


FIGURE 2 The conductometric titration curve of a strong base being added to a weak acid

As the ethanoic acid dissociates, the hydrogen ions react with the hydroxide ions in the added sodium hydroxide solution to form water. This lowers the conductivity of the solution, as effectively protons are being replaced by less conducting sodium ions, resulting in the initial decrease in conductivity on the graph (Figure 2) until all the hydrogen ions have reacted.

At this point, the ethanoic acid equilibrium reaction responds to the removal of product by shifting in the forwards direction to replace the hydrogen ions that were removed when they reacted. The hydroxide will again remove these ions but as the reaction continues to move forward, the ethanoate ion (CH_3COO^-) and sodium ion concentrations increase, which results in a steadily increasing conductivity.

At the equivalence point, all the ethanoic acid is dissociated and all the hydrogen ions produced have reacted with the hydroxide ions to form water. Therefore, there is only sodium ions, ethanoate ions and water according to the overall equation:

$$NaOH(aq) + CH_3COOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$$

The equivalence point occurs when sodium hydroxide is in excess, and conductivity increases at a faster rate. The two straight lines on the graph intersect.

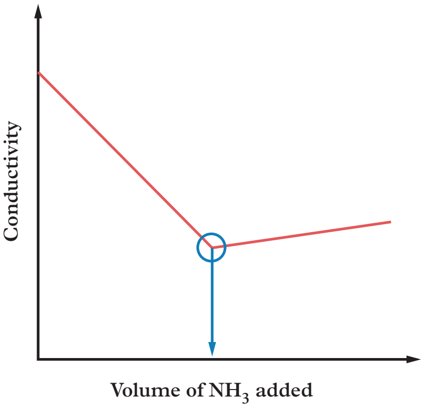


FIGURE 3 The conductometric titration curve of a weak base being added to a strong acid

What happens when a strong acid and a weak base react?

Weak bases are proton acceptors and will react completely with strong acids to gain hydrogen ions (protons) to form the conjugate acid. For example, the reaction between ammonia and a strong acid produces ammonia ions. As hydrochloric acid is a strong acid and completely dissociates, there is an abundance of hydrogen ions to react with the ammonia.

$$NH_3(aq) + H^+(aq) + Cl^-(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

In Figure 3, the strong acid is the starting reactant, causing the solution to have a high conductivity. As ammonia is added, the conductivity decreases because the hydrogen ions are being replaced by less conductive ammonia ions. At the equivalence point, the two straight lines in Figure 3 intersect.

As soon as there is excess ammonia, the conductivity increases only slightly as the ammonia molecule continues to be only partially ionised by water, with the left-hand side of the equilibrium being favoured:

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

How do we perform calculations for conductometric titrations?

Calculations in a conductometric titration are similar to those for an acid–base titration. An accurate volume of one solution is placed in the beaker and the volume of the burette solution is determined by the turning point on the graph. As long as one of the solutions has an accurately known concentration, the concentration of the other solution can be calculated.

Worked example 5.4A

Calculating concentration in conductometric titrations

A 50.0 mL solution of hydrochloric acid (HCl) is titrated with a 0.15 M sodium hydroxide (NaOH) solution using a conductivity meter. The equivalence point is reached after adding 40.0 mL of NaOH.

a **Construct** the balanced chemical equation for the reaction. (1 mark)

b **Calculate** the molar concentration of the HCl solution. (3 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the questions are asking you to do.	“Construct” means to display information in a diagrammatical or logical form. “Calculate” means to determine or find a number or answer by using mathematical processes. We need to calculate the final answer to the correct number of significant figures, showing all working throughout the process.
Step 2: For part **a**, write the equation.	**a** $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$ (1 mark)

Think	Do
Step 3: For part **b**, calculate the number of moles of the known solution, NaOH.	**b** $n(\text{NaOH}) = c \times V = 0.15\ \text{mol L}^{-1} \times 0.040\ \text{L} = 0.0060\ \text{mol}$ (1 mark)
Step 4: Use the stoichiometric ratio to calculate the moles of the unknown solution; HCl	$n(\text{HCl}) = n(\text{NaOH}) = 0.0060\ \text{mol}$ (1 mark)
Step 5: Calculate the concentration of HCl (in M) and express the answer to 2 s.f.	$c(\text{HCl}) = \frac{n}{V} = \frac{0.0060\ \text{mol}}{0.050\ \text{L}} = 0.12\,\text{M}$ (1 mark)

Your turn

A 25.0 mL solution of hydrochloric acid (HCl) is titrated with a 0.10 M sodium hydroxide (NaOH) solution using a conductivity meter. The equivalence point is reached after adding 35.0 mL of NaOH.

a **Construct** the balanced chemical equation for the reaction. (1 mark)

b **Calculate** the concentration, in mol L^{-1}, of the hydrochloric acid solution. (3 marks)

Worked example 5.4B

Interpreting conductometric curves

The data in Figure 4 was obtained from a conductometric titration of 50.0 mL of hydrochloric acid (HCl) with 0.100 M sodium hydroxide (NaOH).

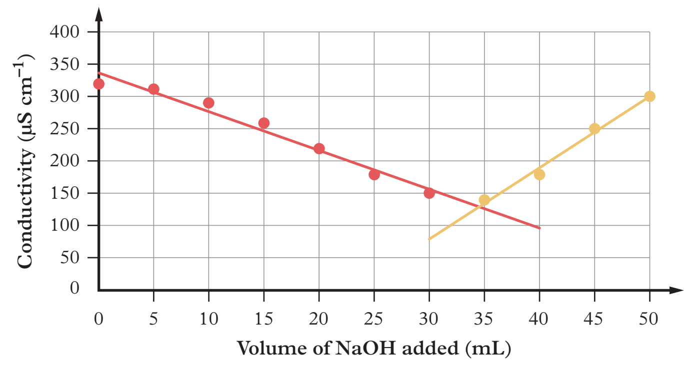


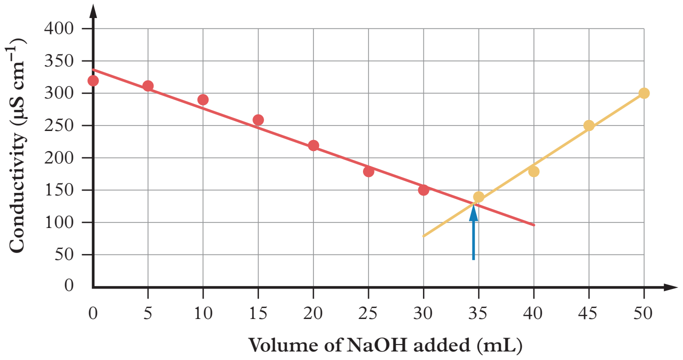
FIGURE 4 Conductometric titration of HCl with NaOH

a **Identify** the volume at the equivalence point from the conductivity curve. (1 mark)

b **Explain** why the conductivity decreases initially and then increases after the equivalence point. (4 marks)

c **Calculate** the molar concentration of HCl solution using the volume of NaOH required to reach the equivalence point. (4 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Identify" means locate, recognise and name. This is worth 1 mark, so once located, the volume needs to be written. "Explain" means make an idea or situation plain or clear by describing it in more detail or revealing relevant facts. We need to state why the lines on the graph take the shape that they do. "Calculate" means to determine or find a number or answer by using mathematical processes. We need to calculate the final answer to the correct number of significant figures, showing all working throughout the process.

Think	Do
Step 2: For part **a**, identify the equivalence point. Use lines of best fit to identify the equivalence point, these are the lines in blue and orange. Where they cross is the equivalence point. Follow this point to the *x*-axis to find the volume of NaOH added.	**a**  Approximately 34.5 mL (1 mark)
Step 3: For part **b**, explain the trend in the graph using chemical equations. There are four marks available, one each for: analysing conductivity initial, decrease, equivalence point and increase.	**b** HCl is a strong acid and is ionised completely to H(aq) and Cl^-(aq). Therefore, initial conductivity is high. (1 mark) As NaOH solution is added, this is a source of Na^+ and OH^-. the OH^- reacts with the H^+ present, forming water, decreasing the conductivity of the solution. (1 mark) In effect, less conductive Na^+ ions are replacing the more conductive H^+ ions. When no more H^+ remains, as it has all reacted with OH^- to form H_2O, the conductivity is at its lowest, the equivalence point. (1 mark) As the NaOH becomes excess, the ion concentration increases and so does the conductivity. (1 mark)
Step 4: For part **c**, write a balanced chemical equation.	**c** $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ (1 mark)
Step 5: Calculate the moles of the known quantity; the NaOH.	$n(NaOH) = c \times V$ $= 0.10 \times 0.0345 = 0.00345$ mol (1 mark)
Step 6: Use a stoichiometric ration to find the amount of HCl.	$n(HCl) = n(NaOH) = 0.00345$ mol (1 mark)
Step 7: Find the concentration of HCl (in M) and give your answer to an appropriate number of significant figures (in this case 3 s.f.)	$c(HCl) = \frac{n}{V}$ $= \frac{0.00345 \text{ mol}}{0.0500 \text{ L}} = 0.0690\text{ M}$ $= 0.0690\text{ M}$ (1 mark)

Your turn

In a conductometric titration of 40.0 mL of ammonia (NH_3) with 0.15 M hydrochloric acid (HCl), the data in Figure 5 was recorded.

a **Identify** the volume at equivalence point from the conductivity curve. (1 mark)

b **Explain** the trend in conductivity during the titration and the reasons for the changes. (4 marks)

c **Calculate** the concentration of NH_3 solution based on the volume of HCl required to reach the equivalence point. (4 marks)

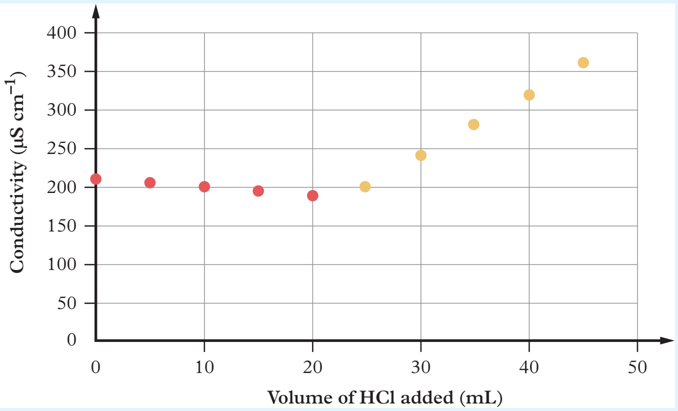


FIGURE 5 Conductometric titration of NH_3 with HCl

How can ion concentrations and solubility of ionic substances be determined using titrations?

Insoluble ionic compounds have extremely low solubilities. If the K_{sp} is known, ion concentrations can be calculated (Lesson 2.6). Experimental data from titrations can be used to determine ion concentrations, solubilities and the K_{sp} of these compounds. This type of titration is called a **solubility titration**. The solutions chosen and the methodology depend on the particular insoluble salt. Due to the large variety of possible reactants, several examples will be considered. However, if presented with a different example, identify the reaction that will take place as well as the insoluble compound being considered, and analyse the data given. Recall that even though compounds with very small K_{sp} values are classed as being insoluble, they do dissolve in extremely small amounts, to form saturated solutions with very low concentrations of ions.

solubility titration
a titration performed to determine the ion concentrations, solubility and K_{sp} of an insoluble ionic compound

How can ion concentrations and K_{sp} be determined for an insoluble hydroxide?

Many metal hydroxides are insoluble and so form extremely dilute solutions of the metal ion and the hydroxide ion. Since these compounds are bases, it is convenient to use an acid–base titration with a standardised solution of an acid such as hydrochloric acid. A saturated solution of the insoluble hydroxide is prepared by mixing a small amount of the insoluble hydroxide in water and allowing it to reach equilibrium; some solid remains. The **supernatant solution** is filtered, to ensure that a saturated solution is used, but no additional solid hydroxide is present. This solution is then titrated with the very dilute acid using an acid–base indicator to show equivalence point.

supernatant solution
the saturated solution lying above the solid residue that did not dissolve

Worked example 5.4C

Determining ion concentrations and K_{sp} of an insoluble hydroxide using a solubility titration

A saturated solution of $Mg(OH)_2$ is filtered and 25.00 mL of this solution is titrated with 0.00020 mol L^{-1} HCl. The volume required to reach the equivalence point of this solution is 32.6 mL. **Determine** the

a concentration of OH^- in the saturated solution (4 marks)

b K_{sp} of magnesium hydroxide. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the questions are asking you to do.	"Determine" means establish, conclude or ascertain after consideration, observation, investigation or calculation. We need to consider the reaction occurring and the titration data to inform calculations. Part **a** is worth 4 marks, and part **b** is worth 2 marks so we must express the concentration for part **a** in mol L^{-1} for part **a** and the K_{sp} for part **b** to an appropriate number of significant figures.
Step 2: Select the appropriate formulas and gather the required data.	$V(Mg(OH)_2) = 25.00\,mL = 0.02500\,L$ $V(HCl) = 32.6\,mL = 0.0326\,L$ $c(HCl) = 0.00020\ mol\ L^{-1}$

Think	Do
Step 3: For part **a**, write the equation for the reaction.	**a** $2HCl(aq) + Mg(OH)_2(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$ (1 mark)
Step 4: Calculate the number of moles of hydrochloric acid required.	$n(HCl) = c \times V$ $n = 0.00020 \times 0.0326$ $= 6.52 \times 10^{-6}$ mol (1 mark)
Step 5: Use the stoichiometric ratio to calculate the number of moles of hydroxide ion present.	Ratio of H^+ (from HCl):OH^- = 1:1 Therefore, $n(OH^-) = 6.52 \times 10^{-6}$ mol (1 mark)
Step 6: Calculate the concentration of hydroxide ions in the solution to complete part a. Round to 2 s.f. as the concentration of HCl is the least precise measurement with 2 s.f.	$[OH^-] = \frac{n}{V}$ $= \frac{6.52 \times 10^{-6}}{0.02500}$ $= 0.0002608$ mol L^{-1} (1 mark)
Step 7: For part **b**, use the ratio of ions in the formula to calculate the concentration of magnesium ions.	**b** Mg^{2+}:OH^- = 1:2; therefore: $[Mg^{2+}] = \frac{[OH^-]}{2}$ $[Mg^{2+}] = 0.0001304$ mol L^{-1} (1 mark)
Step 8: Use the K_{sp} expression and the concentrations of magnesium and hydroxide ions, to determine K_{sp}. Round to 2 s.f.	$K_{sp} = [Mg^{2+}] \times [OH^-]^2$ $= 0.0001304 \times 0.0002608^2$ $= 8.8 \times 10^{-12}$ (1 mark)

Your turn

A saturated solution of $Pb(OH)_2$ is filtered and 20.00 mL of this solution is titrated with 0.000010 mol L^{-1} HCl. The volume required to reach the equivalence point of this solution is 26.8 mL. **Determine** the

a concentration of OH^- in the saturated solution (4 marks)

b K_{sp} of lead(II) hydroxide. (2 marks)

How can ion concentrations be determined using solubility titrations?

In Worked example 5.4C, the concentrations of hydrochloric acid selected were quite different for each metal hydroxide. Concentrations of acid need to be chosen to produce reasonable titration volumes. If the volume was too small in an experimental procedure, it is less precise. The volume of acid would need to be diluted, and the titration conducted again. The step of filtering a supernatant solution is vital in this procedure, as if any solid metal hydroxide was present, it would gradually dissolve as added acid reacted with and removed hydroxide ions from the solution. Insoluble hydroxides are said to have a pH-dependent solubility and are more soluble at a lower pH.

The concentration of specific ions can be determined using a solubility titration, in which the product is a precipitate. In this case, the analyte is a water sample with an unknown concentration of an ion to be determined. A solution that reacts with that ion to form a precipitate is placed in the burette to be used as the titrant. As the titrant is added, precipitation occurs. When the precipitation finishes, the equivalence point is reached. In some cases, another chemical must be used as an indicator, while in other cases, due to the colour of the titrant solution, the titration is self-indicating. Again, there are many different examples of this type of titration, with a variety of substances used as indicators, and just a few examples will be considered.

Frequently, the concentration of chloride ion in water samples is needed as part of salinity-testing. A method known as Mohr's method is useful. A sample of the water to be tested is titrated with a solution of silver nitrate, $AgNO_3$. The silver ions and the chloride ions react and silver chloride precipitates according to:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

$AgNO_3$ is colourless, so it is very difficult to detect when AgCl stops precipitating. To detect the endpoint, 1 to 2 mL of 5%(w/v) potassium chromate KCr_2O_4 solution is added at the start of the titration as an indicator. Silver chromate is more soluble in mol L^{-1} than silver chloride. While there are chloride ions remaining, AgCl continues to precipitate, and there are no excess Ag^+ ions in the reaction mixture. Once practically all the chloride ions have precipitated, the added Ag^+ is in excess and reacts with chromate ions, CrO_4^{2-} according to:

$$2Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s)$$

Silver chromate has a distinctive reddish-brown colour, in contrast to the white colour of silver chloride. Once this colour appears, the titration is stopped. The concentration and volume of silver nitrate solution added is used to calculate the concentration of chloride ions in the sample. Although silver forms insoluble salts with other ions, their endpoint relies on other indicators; potassium chromate is not generally a suitable indicator, due to wider differences in solubilities.

Another ion whose concentration can be determined using solubility is the sulfide ion. By titrating the sample solution with a copper(II) sulfate solution, a black precipitate of copper(II) sulfide forms according to:

$$Cu^{2+}(aq) + S^{2-}(aq) \rightarrow CuS(s)$$

While precipitation is occurring, the blue Cu^{2+} ions disappear as soon as they are added. Once all of the sulfide ion has reacted, additional copper(II) sulfate solution is in excess and the blue colour persists in the reaction mixture, to indicate the endpoint.

Worked example 5.4D

Determining ion concentrations in water samples using solubility titrations

A 20.00 mL sample of water from a town water bore is titrated with 15.6 mL of 0.0010 M $AgNO_3$ to completely precipitate the chloride ion. **Determine** $[Cl^-]$ in the bore water. (4 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Determine" means establish, conclude or ascertain after consideration, observation, investigation or calculation. We need to consider the reaction occurring and the titration data to inform calculations. The question is worth 3 marks, so we must express the concentration in mol L^{-1} to an appropriate number of significant figures.
Step 2: Select the appropriate formulas and gather the required data.	V(sample with Cl^-) = 20.00 mL = 0.02000 L $V(AgNO_3)$ = 15.6 mL = 0.0156 L $c(AgNO_3)$ = 0.0010 M
Step 3: Write a balanced equation for the reaction. One mole of $AgNO_3$ dissociates to produce 1 mole of Ag^+ ions which react in a 1:1 ratio with Cl^- ions.	$AgNO_3(aq) + Cl^-(aq) \rightarrow AgCl(s) + NO_3^-(aq)$ Note: The spectator ion is nitrate and can be omitted, so long as it is realised that the mole ratio between silver nitrate and chloride ion is 1:1. (1 mark)

Think	Do
Step 4: Calculate the number of moles of silver nitrate used.	$n(AgNO_3) = c \times V$ $= 0.0010 \times 0.0156$ $= 1.56 \times 10^{-5}$ mol (1 mark)
Step 5: Use the mole ratio to determine the number of moles of chloride ions in the sample.	Mole ratio $AgNO_3$:Cl^- = 1:1 $n(Cl^-) = 1.56 \times 10^{-5}$ mol (1 mark)
Step 6: Use the amount in mol and the volume of the sample to determine the concentration of chloride ions in the sample.	$c(Cl^-) = \frac{n}{V}$ $= \frac{1.56 \times 10^{-5}}{0.02000}$ $= 0.00078$ mol L^{-1}
Step 7: Finalise your answer by rounding the numbers to 2 s.f. and include the units.	$c(Cl^-) = 0.00078$ mol L^{-1} (1 mark)

Your turn

A 25.00 mL sample of water from a mine tailings dam is titrated with 22.1 mL of 1.0×10^{-4} M $CuSO_4$ to completely precipitate the sulfide ion. **Determine** $[S^-]$ in the tailings water. (4 marks)

Challenge

Acid–base titrations producing insoluble salts

Some acid–base titrations produce insoluble salts. **Predict** the conductivity graph for a conductometric titration of barium hydroxide with sulfuric acid, which produces insoluble barium sulfate in the reaction. **Justify** your prediction. (4 marks)

Real-world chemistry

Ensuring wastewater is safe for the environment

Water treatment is a critical process for protecting public health and the environment. One of its key components is the management of chemical reactions that remove contaminants, adjust pH and reduce hardness or nutrient loads. It is essential that wastewater is treated before being released into the environment because ecosystems are affected adversely by contaminants and abnormal pH levels. The contamination that causes pH changes is due to animal and human waste, pesticide use and the improper disposal of chemicals.

Wastewater frequently contains contaminants that make it turbid (opaque or cloudy) so pH indicators that change colour are unsuitable. A conductometric titration is an analytical technique designed to determine the equivalence point of a reaction by measuring electrical conductivity. As acidic or basic titrants are added to wastewater, they react with the ions in the solution, altering its conductivity. Such titrations are automated, making them both rapid and reliable.

Once the amount of titrant required for a small sample is known, large amounts of wastewater can be treated to reach an appropriate pH.

The ideal pH of treated wastewater is typically between 6.5 and 8.5. When outside of its optimal range, an acid or a base is added to neutralise the solution back into an acceptable range.

For acidic water, a base ($Ca(OH)_2$ or occasionally NaOH) is added. To illustrate the neutralisation process, carbonic acid has been used in the equation below, but wastewater can contain a variety of acids, depending on the source.

$$H_2CO_3(aq) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + 2H_2O(l)$$
$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

Calcium hydroxide is much less expensive than sodium hydroxide for treating large amounts of wastewater. Unfortunately, the calcium carbonate produces a solid product with some acids present, in the form of a sludge.

For alkaline water, carbon dioxide is added. This forms carbonic acid as shown:

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq) \rightarrow H^+(aq) + HCO_3^-(aq)$$

Carbonic acid can neutralise any alkalis. This reaction can also be tracked using a conductometric titration.

A conductometric titration can detect the equivalence point of these reactions to ensure that an accurate quantity is added to correct the pH to a level that meets environmental regulations.

Apply your understanding

1 **Identify** the main benefits of using a conductometric titration over a pH indicator for wastewater. (1 mark)

2 Treatment of acidic wastewater with calcium hydroxide can produce a solid sludge depending on the acid anion in the water. Use the solubility table in the QCAA Formula and data book to **determine** which acids result in a precipitate forming. (3 marks)

3 **Predict** the shape of the graph for the conductometric titration of weak carbonic acid with calcium hydroxide. Justify your predicted graph. (3 marks)

Check your learning 5.4

Check your learning 5.4: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain** the difference in conductivity between a strong acid and a weak acid. (2 marks)

2 **Explain** the appearance of the equivalence point on a conductivity graph and its significance in a conductometric titration. (2 marks)

3 25.0 mL of a solution of ethanoic acid (CH_3COOH) was titrated with a 0.100 M solution of sodium hydroxide (NaOH). The equivalence point was observed after adding 35.0 mL of NaOH.

 a **Construct** the balanced chemical equation for the reaction between ethanoic acid and sodium hydroxide. (1 mark)

- **b** **Calculate** the concentration of the ethanoic acid solution. (3 marks)
- **c** **Explain** how the conductivity of the solution changes during the titration. (2 marks)

4 30.0 mL of a solution of ammonia (NH_3) was titrated with a 0.200 M solution of hydrochloric acid (HCl). The equivalence point was observed after adding 25.0 mL of HCl.

- **a** **Construct** the balanced chemical equation for the reaction between ammonia and hydrochloric acid. (1 mark)
- **b** **Calculate** the molar concentration of the ammonia solution. (3 marks)
- **c** **Describe** the change in conductivity during the titration and **explain** why it behaves differently from the titration of a strong base with a strong acid. (3 marks)

Knowledge utilisation

5 While conducting a conductometric analysis of a strong acid with a strong base, water is not rinsed effectively out of the burette. If the titre volumes are about 25 mL each time the experiment is repeated, **justify**

- **a** whether this would be a systematic or random error (2 marks)
- **b** the accuracy of the data by comparing it to the theoretical value (2 marks)
- **c** the precision of the data (2 marks)
- **d** whether the experiment is reliable (2 marks)
- **e** whether the experiment is valid. (2 marks)

Practical

Lesson 5.5

Conductometric titration

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Learning intentions and success criteria

MODULE 5

Lesson 5.6

Review: Volumetric analysis

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.
- A standard solution is a solution whose concentration is known to a high degree of accuracy. It is reacted in a titration to determine the concentration of a second reactant.
- The equivalence point of a titration is reached when amounts of both reactants are in the stoichiometric ratio and no reactant remains. The end point of a titration is a chemical observation that scientists use to determine when to end the titration. The end point can be found by observing a suitable indicator or changes in conductivity and should be close to equivalence point.

5.2
- 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 base or acid, demonstrate a buffer region, an almost flat portion of the titration curve, 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. The volume of the titre is half the volume at equivalence point. This pK_a value can be used to accurately determine the K_a of a weak acid.

5.3
- Practical: Determining the concentration of ethanoic acid in white vinegar

5.4
- The equivalence point of a conductometric titration can be determined from a graph of conductivity vs. volume of titrant.
- The equivalence point is identified by where the two linear regions of the graph intersect.
- A conductometer or multimeter, on a resistance setting, can be used to measure conductivity to generate a graph and determine the equivalence point.
- Strong acids and bases completely ionise in water and therefore have high ion concentrations and high conductivity. Weak acids and bases only partially ionise in water and therefore have low ion concentrations and low conductivity.
- The K_{sp} of an insoluble salt can be determined using a solubility titration.
- Insoluble salts have very low solubilities and form very dilute solutions. A solubility titration can titrate a solution of known concentration until a precipitate appears. Alternatively, a solubility titration can be used to titrate a saturated solution of an insoluble salt, to determine the concentration of one of the ions.

5.5
- Practical: Conductometric titration.

Key formulas

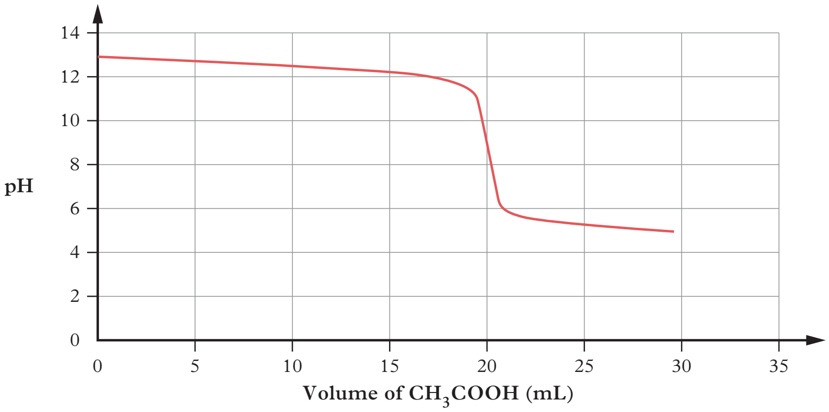
Number of moles	$n = c \times V$
Number of moles	$n = \frac{m}{M}$
pK_a	$pK_a = -\log_{10}K_a$ $K_a = 10^{-pK_a}$
Acid dissociation constant	$K_a = \frac{[H_3O^+][A^-]}{[HA]}$

Review questions 5.6A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

Use the following graph to answer questions 1 and 2.



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.

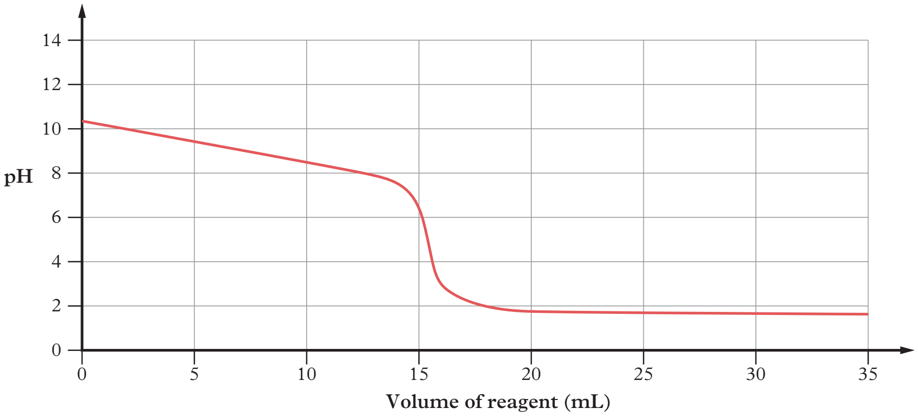
2 Assuming that the average titre is 20.00 mL, what is the concentration of CH_3COOH?

- **A** 5 M
- **B** 0.5 M
- **C** 0.20 M
- **D** 0.05 M

3 What volume of 0.350 M HCl is required to react completely with 18 mL of 0.6 M Na_2CO_3 solution?

- **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 following 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 observation that shows the end point of an acid-base titration?
- **A** Bubbling of solution
- **B** Temperature change
- **C** Colour change of an indicator
- **D** The solution has a neutral pH

6 What is the correct definition of a titre?
- **A** The volume of solution dispensed from the burette
- **B** A graduated glass cylinder that dispenses highly accurate volumes of a standard solution
- **C** The standard solution in the burette that is added to the solution of unknown concentration
- **D** A glass tube that dispenses highly accurate volumes of a solution of unknown concentration

7 A titration curve shows that the equivalence point has a pH of 5.26 and the half-equivalence point has a pH of 9.22. The analyte must be a
- **A** weak acid with pK_a 4.78.
- **B** weak acid with pK_a 9.22.
- **C** weak base with pK_b 4.78.
- **D** weak base with pK_b 9.22.

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 up to the meniscus.
- **C** an angle looking down to the meniscus.
- **D** eye level to the bottom of the meniscus.

9 To determine the titre, you have to
- **A** add the initial volume to the final volume to determine the total volume of standard solution dispensed from the burette.
- **B** divide the initial volume by the final volume to determine the total volume of standard solution dispensed from the burette.
- **C** subtract the initial volume from the final volume to determine the total volume of standard solution dispensed from the burette.
- **D** subtract the final volume from the initial volume to determine the total volume of standard solution dispensed from the burette.

10 In a conductometric titration of ethanoic acid (CH_3COOH), where sodium hydroxide (NaOH) is added from the burette, how does the conductivity of the solution change during the titration?
- **A** Conductivity increases steadily throughout the titration.
- **B** Conductivity decreases steadily to the equivalence point then increases significantly after it.
- **C** Conductivity increases initially, remains constant to the equivalence point, and then increases.
- **D** Conductivity decreases very slightly at the start, increases gradually to the equivalence point then increases at a faster rate after the equivalence point.

Review questions 5.6B Short response

Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

11 **Define** "buffer region" and **describe** how it relates to pK_a and half-equivalence point. (3 marks)

12 **Define** "parallax error" and **explain** why it must be avoided when measuring. (2 marks)

13 **Explain** the relationship between an end point and an equivalence point. **Sketch** a titration curve to support your answer. (3 marks)

14 **Identify** five ways that errors may occur in the titre volume. (5 marks)

15 **Explain** why there are many ways that errors may occur in a titration experiment. (2 marks)

16 **Explain** why strong acids and bases conduct electric current better than weak acids and bases. (2 marks)

17 **Explain** why a conductometric titration is preferable over an acid–base titration when a solution is coloured. (2 marks)

18 **Calculate** 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. (3 marks)

19 An aliquot of weak base (initial pH 11.1) is titrated against a strong monoprotic acid. 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_b. (4 marks)

20 An aliquot of weak monoprotic acid (initial pH 2.8) is titrated against a strong base. 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. (4 marks)

21 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.

$$NaOH(aq) + KHC_8H_4O_4(aq) \rightarrow KNaC_8H_4O_4(aq) + H_2O(l)$$

If an average titre of 12.07 mL was obtained, **calculate** the concentration of the NaOH solution. (4 marks)

22 A 25.0 mL solution of ethanoic acid (CH_3COOH) was titrated with a 0.10 M sodium hydroxide (NaOH) solution using a conductivity meter. The equivalence point was reached after adding 30.0 mL of NaOH.

a **Construct** the balanced chemical equation for the reaction. (1 mark)

b **Calculate** the concentration of the ethanoic acid solution. (3 marks)

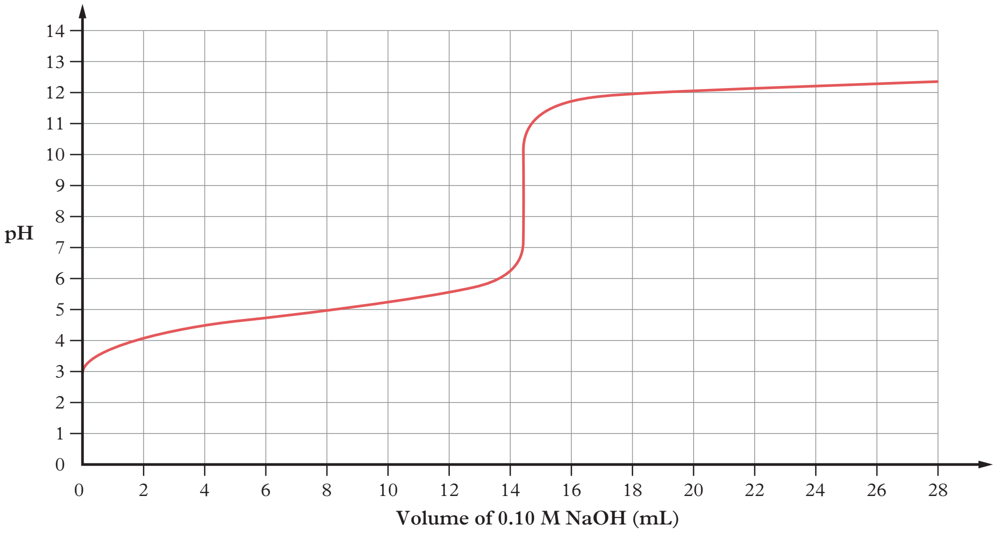
23 In a conductometric titration, a 50.0 mL sample of water was titrated with a 0.01 M EDTA solution to determine its total hardness. The equivalence point was reached after 20.0 mL of EDTA was added.

a **Construct** the balanced chemical reaction for the complexation of Ca^{2+} and Mg^{2+} with EDTA. (1 mark)

b **Calculate** the total hardness of the water sample in mg L^{-1} of $CaCO_3$. (3 marks)
Hint: The molar mass of $CaCO_3$ is 100.1 g mol^{-1}, and 1 mol of $CaCO_3$ is equivalent to 1 mol of Ca^{2+} or Mg^{2+}.

Analytical processes

24 Use your knowledge of acid–base titrations and 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 shown is produced.



Use the information on the graph to **determine**

a the volume of NaOH used to neutralise the solution of HA (1 mark)

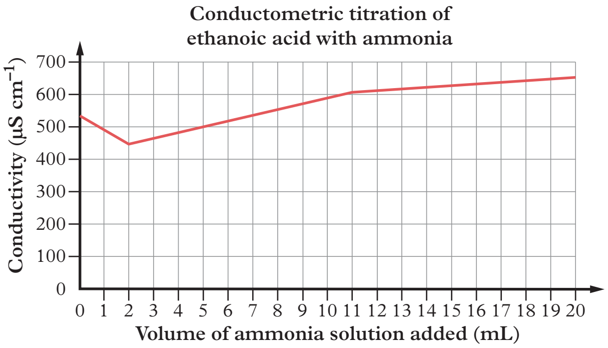
b [HA] (1 mark)

c the concentration of hydronium ions (H_3O^+) in the solution of HA before it reacts with NaOH (1 mark)

d K_a for the weak acid HA by calculating using answers from parts **b** and **c**. (1 mark)

e whether your answer for part **d** correlates with the titration curve. (1 mark)

25 In a conductometric titration, a 10.0 mL sample of 0.0120 M ethanoic acid was titrated with a solution of ammonia. The results are shown.



- **a** **Determine** the volume at equivalence point of the titration. (1 mark)
- **b** **Explain** why a conductometric titration is suitable in this instance but a titration with an indicator would not be feasible. (2 marks)
- **c** **Construct** the balanced chemical reaction the reaction. (1 mark)
- **d** **Calculate** the concentration of the ammonia solution. (3 marks)

Knowledge utilisation

26 **Create** a mind map of the different sources errors in titrations and the effect each error has on the titre. (6 marks)

27 In a titration, a student prepares 250.0 mL of a standard solution of potassium hydrogen phthalate by weighing 5.106 g and dissolving, then making up to the mark in a volumetric flask. This solution is used to standardise a solution of NaOH. A 20.00 mL aliquot of potassium hydrogen phthalate results in an average titre of 23.9 mL of NaOH solution. The standardised solution of NaOH is then used to titrate a solution of HCl. A 20.00 mL aliquot of the HCl results in an average titre of 26.54 mL.

A second student follows the same procedure to and standardises the NaOH solution in the same way but leaves the NaOH solution on the bench over the school holidays. On 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. (12 marks)

28 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 second student's claim and provide a justification. (3 marks)

Data drill

Analysing titration curves

A student used a pH meter to produce a titration curve and recorded their results in Figure 1.

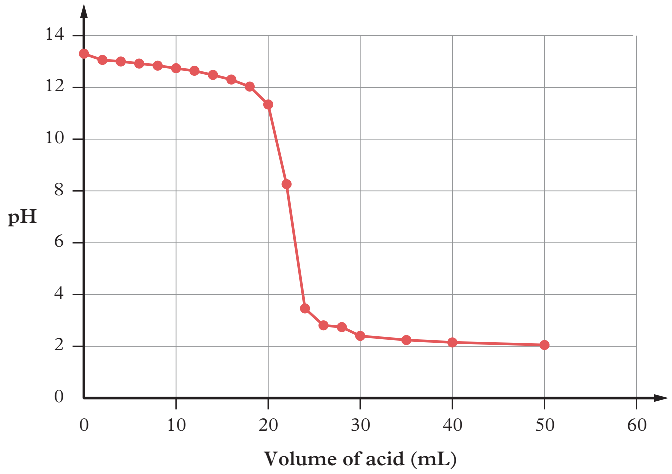


FIGURE 1 Titration curve

Apply understanding

1 Use the graph to **identify** the
  - **a** types of acid and base present (2 marks)
  - **b** equivalence point on the titration curve (1 mark)
  - **c** volume of titrant required to reach the equivalence point. (2 marks)

2 **Determine** a suitable indicator for this titration and justify your answer. (2 marks)

Analyse data

3 Based on the vertical slope of the titration curve, **identify** whether this experiment result is precise. (2 marks)

4 **Identify** how the accuracy of this experiment may be determined. (2 marks)

Interpret evidence

5 The experiment was repeated and resulted in a lower volume of acid at the equivalence point. **Justify** what may have happened to cause this discrepancy in data. (2 marks)

6 The experiment was repeated a second time but the student did not label the beakers that they were using for their aliquot and the group next to them were using an unlabelled beaker of ammonia. **Predict** the titration curve for the alternative reaction and **justify** how you would know which beaker was the correct one. (3 marks)

Module 5 checklist: Volumetric analysis

UNIT 3

Topic 1 review

Multiple choice

(1 mark each)

1 Which of the following implies that a chemical system at equilibrium is dynamic?

A The position of the equilibrium constantly changes.

B The rate of the forward reaction decreases but the rate of the reverse reaction increases, as the mixture reaches equilibrium.

C The concentrations of the reactants and products continue to change.

D The reactants and products continue to react. The amounts of the reactants and products are unchanged.

Use the following information to answer questions 2 and 3.

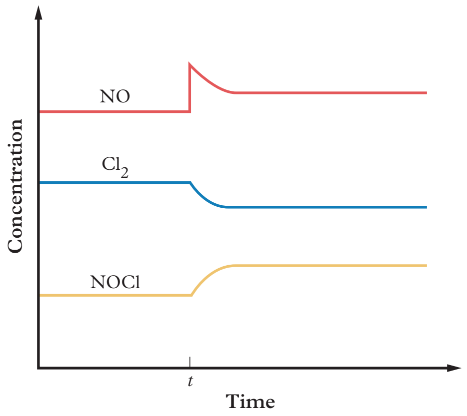
$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g) \quad \Delta H = +75.5 \text{ kJ mol}^{-1}$

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 A catalyst was added.

B The volume of the system was halved.

C Additional NO was added to the system.

D The temperature of the system was increased.

4 For the reaction

$H_2 + Br_2 \rightleftharpoons 2HBr$, $K_c = 3.5 \times 10^4$ at 1495 K.

Identify K_c for the reverse reaction.

A 7.2×10^5 **B** 3.5×10^{-4}

C 2.86×10^5 **D** 2.86×10^{-5}

5 The equilibrium between carbon monoxide (CO) and oxygen gas (O_2) to form carbon dioxide is shown below.

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

$\Delta H = -566$ kJ, $K_c = 15.30$

Identify the change in equilibrium when the volume of a mixture at equilibrium is decreased at a constant temperature.

A K_c increases.

B $[CO_2]$ increases.

C [CO] and $[O_2]$ increases.

D The ratio $\frac{[CO_2]}{[CO][O_2]}$ decreases.

Use the following information to answer questions 6 and 7.

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

$\Delta H = 75.3 \text{ kJ mol}^{-1}$, $K_c = 1.0 \times 10^{-5}$ at 30°C

6 Determine the correct relationship at equilibrium at this temperature.

A The concentration of NO equals the concentration of NOCl.

B The concentration of NOCl is double the concentration of Cl_2.

C The concentration of NOCl is greater than the concentration of Cl_2.

D The concentration of NO is greater than the concentration of NOCl.

7 What is the effect of increasing temperature on the equilibrium?

A The position of equilibrium moves to the left and K_c decreases.

B The position of equilibrium moves to the right and K_c increases.

C The position of equilibrium moves to the left and K_c does not change.

D The position of equilibrium moves to the right and K_c does not change.

8 Determine which of the following is not a conjugate acid–base pair.

A H_3O^+ and OH^-

B HNO_3 and NO_3^-

C HSO_4^- and SO_4^{2-}

D CH_3COOH and CH_3COO^-

9 Determine which of the following 0.5 mol L^{-1} solutions would have the lowest conductivity.

A HCl

B NH_3

C HNO_3

D H_2CO_3

10 A solution changes from pH 3 to pH 5. Determine the change in concentration of hydrogen ions during this pH change.

A It increases by a factor of 100.

B It decreases by a factor of 100.

C It increases by a factor of 1,000.

D It decreases by a factor of 1,000.

11 The concentration of ethanoic acid (pK_a 4.75) in vinegar is approximately 1.0 M. What is the pH of vinegar?

A 5.4

B 4.8

C 2.4

D 0.004

12 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 oxalic acid → malic acid → lactic acid.

B oxalic acid → lactic acid → malic acid.

C lactic acid → oxalic acid → malic acid.

D lactic acid → malic acid → oxalic acid.

13 A solution of 0.2 M methanamine (CH_3NH_2) has pK_b 3.36 at room temperature and pressure. Calculate the approximate pH of the solution.

A 12 **B** 8.7 **C** 9.8 **D** 5.4

14 Determine the most suitable indicator to indicate the equivalence point of a titration of 0.2 M methanamine with 0.1 M HCl.

A Phenol red

B Methyl orange

C Phenolphthalein

D Bromothymol blue

15 A solution composed of 0.25 M acetic acid and 0.25 M sodium acetate has pK_a 4.75. Determine the impact of adding small amounts of HCl on the solution.

A The pH will decrease slightly over the time the HCl is being added.

B The pH will increase significantly over the time the HCl is being added.

C The pH will decrease significantly over the time the HCl is being added.

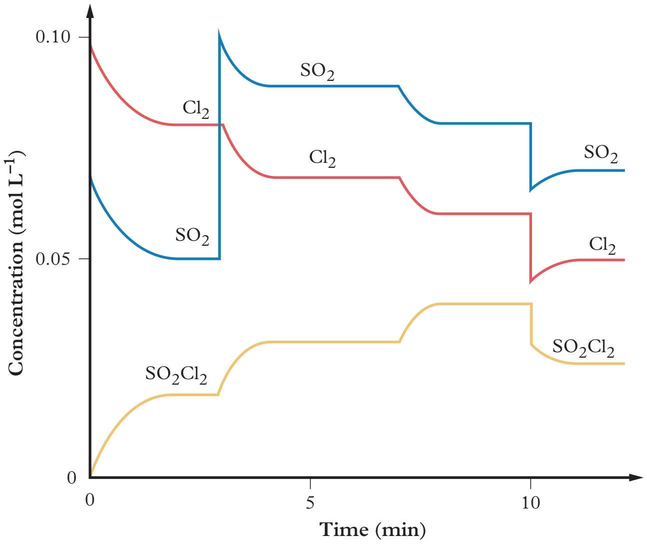
D The pH will change initially and then return to what it was before the acid addition.

Short response

16 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. (1 mark)

b **Determine** during which time intervals the reaction was at equilibrium. (1 mark)

c **Calculate** the value of K at the 2-minute and 9-minute marks. (2 marks)

d **Identify** one possible reason why the values of K calculated in part **c** are different. (1 mark)

- **e** **Determine** what change was made to the system at
  - **i** 3 minutes (1 mark)
  - **ii** 7 minutes (1 mark)
  - **iii** 10 minutes. (1 mark)

17 Chlorine gas is generated in an equilibrium reaction between hydrogen chloride gas and oxygen:

$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$
$\Delta H = -128\ \text{kJ mol}^{-1}, K = 2.46$

- **a** **Construct** an equilibrium expression. (1 mark)
- **b** Initially, 20 mol of HCl and 6 mol of O_2 are injected into a 2 L vessel. After 30 s, the concentration of O_2 was measured to be 1.5 M. **Calculate** Q_c of the reaction at 30 s. (2 marks)
- **c** **Determine** what you can conclude about the equilibrium position of the reaction mixture in part **a** based on the Q_c value that you have calculated. (1 mark)
- **d** In a second mixture, the concentrations of HCl, O_2, H_2O and Cl_2 are found to be 12 M, 3 M, 10 M and 10 M respectively. **Calculate** Q_c for this mixture. (2 marks)
- **e** **Determine** what you can conclude about the equilibrium position of the reaction mixture in part **c** based on the Q_c value that you have calculated. (2 marks)
- **f** Use your answer to part **e** to **deduce** the direction the reaction would need to proceed in order to reach equilibrium. **Justify** your answer. (2 marks)
- **g** Using Le Châtelier's principle, **explain** the effect of increasing the temperature of the system. (2 marks)
- **h** Using Le Châtelier's principle, **explain** the effect of decreasing the volume of the system. (2 marks)

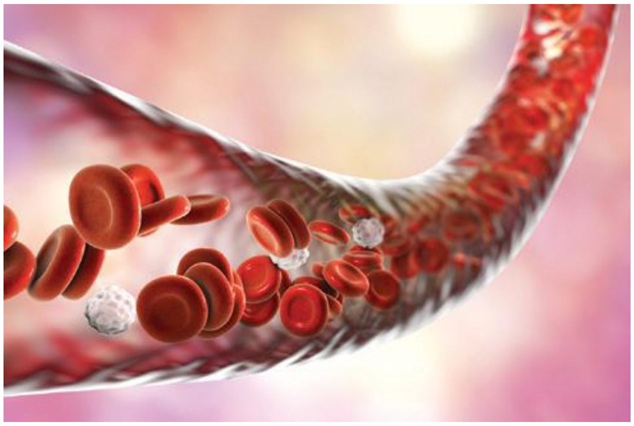
18 Consider the following exothermic reaction taking place at 40°C in a 1 L closed container. A solution of colourless hydrogen peroxide (H_2O_2) is added to a solution of sodium iodide (NaI), which releases iodide ions (I^-), and acidified with hydrochloric acid (HCl), which releases hydrogen ions (H^+). The yellow colour of the iodine (I_2) can be used to determine the rate of reaction as depicted below.

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

- **a** If the temperature of the reaction was changed to 30°C, **predict** the effect on K_c of the reaction and any observations that can be made. (2 marks)
- **b** **Propose,** stating a reason, how the addition of a catalyst at constant temperature will affect the equilibrium concentration of I_2. **Justify** your response. (2 marks)
- **c** The reaction was conducted again with solid NaI instead of a solution of NaI. **Predict** the effect changing the size of NaI particles will have on the equilibrium position and the rate of reaction overall. **Justify** your response. (3 marks)

19 Blood contains a natural carbonic acid/hydrogencarbonate buffer. Carbon dioxide is absorbed into the blood. A simplified representation of this process is provided in the equilibrium equation:

$$CO_2(aq) + 2H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_c = 4.45 \times 10^{-7}$$



- **a** **Explain** how a buffer can stabilise the pH of a solution. (3 marks)
- **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^+. (1 mark)
  - **ii** **Calculate** the equilibrium value of $[HCO_3^-]$. (1 mark)
- **c** Muscles metabolise fats and sugars and produce energy. Both CO_2 and H^+ are produced as by-products. **Explain** the response of the buffer system for a person who regularly exercises excessively. (2 marks)

20 At 57°C, the concentration of hydroxide ions in pure water is 2.95×10^{-7} M.

- **a** **Construct** the ionisation equation for water. (1 mark)
- **b** **Deduce** the concentration of H^+. (1 mark)
- **c** **Calculate** the pOH of the water. (1 mark)
- **d** **Calculate** K_w. (1 mark)

e **Calculate** the pH. (1 mark)

f The self-ionisation of water is an endothermic process. **Explain** what happens to the pH of water as temperature increases. (2 marks)

21 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. (2 marks)

b To analyse the cleaner, 10.0 g of the cleaning solution is diluted 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. (2 marks)

ii **Calculate** the average amount of HCl, in moles, in the 10.00 mL aliquots. (3 marks)

iii **Calculate** the amount of HCl, in moles, in the 250.00 mL volumetric flask. (1 mark)

iv **Calculate** the mass of the HCl in the cleaner. (1 mark)

v **Calculate** the concentration of HCl in % w/w. (1 mark)

vi **Compare** the experimental concentration to the one stated on the cleaner. **Determine** what conclusions you can make. (2 marks)

c **Explain** the colour change that would be observed with a methyl orange indicator. (2 marks)

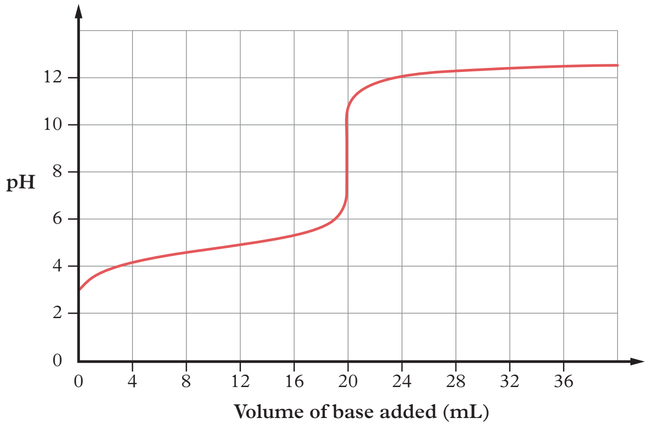
d After the experiment, a student realises that their partner had rinsed the burette with water and then filled it with standard solution before beginning the titration. **Deduce** the effect of this error on the final concentration of HCl calculated in the experiment. (2 marks)

22 Acids can be described as strong or weak.

a **Compare** the difference in dissociation between strong and weak acids of the same concentration. (2 marks)

b **Calculate** the pH of a solution of propanoic (molar mass = 72.08 g mol^{-1}) acid made by dissolving 1.40 g of the acid in distilled water to make a 0.500 L solution. ($K_a = 1.3 \times 10^{-5}$). (4 marks)

c For the titration of an unknown acid shown in the curve below, **determine** the pH at the equivalence point and the pK_a of the following unknown acid. (2 marks)

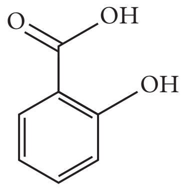


23 At 350°C, $K_c = 1.2$ for the composition of ammonia as described in the following equation.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

When a certain concentration of NH_3 is put into an otherwise empty rigid vessel at 350°C, equilibrium is reached when 50% of the original ammonia has decomposed. **Calculate** the concentration of ammonia before any decomposition occurred. (5 marks)

24 Salicylic acid is commonly used in the production of aspirin and as a key component of acne treatments because of its anti-inflammatory properties. Assume that it behaves as a monoprotic acid with $K_a = 1.06 \times 10^{-3}$ at room temperature and pressure. 0.02500 L of 0.150 M salicylic acid is titrated with 0.100 M standardised NaOH solution.



Salicylic acid
$C_7H_6O_3$

a **Determine** the formula of the conjugate acid and conjugate base formed when salicylic acid reacts with sodium hydroxide (NaOH). (2 marks)

b **Identify** the equivalence point volume for the titration. (3 marks)

c **Identify** the pH at equivalence point for the titration. (6 marks)

d **Sketch** the titration curve that would be produced from the titration reaction between salicylic acid with NaOH, indicating the important features identified above. (3 marks).

e **Propose** a suitable indicator for this titration. **Justify** your response. (2 marks)

25 K_{sp} of silver iodide is 8.5×10^{-17} and for copper(II) hydroxide it is 2.2×10^{-20}.

a **Calculate** the solubility of silver iodide in pure water. (2 marks)

b **Calculate** the solubility of copper(II) hydroxide in pure water. (2 marks)

c **Identify** $[Cu^{2+}]$ and $[OH^-]$ in a saturated solution of copper(II) hydroxide. (1 mark)

d A student claims that copper(II) hydroxide is less soluble than silver iodide because it has a smaller K_{sp}. **Evaluate** this claim. (2 marks)

e **Calculate** the solubility of silver iodide in a solution of 0.1 M NaI. (2 marks)

f **Calculate** the solubility of copper(II) hydroxide in an acidic solution with a pH of 4. Assume that the solution is buffered and able to maintain this pH. (4 marks)

26 Titration curves are used to depict changes in pH throughout a titration. Conductivity graphs depict the changes in the conductivity throughout a conductometric titration. Each type of graph can be used to find the equivalence point of a titration and has distinctive features depending on whether strong or weak acids and bases are used as well as whether the acid or the base is being titrated.

a Consider the titration of a strong acid with a strong base.

i **Construct** both a titration curve and a graph of a conductometric titration, showing the main features and general shape. (4 marks)

ii **Summarise** the features in the following tables. (Some features have been completed for you.) (2 marks)

Titration curve features	
Initial pH	
pH change as base is added, but somewhat before equivalence point	pH rises steadily, as shown by a small positive gradient.
pH changes as equivalence point is approached and passed	pH rises more rapidly, as shown by the gradient increasing then the curve being almost vertical; then the pH rises less rapidly after equivalence point is pased, so the gradient is positive, but the curve is less steep again.
pH at equivalence point and how equivalence point is recognised on the curve	
pH changes somewhat after equivalence point	

Conductometric titration features	
Initial conductivity	
Change in conductivity as equivalence point is approached	Conductivity falls rapidly and linearly as base is added, towards the minimum value (gradient is negative and has a large magnitude).
Conductivity at equivalence point and how equivalence point is recognised on the graph	
Conductivity changes after equivalence point	

b Consider the titration of a weak acid with a strong base.

i **Construct** both a titration curve and a graph of a conductometric titration, showing the main features and general shape. (4 marks)

ii **Summarise** the features in the following tables. (Some features have been completed for you.) (2 marks)

Titration curve features	
Initial pH	
pH change as base is added, but somewhat before equivalence point	pH rises rapidly at first, shown by a steeper section, then rises very little for some time as base is added, as shown by a very small positive gradient (buffer zone).
pH changes as equivalence point is approached and passed	
pH at equivalence point and how equivalence point is recognised on the curve	
pH changes somewhat after equivalence point	

Conductometric titration features	
Initial conductivity	Fairly low, much lower than for the strong acid
Change in conductivity as equivalence point is approached	
Conductivity at equivalence point and how equivalence point is recognised on the graph	
Conductivity changes after equivalence point	

c Consider the titration of a weak base with a strong acid.

- **i** **Construct** both a titration curve and a graph of a conductometric titration, showing the main features and general shape. (4 marks)
- **ii** **Summarise** the features in the tables below. (Some features have been completed for you.) (2 marks)

Titration curve features	
Initial pH	pH is moderately high, about 11 or 12 (not 13 or 14)
pH change as acid is added, but somewhat before equivalence point	
pH changes as equivalence point is approached and passed	
pH at equivalence point and how equivalence point is recognised on the curve	
pH changes somewhat after equivalence point	

Conductometric titration features	
Initial conductivity	
Change in conductivity as equivalence point is approached	
Conductivity at equivalence point and how equivalence point is recognised on the graph	Conductivity is at the lowest point, where two straight lines intersect.
Conductivity changes after equivalence point	

d Consider the titration of a strong base with a strong acid, where the salt formed is insoluble.

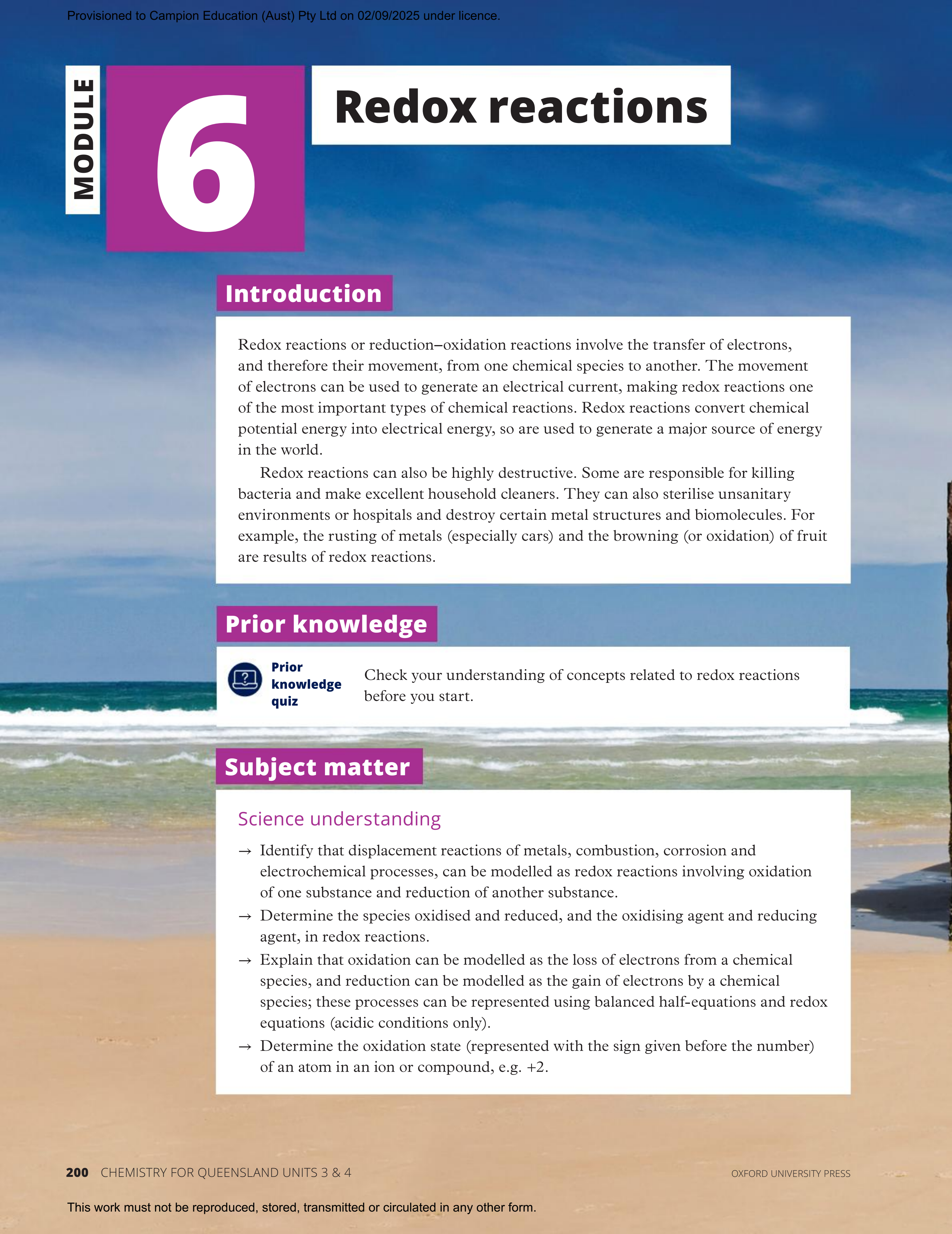
- **i** **Construct** both a titration curve and a graph of a conductometric titration, showing the main features and general shape. (4 marks)
- **ii** **Summarise** the features in the tables below. (Some features have been completed for you.) (2 marks)

Titration curve features	
Initial pH	pH is high, about 13 or 14 (depending on concentration)
pH change as base is added, but somewhat before equivalence point	
pH changes as equivalence point is approached and passed	
pH at equivalence point and how equivalence point is recognised on the curve	
pH changes somewhat after equivalence point	

Conductometric titration features	
Initial conductivity	
Change in conductivity as equivalence point is approached	
Conductivity at equivalence point and how equivalence point is recognised on the graph	
Conductivity changes after equivalence point	

TOTAL MARKS

/136



MODULE 6 Redox reactions

Introduction

Redox reactions or reduction–oxidation reactions involve the transfer of electrons, and therefore their movement, from one chemical species to another. The movement of electrons can be used to generate an electrical current, making redox reactions one of the most important types of chemical reactions. 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 results of redox reactions.

Prior knowledge

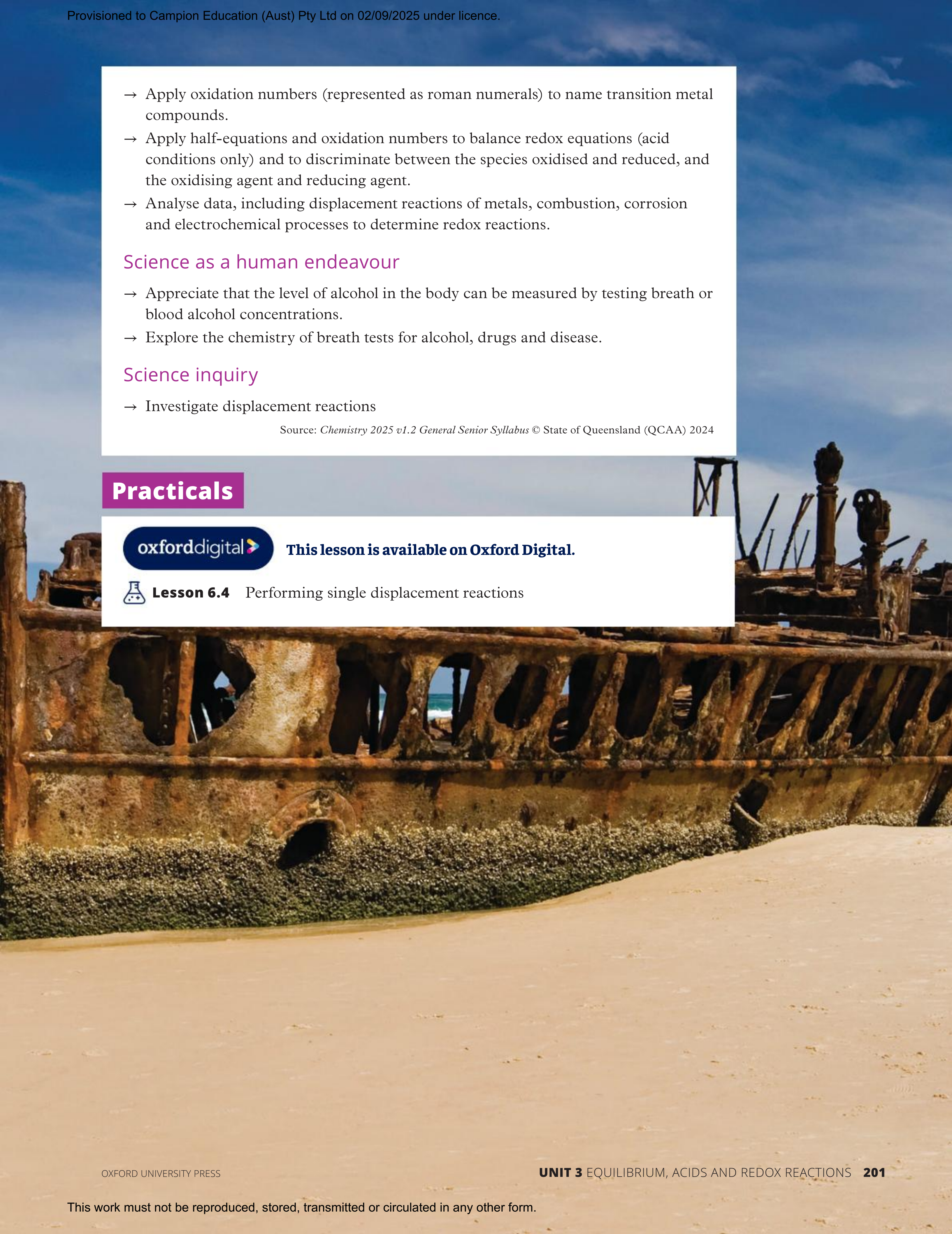
Prior knowledge quiz

Check your understanding of concepts related to redox reactions before you start.

Subject matter

Science understanding

- Identify that 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.
- Determine the species oxidised and reduced, and the oxidising agent and reducing agent, in redox reactions.
- Explain 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).
- Determine the oxidation state (represented with the sign given before the number) of an atom in an ion or compound, e.g. +2.



- → Apply oxidation numbers (represented as roman numerals) to name transition metal compounds.
- → Apply half-equations and oxidation numbers to balance redox equations (acid conditions only) and to discriminate between the species oxidised and reduced, and the oxidising agent and reducing agent.
- → Analyse data, including displacement reactions of metals, combustion, corrosion and electrochemical processes to determine redox reactions.

Science as a human endeavour

- → Appreciate that the level of alcohol in the body can be measured by testing breath or blood alcohol concentrations.
- → Explore the chemistry of breath tests for alcohol, drugs and disease.

Science inquiry

- → Investigate displacement reactions

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Practicals

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Lesson 6.4 Performing single displacement reactions

Lesson 6.1
Reduction and oxidation reactions

Key ideas

- → 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 outermost orbitals of the reactants.
- → The reactant that loses one or more electrons causes the reduction of the other reactant and so is called the reductant.
- → The reactant that takes one or more electrons causes the oxidation of the other reactant and so is called the oxidant.
- → Single displacement reactions, oxidation and corrosion are examples of redox reactions.

Learning intentions and success criteria

What is a redox reaction?

When negatively charged electrons move between chemical species, energy is exchanged. This exchange of electrons between chemicals is like a financial transaction in which money is exchanged. When a substance loses one or more electrons, another substance accepts them. Electrons cannot be destroyed in a chemical reaction, merely transferred.

redox
a chemical reaction involving the transfer of electrons from one reactant to another

reduction
a gain of electrons

oxidation
a loss of electrons

Redox is an abbreviation for a pair of reactions in which electrons are exchanged between reactants. The reactions are called **reduction** and **oxidation** reactions, and one cannot occur without the other, i.e. they occur simultaneously.

How do we know that a redox reaction has occurred?

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.

Valence electrons

The reaction between sodium and oxygen to form sodium oxide is an example of a redox reaction:

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

valence electron
an electron in the outermost shell of an atom, according to the Bohr model of electron configuration

The Bohr model of the electron configuration of sodium and oxygen atoms (Figure 1) demonstrates that sodium has one **valence electron**, which it must lose to become stable. Each oxygen atom 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. As oxygen is present in molecular form, the two atoms in a molecule accept four electrons altogether, so four sodium atoms are required.

This example demonstrates the transfer of electrons between reactants. Each of the four sodium atoms loses an electron and each of the two oxygen atoms gains two electrons. The transfer of electrons results in Na becoming the ion Na^+ and O becoming the ion O^{2-}. Each sodium loses an electron and develops a positive charge. Each 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.

In some redox reactions, particularly when two non-metals react with each other, the electrons are only partially transferred. For example, when hydrogen and nitrogen react to form ammonia, the bonds formed are polar covalent bonds, rather than ionic, where the N atom in ammonia has more of the share of the electrons in each bond, because it is more electronegative than hydrogen. The nitrogen atom gains a partial negative charge and has been reduced, while each hydrogen partly loses its electron and has been oxidised.

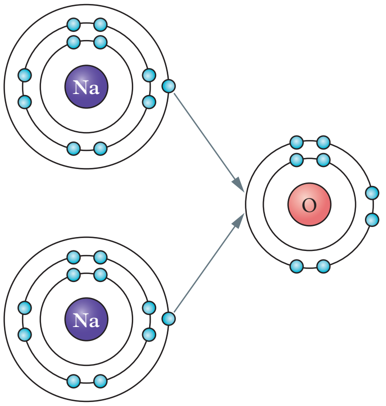


FIGURE 1 Sodium has one valence electron. Oxygen has six valence electrons. Two sodium atoms each transfer an electron to an oxygen atom to form sodium oxide, Na_2O, made up of Na^+ and O^{2-} ions.

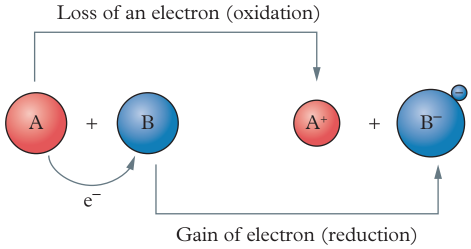


FIGURE 2 The transfer of an electron from A to B results in a positive cation (A^+) and negative anion (B^-), forming an ionic compound (AB).

Study tip

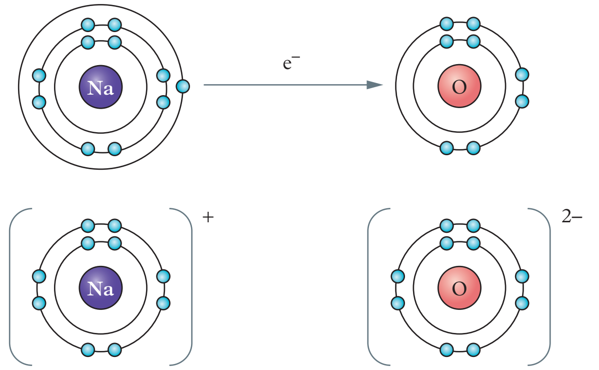
A useful method of remembering oxidation and reduction is OIL RIG. This stands for "Oxidation is Loss (of electrons)" and "Reduction is Gain (of electrons)".

oxidised
to lose electrons

reduced
to gain electrons

Terminology

In the example of sodium and oxygen reacting to form sodium oxide, sodium is oxidised and oxygen is reduced. However, sodium will not lose its valence electron unless oxygen is able to accept it. For this reason, oxygen causes sodium to lose an electron and, similarly, sodium causes oxygen to gain an electron. The chemical species responsible for causing oxidation and reduction are called **oxidising agents** and **reducing agents** (Figure 3).



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

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

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.

You will not be required to explain why some substances can more easily be oxidised than others. However, ionisation energy, which you learnt about in Unit 1, is a measure of the energy required to remove an electron from a gaseous ion. Broadly speaking, elements with low ionisation energies are more easily oxidised. Note that the second and higher ionisation energies of an element are always larger than the first ionisation energy, and which is why some elements lose more than one electron when oxidised. Electron affinity provides a measure of the energy change when an atom in the gaseous phase gains an electron. Generally, elements with a lower, more negative electron affinity can gain an electron more easily.

Worked example 6.1A

Applying terminology when determining electron transfer

Consider the chemical reaction between fluorine atoms and lithium atoms in the gas phase to form solid lithium fluoride:

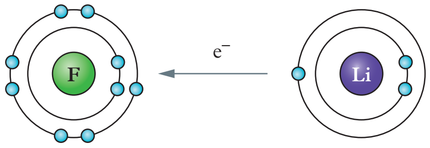
$$F(g) + Li(g) \rightarrow LiF(s)$$

a **Construct** the Bohr electron configurations of lithium and fluorine and show the electron transfer. (2 marks)

b **Identify** the chemicals that gain and lose electrons. (1 mark)

c **Identify** the chemicals oxidised and reduced. (1 mark)

d **Identify** the oxidising agent and the reducing agent. (1 mark)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	“Construct” means to display information in a diagrammatical or logical form. “Identify” means to recognise and name. We need to determine which chemical donates and accepts electrons to name the processes involved. The first question is worth 2 marks because two pieces of information are required; however, each subsequent question is worth 1 mark, so there is no need for working, only stating the answer.
Step 2: For part **a**, draw the electron configuration of both reactants.	**a**  (1 mark for drawing both correctly)
Step 3: Determine how they will transfer electrons to complete their valence shell.	Fluorine gains an electron from lithium, which loses an electron. (1 mark for drawing the electron moving from lithium to fluorine)
Step 4: Assign terminology based on your answer to part **a**, in steps 2 and 3.	**b** The fluorine atom gains an electron. The lithium atom loses an electron. (1 mark) **c** Lithium is oxidised. Fluorine is reduced. (1 mark) **d** Fluorine is the oxidising agent. Lithium is the reducing agent. (1 mark)

Your turn

Consider the chemical reaction between chlorine atoms and sodium atoms in the gas phase to form sodium chloride:

$$Cl(g) + Na(g) \rightarrow NaCl(s)$$

a **Construct** the Bohr electron configurations of sodium and chlorine atoms and show the electron transfer. (2 marks)

b **Identify** the chemicals that gain and lose electrons. (1 mark)

c **Identify** the chemicals oxidised and reduced. (1 mark)

d **Identify** the oxidising agent and the reducing agent. (1 mark)

What are some examples of redox 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:

- **single displacement** reactions
- **combustion** reactions
- **corrosion** reactions.

single displacement
a chemical reaction in which a more reactive metal ion replaces a less reactive metal ion in a compound

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

Displacement reactions of metals

Displacement reactions of metals are often called single displacement reactions. This reaction is covered in detail in Units 1 & 2. Single displacement reactions occur when a stronger reducing agent replaces a weaker reducing agent. Figure 4 shows the reactivity series of the metals.

Consider the reaction of magnesium metal with zinc nitrate in aqueous solution:

$$Zn(NO_3)_2(aq) + Mg(s) \rightarrow Mg(NO_3)_2(aq) + Zn(s)$$

Magnesium is a stronger reducing agent – it gives away its electrons more readily than zinc does. Therefore, magnesium donates electrons to zinc to form magnesium ions in solution and zinc metal. Nitrate ions are spectator ions in the solution.

Zn^{2+} or zinc ions are the cations in the ionic compound zinc nitrate. These ions gain electrons from the magnesium metal to form zinc metal. Therefore, the zinc ions undergo reduction.

Magnesium metal loses electrons to form a positive metal cation, Mg^{2+}, in the ionic compound. Therefore, magnesium undergoes oxidation.

A summary of this reaction showing just the reacting species is:

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

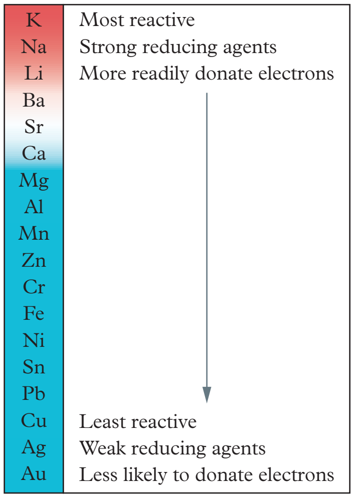


FIGURE 4 The metal reactivity series

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 magnesium and oxygen:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

Magnesium metal loses electrons to form a positive metal cation, Mg^{2+} in this case. Therefore, magnesium undergoes oxidation. Oxygen gas gains electrons to form a negative non-metal anion, O^{2-}. Therefore, oxygen undergoes reduction.

Corrosion

Corrosion is a process in which metals react with chemicals in the atmosphere (including water from 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. As an ion, the metal readily donates an electron according to the general equation (where M represents the metal):

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

This type of reaction is called a half-reaction, because it represents only one half of the redox reaction, which in this case is the oxidation half-reaction. For example, iron is a metal highly susceptible to corrosion. When water interacts with the surface of the iron metal (Figure 5), iron loses two electrons to form aqueous Fe^{2+} 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:

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

Note here how the electrons in this reduction half-reaction are on the left-hand side, whereas they are on the right-hand side in the oxidation half reaction. The Fe^{2+} ions and hydroxide ions react with each other to form iron(II) hydroxide, where the Roman numeral II tells us how many electrons have been lost compared to iron metal:

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$$

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 in a further redox reaction:

$$4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$$

The iron(III) hydroxide decomposes because of the presence of oxygen to form a brown hydrated iron oxide complex:

$$4Fe(OH)_3(s) \rightarrow 2Fe_2O_3.H_2O(s)$$

Iron(III) oxide is the chemical that gives rust its characteristic brown colour (Figure 5).

FIGURE 5 The corrosion of iron metal forms rust, seen here as red-brown patches.

Challenge

Ionisation energy and redox

Analyse, using Figure 6, how the ionisation energies of atoms relate to an atom's ability to lose electrons, and therefore their strength as a reductant. Use francium and fluorine as examples to support your answer. (3 marks)

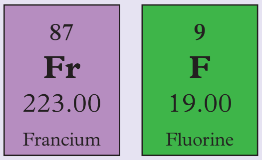


FIGURE 6 Francium and fluorine are both chemical elements.

Skill drill

Analysing the reactivity data of metals

Science inquiry skill: Understanding the scientific method (Lesson 1.3); Processing and analysing data (Lesson 1.7)

A design company wants to determine the best material to use for metal piping. They know that metals are corroded when they react with oxygen and water and therefore want to use a material that is corrosion resistant.

The materials tested ranged from the cheapest mild steel to the most expensive coated stainless steel. To measure the corrosion, a sample of each material was placed in aerated water for up to 30 days with the mass loss of each material recorded every week (Table 1). Each sample had the same mass and surface area.

TABLE 1 Corrosion data for various materials

Metal	Mass loss (g) on			
	Day 7	Day 14	Day 21	Day 30
Mild steel	0.0114	0.0146	0.0152	0.0185
Coated mild steel	0.0008	0.0010	0.0013	0.0018
Aluminium	0.0018	0.0022	0.0025	0.0028
Coated aluminium	0.0008	0.0010	0.0013	0.0018
Copper	0.0210	0.0420	0.0630	0.1260
Coated copper	0.0126	0.0252	0.0378	0.0756
Stainless steel	0.0001	0.0001	0.0001	0.0001
Coated stainless steel	0.0000	0.0000	0.0000	0.0001

Practise your skills

1 **Identify** the dependent and independent variables. (2 marks)
2 Using the variables, **identify** two trends in the data. (2 marks)
3 Consider copper and aluminium.
  a **Explain** whether these metals will undergo oxidation or reduction when they corrode. (2 marks)
  b **Determine** which is more reactive. **Justify** your reasoning using the data. (2 marks)

Check your learning 6.1

Check your learning 6.1: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain** the processes of reduction and oxidation. How are they related? (2 marks)

2 **Describe** what happens to the valence shell electrons during redox reactions. (2 marks)

Analytical processes

3 Use your knowledge of valence shell diagrams to **demonstrate** the transfer of electrons between the following pairs of atoms. (2 marks each)

  a Lithium metal (Li) and sulfur (S)
  b Magnesium metal (Mg) and fluorine (F)
  c Aluminium metal (Al) and oxygen (O)

  For each of **a**, **b** and **c**, **determine**

    i which atom is oxidised and which atom is reduced (1 mark each)
    ii the reducing and oxidising agent (1 mark each)
    iii the product of the reaction. (1 mark each)

4 **Determine** the oxidised and reduced species in the following reactions. (2 marks each)

  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 $2AgNO_3(aq) + Pb \rightarrow Pb(NO_3)_2(aq) + 2Ag(s)$

Knowledge utilisation

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. (4 marks)

Using this information, **devise** a more accurate definition for oxidation and reduction. (2 marks)

6 Your teacher claimed that the corrosion of a metal can sometimes be beneficial but did not explain why. Your friend was absent from this Chemistry lesson and asks you to explain this concept to them. **Investigate** a circumstance where this is true, and **construct** an answer that you would give to your friend. (2 marks)

Lesson 6.2
Oxidation numbers

Key ideas

→ 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, then reduction has occurred.

→ If the oxidation number increases, then oxidation has occurred.

→ The oxidation states of transition metals are represented by capital Roman numerals after the element's name or symbol, e.g. chromium(III), Cr(III).

How do we identify the chemical species that undergo oxidation and reduction?

Often, redox reactions are complex, and their **overall equations** involve 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 the reaction has occured.

Learning intentions and success criteria

overall equation
a reaction that combines the two half-equations after electrons have been balanced and cancelled out

oxidation state
oxidation number

How are oxidation numbers assigned?

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
1	Elements have an oxidation number of 0.	O_2, O_3, F_2, He, Fe, Zn, Li, C_{60}
2	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 peroxides, e.g. H_2O_2, where it is –1, and F_2O, where it is +2 due to the partial transfer of electrons to F).
3	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. Cl^- has an oxidation number of –1.
4	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.

Study tip

Oxidation numbers must always be written as a positive or negative number; for example, the sodium ion has an oxidation state of +1, not 1 or +. The sign comes before the number to distinguish it from ionic charge.

Rule	Examples
5 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 × O) = –3. Oxygen is –2 and 4 × –2 = –8. P + –8 = –3, so phosphorus has an oxidation number of +5.
6 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 × –2 = –2. The sum of the oxidation numbers is 0, so nitrogen has an oxidation number of +4.

Oxidation and reduction using oxidation numbers

oxidation number the number of electrons gained or lost by an atom, relative to the element

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 other words, during a reduction reaction, 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 the oxidation number. In other words, during an oxidation reaction, 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

Determining oxidation numbers using rule 1

Determine the oxidation state of chlorine gas (Cl_2). (1 mark)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Determine" means to conclude or ascertain after consideration. We need to apply the oxidation rules to make a conclusion regarding the oxidation number of Cl_2. This is worth 1 mark so you must state the answer.
Step 2: Apply oxidation number rules. Note: Reasoning does not have to be in written sentence form, unless asked.	**1** $Cl_2(g)$ is an uncharged molecule, because it is in its elemental form. **2** Therefore, the oxidation state of a chlorine atom is 0.
Step 3: State the final answer.	Cl has an oxidation state of 0. (1 mark)

Your turn

Determine the oxidation state of iron (Fe). (1 mark)

Worked example 6.2B

Determining oxidation numbers using rule 3

Determine the oxidation state of a magnesium ion. (1 mark)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Determine" means to conclude or ascertain after consideration. We need to apply the oxidation rules to make a conclusion about the oxidation number of Mg. This is worth 1 mark so you must state the answer.

Think	Do
Step 2: Apply oxidation number rules.	**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.
Step 3: State the final answer.	Mg has an oxidation state of +2. (1 mark)

Your turn

Determine the oxidation state of an oxygen (oxide) ion. (1 mark)

Worked example 6.2C

Determining oxidation numbers using rules 2 and 4 combined

Determine the oxidation state of all the elements in an ammonia molecule (NH_3). (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Determine" means to conclude or ascertain after consideration. We need to apply the oxidation rules to determine the oxidation numbers of H and N in NH_3. This is worth 2 marks because there are two elements to determine oxidation number.
Step 2: Apply oxidation number rules. Rule 2 is used for hydrogen. Rule 4 is used for nitrogen.	Oxidation state (H^+) = +1 (rule 2) For NH_3, the total of the oxidation numbers is 0 (rule 4) $(N) + 3 \times (+1)=0$ Solving: $(N) = -3$
Step 3: State the final answer.	H has an oxidation state of +1. (1 mark) N has an oxidation state of –3. (1 mark)

Your turn

Determine the oxidation state of all the elements in carbon dioxide (CO_2). (2 marks)

What are the oxidation states of transition metals?

Some metals, particularly transition metals and some non-metallic elements in polyatomic ions and molecules, can have multiple oxidation states. When determining oxidation numbers, if there is no rule for an atom, then its oxidation number must be determined by using other atoms in the chemical species.

Oxidation states of transition metals are indicated by capital Roman numerals in parentheses after the atom. For example, manganese +7 is written manganese(VII) (or Mn(VII)). Roman numerals are also used in the name of a molecule to identify the oxidation state of the metal. Additionally, you may see the oxidation state written in superscript and roman numeral (e.g. Mn^{VII}).

For example:

- Copper has an oxidation state of +1 or +2 (rarely +3) in compounds. Therefore, it is Cu(I) or Cu(II). When naming copper in "copper sulfate", it is either copper(I) sulfate (Cu_2SO_4) or copper(II) sulfate ($CuSO_4$). Including the oxidation state makes it clear which compound is being discussed.

Study tip

The terms "oxidation number" and "oxidation state" are interchangeable. They mean the same thing.

Study tip

Ions with a charge of 1− or 1+ are just written as − or + (e.g. Cl^- or K^+), but their oxidation states are written as −1 or +1 respectively.

- Iron usually has an oxidation state of +2 or +3 in compounds. Therefore, it is Fe(II) or Fe(III). When naming iron in "iron nitrate", it is either iron(II) nitrate ($Fe(NO_3)_2$) or iron(III) nitrate ($Fe(NO_3)_3$).

Worked example 6.2D shows how to determine the oxidation state of all the elements in a polyatomic ion.

Worked example 6.2D

Determining oxidation numbers using rule 5

Determine the oxidation states of all the elements in the

a dichromate ion ($Cr_2O_7^{2-}$) (2 marks)

b nitrate ion (NO_3^-). (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Determine" means to conclude or ascertain after consideration. We need to apply the oxidation rules to make a conclusion about the oxidation number of chromium and oxygen in $Cr_2O_7^{2-}$. Each part is worth 2 marks because there are two elements, so you must state the answer.
Step 2: Apply oxidation number rules for part **a**. Lengthy written explanations are not required for marks, although some working will avoid errors.	**a** 1 $Cr_2O_7^{2-}$ is an ion; therefore, the sum of all the oxidation numbers must be equal to its charge (−2) (rule 5). 2 The oxidation state of oxygen when in a compound is always −2 (unless in a peroxide) (rule 2); chromium is a transition metal and has multiple possible oxidation states. Therefore, determine the oxidation state of chromium. $(2 \times Cr) + (7 \times -2) = -2$ $(2 \times Cr) + (-14) = -2$ $(2 \times Cr) + (-14) + 14 = -2 + 14$ $2 \times Cr = +12$ $Cr = +6$ 3 Therefore, chromium has an oxidation state of +6. (Note: Because chromium is a transition metal, it can be identified as Cr(VI)).
Step 3: State the final answer for part **a**.	The oxidation number of oxygen is −2. (1 mark) The oxidation number of chromium is +6. (1 mark)
Step 4: Apply oxidation number rules for part **b**.	**b** 1 NO_3^- is an ion; therefore, the sum of all of the oxidation numbers must be equal to its charge (−1) (rule 5). 2 The oxidation state of oxygen in a compound is always −2 (unless in a peroxide) (rule 2). Nitrogen can have multiple potential oxidation states. Therefore, determine the oxidation state of nitrogen. $N + (3 \times -2) = -1$ $N + -6 = -1$ $N = +5$ 3 Therefore, nitrogen in the nitrate ion has an oxidation state of +5.
Step 5: Final answer for part **b**.	O has an oxidation state of −2. (1 mark) N has an oxidation state of +5. (1 mark)

Your turn

Determine the oxidation states of all the elements in the

a permanganate ion (MnO_4^-) (2 marks)

b ammonium ion (NH_4^+). (2 marks)

Challenge

Oxidation of alcohol

The alcohol ethanol undergoes oxidation by the permanganate ion in an acidic environment according to the equation:

$$3CH_3CH_2OH(aq) + 2MnO_4^-(aq) + 4H^+(aq) \rightarrow 3CH_3COOH(aq) + 2Mn^{2+}(aq) + 5H_2O(l)$$

Identify the species that is oxidised and the species that is reduced as well as the oxidising and reducing agents. (4 marks)

Real-world chemistry

Maria Skyllas-Kazacos – Australia's battery queen

Maria Skyllas-Kazacos, an accomplished Australian electrochemist and professor at the University of New South Wales, has gained international recognition for her groundbreaking work on the development of the vanadium redox flow battery. Her contributions have transformed energy storage technology, paving the way for renewable energy systems to become more practical and efficient.

A vanadium redox flow battery uses vanadium ions in different oxidation states (Figure 1) to store and release energy.

The battery consists of two electrolyte tanks containing solutions of vanadium-based electrolytes, which are pumped through an electrochemical cell stack during charge and discharge cycles (Figure 2).

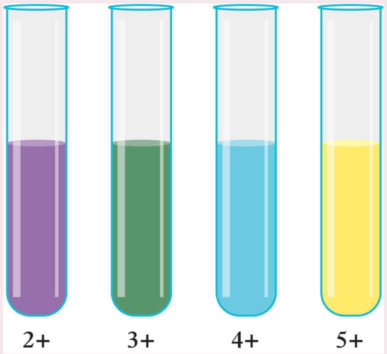


FIGURE 1 The various oxidation states of vanadium in solution

While generating electricity (discharge), one tank converts VO_2^+ into VO^{2+} while the other converts V^{2+} into V^{3+}. One loses electrons while the other gains them, producing an electrical current that is essential for the battery.

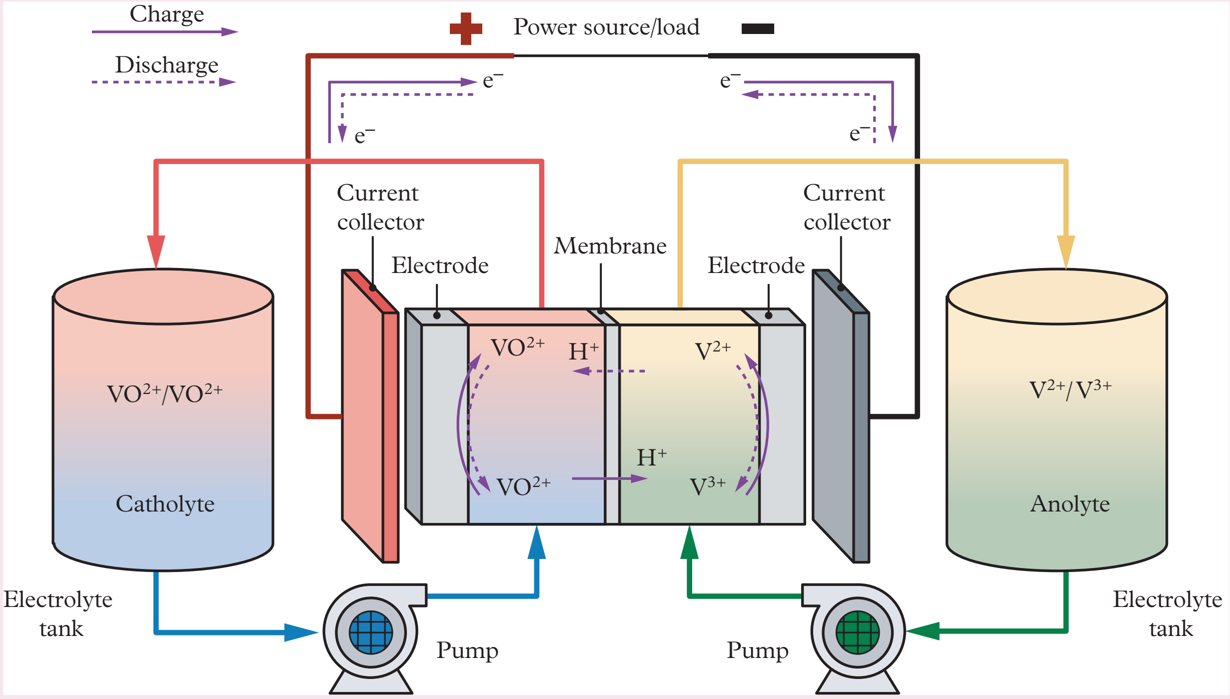


FIGURE 2 The vanadium redox flow battery

The vanadium redox flow battery has several advantages over traditional batteries:

1 Scalability: The energy storage capacity can be increased by simply enlarging the electrolyte tanks.
2 Longevity: Unlike lithium-ion batteries, the vanadium redox flow battery can operate for decades with minimal degradation.
3 Safety: The aqueous electrolyte is non-flammable, reducing the risk of fire.
4 Sustainability: Vanadium is recyclable, making the system environmentally friendly.

Apply your understanding

1 **Calculate** the oxidation state of vanadium in VO^{2+}. (1 mark)
2 **Calculate** the oxidation state of vanadium in VO_2^+. (1 mark)
3 In the VO_2^+/VO^{2+} tank, VO_2^+ is converted into VO^{2+} when the battery generates electricity. **Justify** whether this is an oxidation or reduction process using the oxidation numbers from questions **1** and **2**. (2 marks)

Check your learning 6.2

Check your learning 6.2: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Define** "oxidation state". (1 mark)
2 **Explain** what happens to oxidation numbers in reduction reactions. (1 mark)

Analytical processes

3 **Determine** the oxidation numbers of each of the atoms in the following chemical substances.
  a O_2 (1 mark)
  b NO_2 (2 marks)
  c SO_4^{2-} (2 marks)
  d CH_3COO^- (3 marks)
  e NaOH (3 marks)
  f H_2O_2 (2 marks)
  g NaH (2 marks)
  h PO_4^{3-} (2 marks)

Knowledge utilisation

4 **Determine** the oxidised and reduced atoms in the following equations. Use their oxidation numbers to **justify** your answers.
  a $2Fe(OH)_3(aq) + 3OCl^-(aq) \rightarrow 2FeO_4^{2-}(aq) + 3Cl^-(aq) + H_2O(l) + 4H^+(aq)$ (3 marks)
  b $Fe^{2+}(aq) + 6H^+(aq) + VO_4^{3-} \rightarrow Fe^{3+}(aq) + VO^{2+}(aq) + 3H_2O(l)$ (3 marks)
  c $2Cr_2O_7^{2-}(aq) + 16H^+(aq) + C_2H_5OH(l) \rightarrow 4Cr^{3+}(aq) + 2CO_2(g) + 11H_2O(l)$ (3 marks)
5 **Investigate** steel and stainless steel and **determine**
  a what both materials are made of (2 marks)
  b what the materials are used for (2 marks)
  c whether the materials corrode; **justify** your answer with a chemical equation or an explanation (2 marks)
  d what the advantages and disadvantages are of using both materials. (4 marks)
6 **Investigate** the first row of the transition metals in the periodic table. **Identify** which of these transition metals have multiple oxidation states apart from their neutral metallic form. Which of these metals has the most oxidation states? (3 marks)

Lesson 6.3

Half-equations and overall redox equations

Key ideas

→ 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.

→ Balanced complex oxidation and reduction half-equations and complex overall redox equations can be written for reactions occurring in acidic conditions.

→ 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.

How do we construct redox reaction equations?

Redox equations can become complicated due to the number of chemical species involved. For this reason, they are balanced in **half-equations**, where the oxidation equation is represented as one half-equation and the reduction equation is represented as the second half-equation. These equations are then combined to form an **overall redox equation**.

These equations show the chemical species that participate in the redox reaction. All other species act as **spectator ions**, which do not participate in the electron transfer and are therefore not included.

Learning intentions and success criteria

half-equation
an equation that represents either an oxidation or a reduction half of a chemical equation; it includes electrons to demonstrate electron transfer

overall redox equation
an equation found by balancing electrons in both half-equations, cancelling the electrons, and adding the half-equations together

spectator ion
any ion in a reaction mixture that does not take part in the reaction; they are omitted from the half-equations and overall equation, e.g. when $KMnO_4$ is used, K^+ is a spectator ion and MnO_4^- is the ion that reacts

How are half-equations constructed?

Every redox reaction is made up of two half-reactions. The oxidation half-equation shows an atom losing electrons and the electrons are on the product side. The reduction half-equation shows an atom gaining electrons and the electrons appear on the reactant side. To properly balance overall redox equations (which you will look at later), it is essential to represent the electrons in the half-equations.

Simple half-equations

Simple half-equations are straightforward to balance. Each half-equation shows the conjugate redox pair and the electrons being transferred. Let's look at the reaction between the copper ions in a solution of copper(II) sulfate and zinc metal, with oxidation numbers assigned.

$$\overset{+2}{Cu^{2+}}(aq) + \overset{0}{Zn}(s) \rightarrow \overset{0}{Cu}(s) + \overset{+2}{Zn^{2+}}(aq)$$

Copper ions are reduced because their oxidation number has decreased. $Cu^{2+}(aq)$ gains two electrons to become Cu(s). The electrons are shown on the left-hand side of the reaction arrow to balance the 2+ charge. Half-reactions will have an equal charge on both sides of the half-reaction. Therefore, the half-equation is:

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

Zinc is oxidised because its oxidation number has increased. Zn(s) loses two electrons to become Zn^{2+}(aq). The electrons are shown on the right side of the reaction arrow to balance the 2+ charge. Therefore, the half-equation is:

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

Sulfate is a spectator ion because its ionic charge and state are the same on both sides of the equation. Therefore, it is excluded from the half-equations and from the overall redox equation.

Study tip

When electrons are on the left of the reaction arrow in a half-equation, the chemical species is gaining electrons and undergoing reduction.

When electrons are on the right of the reaction arrow in a half-equation, the chemical species is losing electrons and undergoing oxidation.

Study tip

Remember to include states for all species in a redox equation (e.g. (g), (l), (aq)), except for electrons, which do not have a state. The electrons are shown as separate particles in half-equations, but in reality they transfer from one chemical species to another.

Study tip

Pay attention to the states in the overall reaction equations. These will determine the states in the half-equations.

Worked example 6.3A

Half-equations and overall equations

Identify and write the oxidation and reduction half-equations in the following reaction. (2 marks)

$$2Ag(s) + Br_2(g) \rightarrow 2AgBr(s)$$

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	“Identify” means to recognise. Although “write” is not a cognitive verb it is often used in chemistry as we need to write chemical equations. These must be balanced and include states. Each half-equation is worth 1 mark.
Step 2: Assign oxidation numbers to identify the species that have been oxidised and reduced.	$2\overset{0}{Ag}(s) + \overset{0}{Br_2}(g) \rightarrow 2\overset{+1}{Ag}\overset{-1}{Br}(s)$ Ag(s) has been oxidised because its oxidation number has increased from 0 to +1. Therefore, it has lost an electron, and e^- must be on the product side of the half-equation. Br_2(g) has reduced because the oxidation number has decreased from 0 to –1. Therefore, it has gained an electron, and e^- must be on the reactant side of the half-equation.
Step 3: Write the oxidation and reduction half-equations to show the transfer of electrons.	Oxidation: $Ag(s) \rightarrow Ag^+(s) + e^-$ (1 mark) Reduction: $Br_2(g) + 2e^- \rightarrow 2Br^-(s)$ (1 mark)

Your turn

Identify and write the oxidation and reduction half-equations in the following reaction. (2 marks)

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

How are complex half-equations constructed?

Often, redox half-equations cannot be balanced by simply adding electrons. In the case of more complex half-equations, where hydrogen or oxygen is included, the balancing of equations follows the KOHES method. Complex redox reactions occur in acidic or basic conditions.

In acidic conditions, the following steps are used (see Worked example 6.3B):

1 K – Balance the **key** elements (everything except oxygen and hydrogen).
2 O – Balance **oxygen** by adding $H_2O(l)$ molecules to the opposite side. Each water molecule contains one oxygen atom.
3 H – Balance **hydrogen** by adding $H^+(aq)$ ions to the opposite side.
4 E – Balance the charge by adding **electrons** to one side.
5 S – Assign **states** to all reactants and products except electrons, which have no state.

Worked example 6.3B

Writing complex half-equations in acidic conditions

Complete the half-equation for permanganate ion (MnO_4^-) forming manganese ion (Mn^{2+}) in acidic conditions and **deduce** whether this is an oxidation or reduction half-equation. (2 marks)

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$$

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Deduce" means to reach a conclusion. In this question you must finish the half-equation by using the KOHES steps. These half-equations are worth 2 marks. 1 mark is assigned for correct chemicals and states; 1 mark is assigned for balancing and correct electrons.
Step 2: Balance the **key** elements.	There is one manganese atom on the left and one on the right. Key elements are already balanced. $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$
Step 3: Balance the **oxygen** by adding H_2O molecules to the opposite side.	There are four oxygen atoms on the left, so we add four H_2O molecules to the right-hand side. $MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O$
Step 4: Balance the **hydrogen** by adding H^+ ions to the opposite side.	There are eight hydrogen atoms on the right, so we add eight H^+ ions to the left-hand side. $MnO_4^-(aq) + 8H^+ \rightarrow Mn^{2+}(aq) + 4H_2O$
Step 5: Balance the charge by adding **electrons** to one side. Note: All of these steps are performed on a single copy of the half-equation, just adding to it as you go. Do not keep rewriting it each time you make a change.	The total charge on the left is –1 (for MnO_4^-) plus +8 (for $8H^+$), which equals +7. The total charge on the right is +2 (for Mn^{2+}) plus 0 (for H_2O), which equals +2. We need $5e^-$ on the left, since 7 – 5 = +2. $MnO_4^-(aq) + 8H^+ + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$ (1 mark)
Step 6: Add **states** to all reactants and products except electrons, which have no state.	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
Step 7: Identify whether the reaction is oxidation or reduction.	Electrons are gained, so this is a reduction half-equation. (1 mark)

Your turn

Complete the half-equation for ethanol (CH_3CH_2OH) forming ethanoic acid (CH_3COOH) in acidic conditions and **deduce** whether this is an oxidation or reduction half-equation. (2 marks)

$$CH_3CH_2OH(aq) \rightarrow CH_3COOH(aq)$$

Study tip

You can look at either the change in oxidation number or the side of the half-equation that the electrons are on, to determine whether it is an oxidation or reduction half-equation.

Study tip

For half-equations to be combined, they must both have the same number of electrons. If the electrons are not balanced, look for the lowest common multiple between the coefficients of the reduction and oxidation half-equations to determine the value that the half-equations must be multiplied by.

How do you construct overall redox equations?

When you have identified the oxidation and reduction half-equations, they can be combined 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. You can see this in Worked example 6.3C.

Worked example 6.3C

Combining half-equations into overall redox reactions

Consider the following reaction:

$$Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$$

a **Identify** and **construct** the oxidation and reduction half-equations. (2 marks)

b **Construct** the overall ionic redox equation. (1 mark)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	“Identify” means to recognise and name. “Construct” means to display information in a diagrammatical or logical form. These chemical equations must be balanced and include states. Each half-equation/equation is worth 1 mark.
Step 2: Assign oxidation numbers to identify the species that have been oxidised and reduced.	$\overset{0}{Fe}(s) + 2\overset{+1\,-1}{HCl}(aq) \rightarrow \overset{+2\,-1}{FeCl_2}(aq) + \overset{0}{H_2}(g)$ Fe(s) has been oxidised because the oxidation number has increased from 0 to +2. H^+(aq) has been reduced because the oxidation number has decreased from +1 to 0. Chloride has had no change in the oxidation number, so it is a spectator ion.
Step 3: For part **a**, write the oxidation and reduction half-equations to show the transfer of electrons.	**a** Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ Reduction: $2H^+(aq) + 2e^- \rightarrow H_2(g)$ (1 mark each)
Step 4: Make sure there is the same number of electrons in both half-equations – if not, multiply the whole half-equation(s) to make them equal.	There are 2 electrons in both half-equations, so they do not need to be multiplied.
Step 5: For part **b**, combine the half-equations to form an overall redox equation.	**b** Cancel out the electrons. $Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$ (1 mark)

Your turn

Consider the following unbalanced reaction:

$$Fe(s) + O_2(g) \rightarrow Fe_2O_3(s)$$

a **Identify** and **construct** the oxidation and reduction half-equations. (2 marks)

b **Construct** the overall ionic redox equation. (1 mark)

Real-world chemistry

Breathalysers

In Australia, 30% of road fatalities are connected to alcohol consumption and blood alcohol concentration (BAC). BAC is the percentage of alcohol in your blood, ranging from 0% to 0.4%, which is potentially fatal.

Breathalysers for use in random breath tests were introduced in Queensland in 1982 and formally commenced in 1988 (Figure 1). This immediately reduced the number of fatalities. Historically, the Drunkometer, Intoximeter and Alcometer used solutions of iodine, acidified permanganate or acidified dichromate. In these cells the following half-equations occur:

Reduction:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

purple colourless

$$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$$

colourless–white blue (in the presence of starch indicator)

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

yellow–orange green

Ethanol in the breath sample is oxidised to form ethanoic acid according to the following half-equation:

$$CH_3CH_2OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$$

All three cells rely on colour-based indicators and are therefore qualitative tests. As an alternative, a fuel cell was developed, where the half-equations involve the transfer of electrons, resulting in the production of an electrical current. This current can be measured and used to determine the concentration of ethanol in the breath and therefore the blood.

Atmospheric oxygen is reduced under acidic conditions to form water:

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

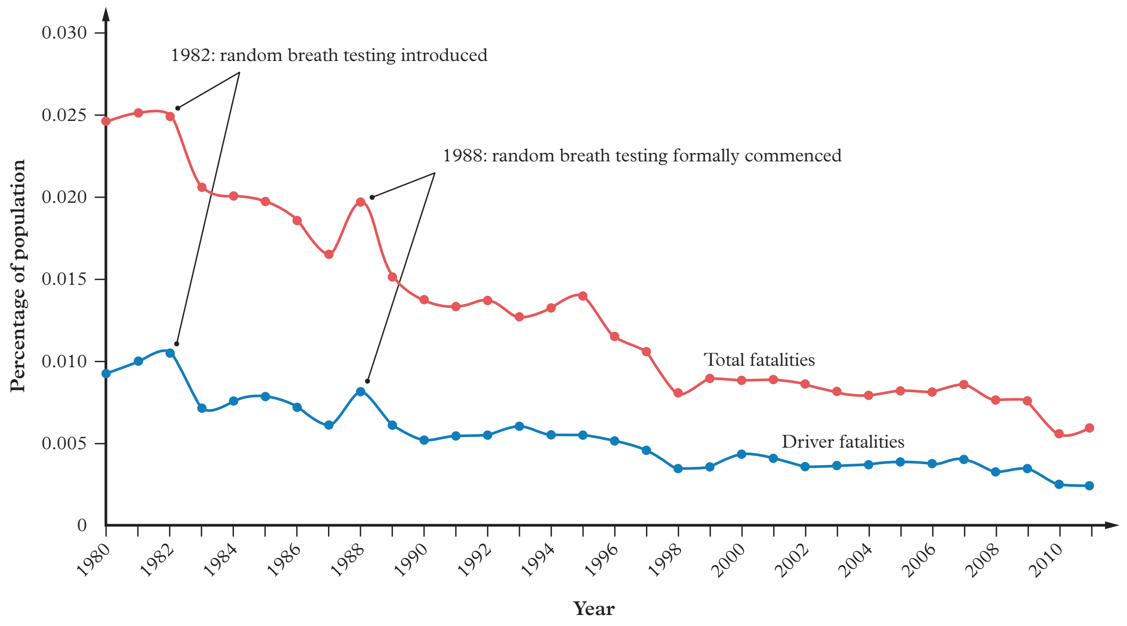


FIGURE 1 Queensland road fatalities as a percentage of the population each year between 1980 and 2011

Apply your understanding

1 **Construct** the overall reaction equations for the Drunkometer, Intoximeter and Alcometer. (3 marks)
2 In the three reactions you developed in question **1**, **identify** the oxidant and reductant. (3 marks)
3 **Apply** your understanding of spectroscopy to **determine** why a permanganate and a dichromate breathalyser must be frequently calibrated. (2 marks)

Skill drill

Analysing qualitative data

Science inquiry skill: Processing and analysing data (Lesson 1.7)

A student conducts an experiment using five different metals and five 0.10 M solutions of metal salts of the same five metals. Samples of each metal were placed in test tubes of each of the five solutions. Observations were made for a time and recorded in Table 1.

TABLE 1 Observations when metals were placed in solutions of metal salts

Solution	Metal				
	Cu	Sn	Ag	Zn	Mg
$Cu(NO_3)_2$	No reaction	Dark deposit on metal and solution turns cloudy	No reaction	Dark deposit on metal and blue colour of solution lightens	Dark deposit on metal and blue colour of solution lightens
$SnCl_2$	No reaction	No reaction	No reaction	Dark deposit on metal	Dark deposit on metal
$AgNO_3$	Deposit on metal and solution turns blue	Deposit on metal and solution turns black	No reaction	Dark deposit on metal	Dark deposit on metal
$ZnSO_4$	No reaction	No reaction	No reaction	No reaction	Dark deposit on metal
$Mg(NO_3)_2$	No reaction	No reaction	No reaction	No reaction	No reaction

Practise your skills

1 Use the data to **justify** which of the metals is the most reactive. (2 marks)
2 Use the data to **justify** which of the metals is the least reactive. (2 marks)
3 **Explain** why the copper nitrate solution colour lightens after reacting with Zn or Mg. (2 marks)
4 Rank the metals and metal ions from most to least reactive. **Identify** the relationship/trend in the data. (3 marks)

Check your learning 6.3

Check your learning 6.3: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** what all oxidation half-equations have in common. (1 mark)

2 **Describe** what all reduction half-equations have in common. (1 mark)

3 **Explain** why overall redox equations must have the same number of electrons on the reactant and product sides. (1 mark)

4 **Construct** the half-equations and overall ionic equations for the following unbalanced reactions. **Identify** the half-equations as reduction or oxidation.

- **a** $Fe(s) + Cl_2(g) \rightarrow FeCl_3(s)$ (4 marks)
- **b** $S(s) + F_2(g) \rightarrow SF_6(g)$ (4 marks)
- **c** $N_2(g) + Cl_2(g) \rightarrow N_2Cl_4(g)$ (4 marks)
- **d** $NO(g) + O_2(g) \rightarrow NO_2(g)$ (4 marks)
- **e** $Cu(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + NO_2(g)$ (acidic solution) (4 marks)
- **f** $Al(s) + Pb^{2+}(aq) \rightarrow Al^{3+}(aq) + Pb(s)$ (4 marks)
- **g** $Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$ (acidic solution) (4 marks)

5 **Identify** the oxidants and reductants in the reaction equations developed in question **4**. (4 marks)

Knowledge utilisation

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. (3 marks)

7 In an experiment, copper metal was placed in a solution of silver nitrate. A silver metal and a blue solution of copper(II) nitrate were formed. **Analyse** this result and **determine** the oxidation and reduction half-equations as well as the balanced overall equation. (5 marks)

8 In an experiment, a purple solution of potassium permanganate is added to a pale green solution of iron(II) chloride. The purple and the pale green colours disappear and the solution develops a reddish-brown colour like rust. **Analyse** these results and **determine** the oxidation and reduction half-equations as well as the balanced overall equation. (5 marks)

Practical

Lesson 6.4

Performing single displacement reactions

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

MODULE 6

Lesson 6.5
Review: Redox reactions

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 the reduction of the other reactant and so is called the reductant.
- The reactant that takes one or more electrons causes the oxidation of the other reactant and so is called the oxidant.
- Single displacement reactions, 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, 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.
- Balanced complex oxidation and reduction half-equations and complex overall redox equations are written for reactions occurring in acidic conditions.
- 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
- Practical: Performing single displacement reactions

Key formulas

Combustion of metal to form a metal oxide	metal + oxygen → metal + oxide

Review questions 6.5A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

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 Br_2 is oxidised; Au is reduced.

B Au is oxidised; Br_2 is reduced.

C Br^{-} is oxidised; Au^{3+} is reduced.

D Au^{3+} is oxidised; Br^{-} is reduced.

2 In this reaction

A Br_2 is the oxidant; Au is the reductant.

B Au is the oxidant; Br_2 is the reductant.

C Au^{3+} is the oxidant; Br^- is the reductant.

D Br^- is the oxidant; Au^{3+} is the reductant.

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 S in H_2S is oxidised; Te is reduced.

B Te is oxidised; S in H_2S is reduced.

C Te in H_2Te is oxidised; S is reduced.

D S is oxidised; Te in H_2Te is reduced.

4 In this reaction

A S is the oxidant; H_2Te is the reductant.

B Te is the oxidant; H_2S is the reductant.

C H_2S is the oxidant; Te is the reductant.

D H_2Te is the oxidant; Se 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 +5

B +6

C +10

D +3.5

7 Identify the oxidation half-equation.

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

B $2Ag(s) + S^{2-}(aq) \rightarrow Ag_2S(s) + 2e^-$

C $AuCl_4^-(aq) + 3e^- \rightarrow Au(s) + 4Cl^-(aq)$

D $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$

8 Identify the reduction half-equation.

A $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

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

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

D $Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^-(aq) + 8H^+(aq) + 5e^-$

9 Reduction means there is

A a negative charge.

B a loss of electrons.

C a gain of electrons.

D an electron in the outermost shell of an atom.

10 For monatomic ions, the oxidation number is

A always +1.

B always neutral.

C always negative.

D the same as the charge on the ion.

Review questions 6.5B Short response

Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

11 Describe why a reducing agent is different from reduction. (2 marks)

12 Explain why corrosion is an example of oxidation. (2 marks)

13 Construct the Bohr electron configuration of Ca(g) + Cl(g). Show the electron transfer between the reactants when they form products $CaCl_2$. (3 marks)

14 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 ________________.” (1 mark)

15 Define “ionisation energy”. (1 mark)

16 Describe how the position of elements on the periodic table affects their ability to gain or lose electrons. (2 marks)

17 Explain the terms “oxidising agent” and “reducing agent”. How would you use them to describe redox reactions? (3 marks)

18 **Describe** what is common to breathalyser redox reactions. Why does this commonality exist? (2 marks)

19 A student placed a piece of iron metal into a solution of lead(II) nitrate and a redox reaction occurred.

- **a** **Construct** two half-equations to demonstrate the oxidation and reduction processes. (2 marks)
- **b** **Construct** a balanced overall equation to represent the chemical reaction. (1 mark)
- **c** **Describe** the observations expected over time. (3 marks)

20 A piece of solid magnesium was placed in a solution of blue copper(II) sulfate. Over time, the solution became paler in colour and a reddish precipitate formed. **Construct** two half-equations to demonstrate the oxidation and reduction processes. **Construct** a balanced overall equation to represent the chemical reaction. (3 marks)

Analytical processes

21 **Distinguish** between the charge of a polyatomic ion and an oxidation state of the elements in that ion. (1 mark)

22 **Determine** the oxidation number of

- **a** nitrogen in NH_3 (1 mark)
- **b** silicon in $CaSiO_3$ (1 mark)
- **c** chromium in $BaCrO_4$ (1 mark)
- **d** vanadium in VO_2^+. (1 mark)

23 **Determine** the oxidation number of

- **a** cadmium in Br_2CdO_6 (1 mark)
- **b** thorium in ThO_2 (1 mark)
- **c** manganese in $MnCO_3$ (1 mark)
- **d** zinc in $Zn(OH)_2$. (1 mark)

24 **Determine** the oxidation number of iron in

- **a** Fe_2O_3 (1 mark)
- **b** FeO (1 mark)
- **c** Fe_2SiO_4 (1 mark)
- **d** Fe. (1 mark)

25 Compounds containing the copper(I) ion can undergo both oxidation and reduction in the same reaction in a process call disproportionation. **Deduce** why this is possible. (2 marks)

26 Consider the following unbalanced chemical equation.

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$$

- **a** **Identify** the oxidation numbers of all atoms. (3 marks)
- **b** **Determine** which chemical species has been oxidised and which has been reduced. (2 marks)
- **c** **Determine** which chemical species are the oxidising and reducing agents. (2 marks)
- **d** **Construct** the oxidation and reduction half-equations. (2 marks)
- **e** **Construct** the balanced overall redox reaction. (1 mark)

27 Consider the following unbalanced chemical equation.

$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$

- **a** **Identify** the oxidation numbers of all atoms. (3 marks)
- **b** **Determine** which chemical species has been oxidised and which has been reduced. (2 marks)
- **c** **Determine** which chemical species are the oxidising and reducing agents. (2 marks)
- **d** **Construct** the oxidation and reduction half-equations. (2 marks)
- **e** **Construct** the balanced overall redox reaction. (1 mark)

28 Consider the following unbalanced chemical equation.

$$Ag(s) + H_2S \rightarrow Ag_2S(g) + H_2(g)$$

- **a** **Identify** the oxidation numbers of all atoms. (3 marks)
- **b** **Determine** which chemical species has been oxidised and which has been reduced. (2 marks)
- **c** **Determine** which chemical species are the oxidising and reducing agents. (2 marks)
- **d** **Construct** the oxidation and reduction half-equations. (2 marks)
- **e** **Construct** the balanced overall redox reaction. (1 mark)

Knowledge utilisation

29 A student claimed that the best method to produce sodium hydroxide is the redox reaction 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** two half-equations to demonstrate the oxidation and reduction processes. (2 marks)

b **Construct** a balanced overall equation to represent the chemical reaction. (1 mark)

c **Evaluate** the student's claim and **discuss** the strengths and weaknesses of this reaction as a method of producing sodium hydroxide. (3 marks)

30 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 module. (3 marks)

31 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 learned in this module. (3 marks)

Data drill

Reading graphs and extrapolating data

Figure 1 shows the blood alcohol concentration (BAC) per number of drinks per hour for an Australian male who is 183 cm (6 feet) tall with an average mass of 86 kg (in 2011 and 2012).

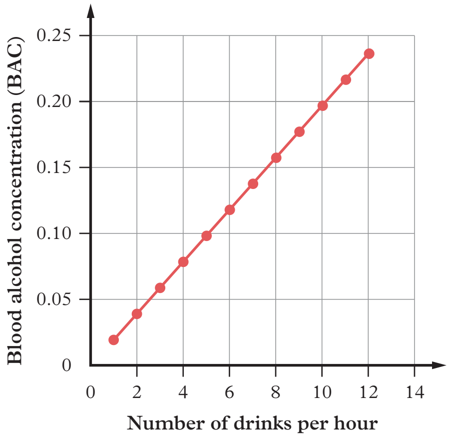


FIGURE 1 BAC per number of drinks for an Australian male with an average mass of 86 kg in 2011 and 2012

Apply understanding

1 **Identify** the independent variable. (1 mark)

2 **Identify** the dependent variable. (1 mark)

Analyse data

3 **Identify** the trend in the data. (2 marks)

4 **Identify** the number of drinks that the man could consume to be classified as over the legal limit. (1 mark)

Interpret evidence

5 **Predict** how different the graph would look for a person of the same height but lower mass. (2 marks)

6 **Predict** how the graph would look different for a person of the same height but greater mass. (2 marks)

Module 6 checklist: Redox reactions

MODULE 7

Galvanic cells

Introduction

Electrochemical cells (galvanic cells) are essential to modern life. They convert chemical potential energy into electrical energy. This technology has many applications but is mainly used in batteries.

The invention of batteries 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 1804–14) volunteered to act as his laboratory assistant.

Today, we use the ability to convert chemical to electrical energy in many ways. Any electrically powered portable device, from small electronics and appliances, to cars, buses and space shuttles, are powered by different versions of galvanic cells. On a small scale, dry cells and button cells make up a large portion of the battery market. The dry cell, a mainly solid battery, is used in the form of AA, AAA, C and D batteries, whereas the button cell is used in hearing aids and electronic car keys. On a large scale, recent advances in technology have been in the space of electric vehicles that are powered by rechargeable lithium batteries. Fuel cells are also being refined and improved for large-scale use in transportation, having been historically used in the Apollo space missions to power capsules and lunar modules.

Prior knowledge

Prior knowledge quiz

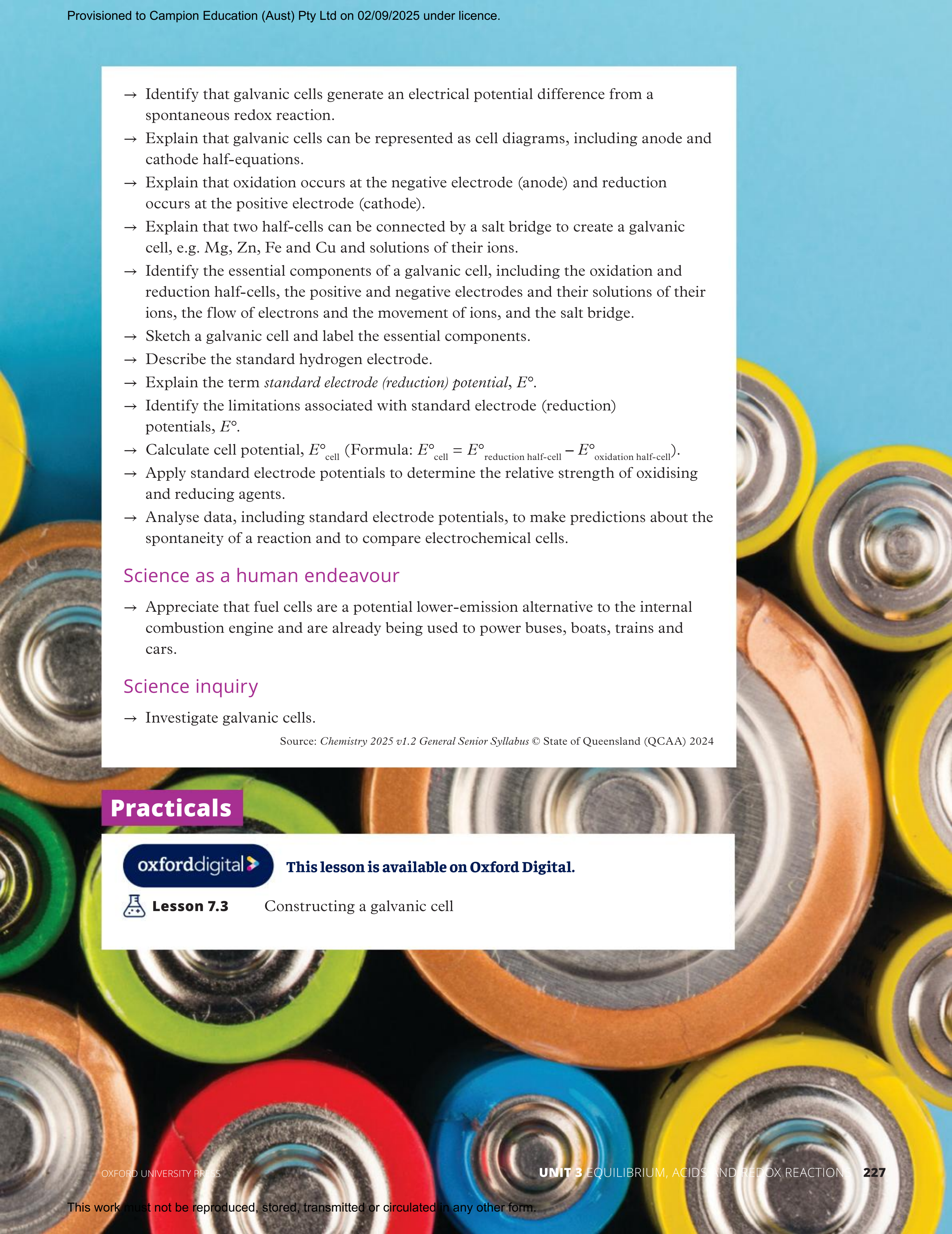
Check your understanding of concepts related to galvanic cells before you start.

Subject matter

Science understanding

→ Explain 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).

→ Discriminate between a galvanic and an electrolytic cell.



- → Identify that galvanic cells generate an electrical potential difference from a spontaneous redox reaction.
- → Explain that galvanic cells can be represented as cell diagrams, including anode and cathode half-equations.
- → Explain that oxidation occurs at the negative electrode (anode) and reduction occurs at the positive electrode (cathode).
- → Explain that two half-cells can be connected by a salt bridge to create a galvanic cell, e.g. Mg, Zn, Fe and Cu and solutions of their ions.
- → Identify 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.
- → Sketch a galvanic cell and label the essential components.
- → Describe the standard hydrogen electrode.
- → Explain the term *standard electrode (reduction) potential*, $E°$.
- → Identify the limitations associated with standard electrode (reduction) potentials, $E°$.
- → Calculate cell potential, $E°_{\text{cell}}$ (Formula: $E°_{\text{cell}} = E°_{\text{reduction half-cell}} - E°_{\text{oxidation half-cell}}$).
- → Apply standard electrode potentials to determine the relative strength of oxidising and reducing agents.
- → Analyse data, including standard electrode potentials, to make predictions about the spontaneity of a reaction and to compare electrochemical cells.

Science as a human endeavour

- → Appreciate that fuel cells are a potential lower-emission alternative to the internal combustion engine and are already being used to power buses, boats, trains and cars.

Science inquiry

- → Investigate galvanic cells.

Source: *Chemistry 2025 v1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

Practicals

oxforddigital **This lesson is available on Oxford Digital.**

Lesson 7.3 Constructing a galvanic cell

Lesson 7.1
Galvanic cells

Key ideas

→ A galvanic cell connects the reduction and oxidation half-reactions 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 contains an unreactive salt solution.

→ Negative ions from the salt bridge move towards the anode half-cell to balance the positive ions that move into the solution from the metal electrode as it undergoes oxidation.

→ Positive ions from the salt bridge move towards the positive cathode half-cell to replace the positive ions that plate as a metal onto the cathode as it undergoes reduction.

Learning intentions and success criteria

redox reaction
a reaction involving oxidation of one reactant and reduction of the other reactant

electrochemical series
a table of 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

electrochemical cell
a device that generates electrical energy from chemical reactions

galvanic cell
an electrochemical cell that converts chemical energy into electrical energy; the reduction and oxidation half-equations are separated and connected through a circuit to generate electricity

electrolytic cell
an electrochemical cell in which electricity is used to drive a non-spontaneous redox reaction

half-cell
half-of an electrochemical cell, where either oxidation or reduction occurs

How is electricity generated from redox reactions?

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**.

Electrochemical cells are devices which can generate chemical energy from electrical energy or electrical energy from chemical energy. There are many different configurations of electrochemical cells, but they are all examples of the two main types of cells:

- **galvanic cells** – which generate electrical energy from chemical energy
- **electrolytic cells** – which generate chemical energy from electrical energy.
  You will learn more about electrolytic cells in Module 8.

What is a galvanic cell?

Galvanic cells use a spontaneous redox reaction that produces thermal energy when reactants are in direct contact and produces electrical energy if they can be separated. For this reason, combustion and general exothermic reactions have the potential to generate electrical energy as they produce heat from their reactants. The half-equations are separated into different half-cells. One half-cell produces electrons and the other consumes them. By separating the half-cells, the reaction occurring in each cannot take place unless electrons are transferred between the two halves, when they are connected in an electric circuit.

What are 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 typically 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 1).

Half-cells are represented as the metal and the metal ion (Figure 2). A copper half-cell containing a solution of copper(II) sulfate and copper metal is represented as $Cu(s)|Cu^{2+}(aq)$. A single vertical line in the notation shows that the chemical species are in a different state.

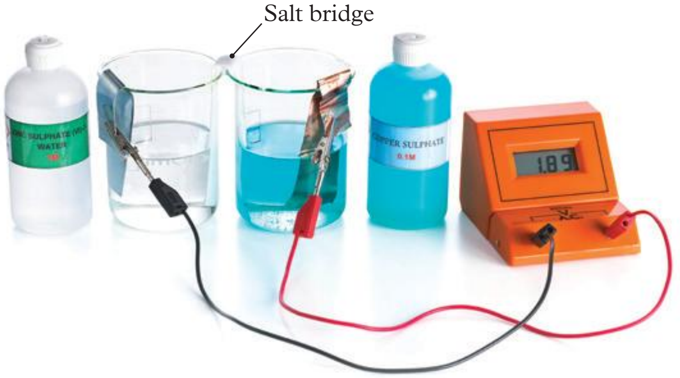


FIGURE 1 The experimental set-up of a galvanic cell

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 into products. For example, chlorine gas is converted into chloride ions. This does not require an electrode made of chlorine, but instead uses an **inert electrode**:

  $$Cl_2(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)$$

  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:

  $$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$$

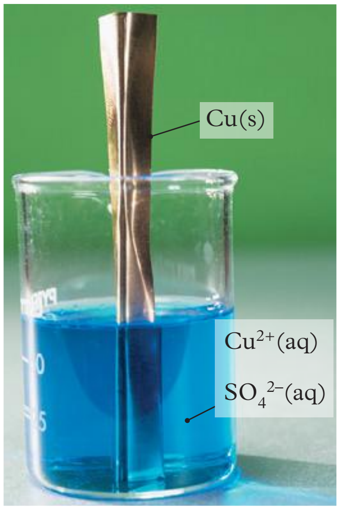


FIGURE 2 A copper half-cell containing copper metal (Cu(s)) and a solution of copper(II) sulfate ($Cu^{2+}(aq)$ and $SO_4^{2-}(aq)$). $SO_4^{2-}(aq)$ acts as a spectator ion.

  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 used when neither of the reactants can be used as an electrode, due to being in aqueous or gas form. They are typically made of platinum, mercury (in which case, the electrode is a liquid, rather than a solid) or carbon. If a half-cell contains an inert electrode such as platinum, the half-cell is represented as $Pt|Fe^{2+}(aq)\ Fe^{3+}(aq)$ with a comma separating the half-equation reactants and products as they are both in solution, or $Pt|Cl_2(g)|Cl^{-}(aq)$ with a vertical line separating the gas from the ions in solution because they are in different states. Any other ions in the solutions are spectator ions and do not react and so are not represented.

- The other half-cell reaction in a complete cell consumes electrons as the ions in the solution gain electrons from the electrode to form a metal. This is the reduction half-cell. If a metal is being produced, it 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 or a less reactive metal.

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

  As for the anode, an inert electrode is used for the cathode if the reactants are in solution or in gas form and neither are solid metals.

Study tip

Electrolytic cells are another example of electrochemical cells and are discussed in detail in Module 8.

electrode
a solid conductor of electricity either into or out of a half-cell

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

What occurs at the 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. **O**xidation **i**s the **l**oss of electrons (OIL) from a reactant. Thus, 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. **R**eduction **i**s the **g**ain of electrons (RIG) by a reactant. Thus, 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.

What are the roles of the external circuit and the salt bridge?

external circuit
the electric circuit (wires) that allow electrons to move 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, set to measure voltage), 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 or there is a potential difference between them due to different reactivities. A voltmeter measures this difference while drawing almost no current.

salt bridge
an electrical connection between the two half-cells of an electrochemical cell; it allows 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

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 breaks 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 3).
- 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 3).

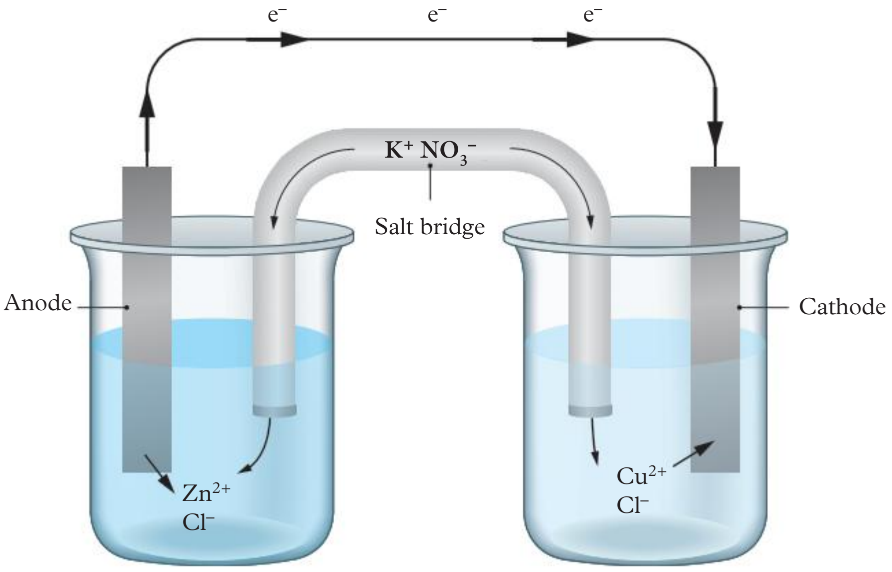


FIGURE 3 The flow of ions through the salt bridge in a galvanic cell. The potassium cations in the salt bridge migrate to the cathode to balance the charge lost when copper cations plate onto the cathode. The nitrate anions in the salt bridge migrate to the anode to balance the charge gained when the 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.

What are 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 movements labelled

Drawing cell diagrams

When drawing a galvanic cell, you must include all aspects of the cell. Consider the example of a redox reaction:

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

This has 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 from the chemical equation. Split the equation into its half-equations and assign oxidation numbers to determine which chemical species undergoes oxidation and which undergoes reduction.

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

You can draw several conclusions from this information.

1 The $Zn(s)|Zn^{2+}(aq)$ half-cell is the oxidation half-cell because electrons are lost and the oxidation number of zinc increases from 0 to +2.

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 because electrons are gained and the oxidation number of copper decreases from +2 to 0.

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.

The cell diagram that can be drawn from this reaction can be seen in Figure 4.

Worked example 7.1 shows you the steps involved in drawing a cell diagram.

The shorthand notation for the complete cell is:

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

In this notation, the anode is on the left, with a single vertical line separating it from the other species involved in the anode half-reaction. Two vertical lines are used to represent the salt bridge. Next are the other species in the cathode half-reaction, a single vertical line, and last, the cathode.

Study tip

Galvanic cells and electrolytic cells (Module 8) label the polarity of electrodes differently. In galvanic cells, the production of a current (electron flow) is what matters, so the anode, which produces electrons for the external circuit, is labelled as negative. Don't get confused.

Study tip

Negative anions from the salt bridge move to the negative anode. Positive cations from the salt bridge move to the positive cathode.

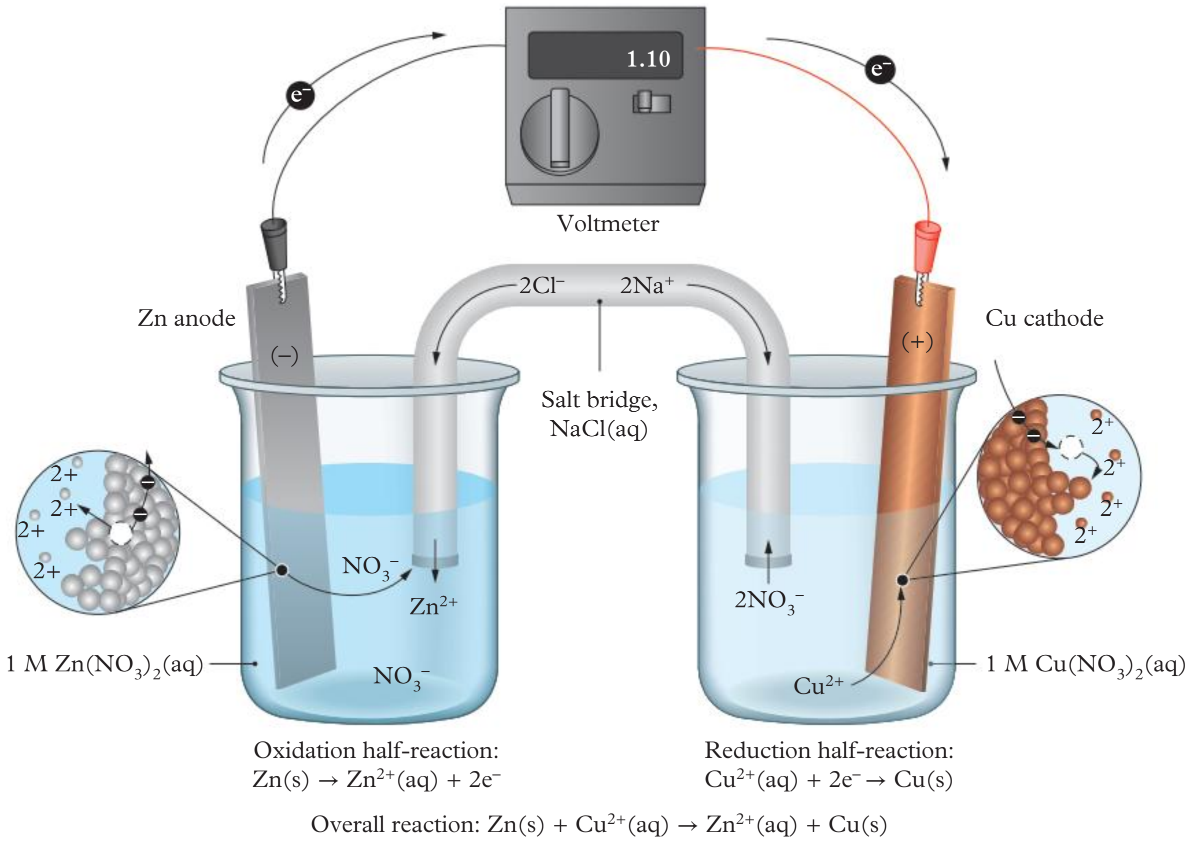


FIGURE 4 The cell diagram for the Cu^{2+} and Zn galvanic cell

Worked example 7.1

Constructing a cell diagram

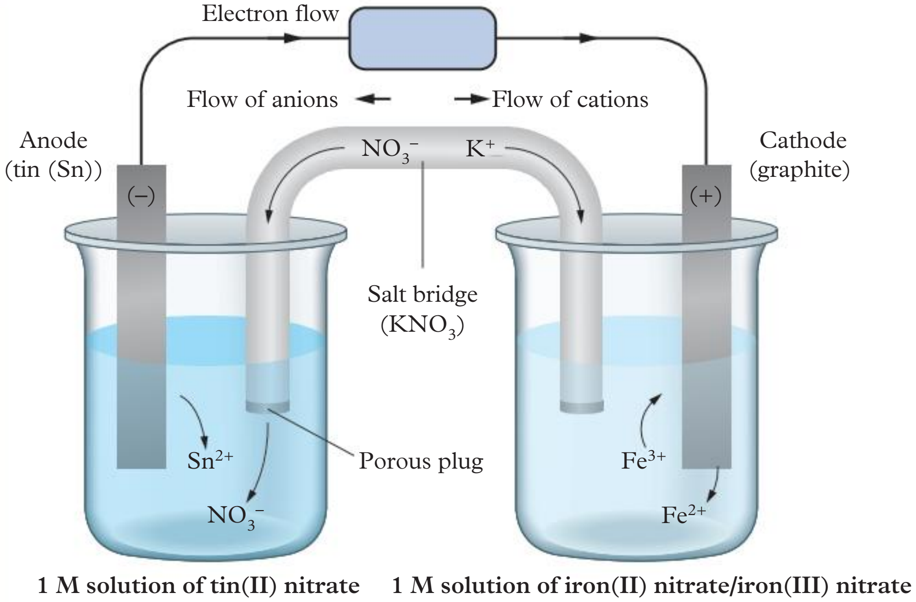
Construct a fully labelled galvanic cell that has the overall redox equation of

$$Sn(s) + 2Fe^{3+}(aq) \rightarrow Sn^{2+}(aq) + 2Fe^{2+}(aq)$$

Your cell diagram must show the

- reduction and oxidation half-equations (2 marks)
- anode and cathode, polarity of electrodes and material that each electrode is made of (1 mark)
- electron movement and a suitable salt bridge solution (1 mark)
- direction of ion movement in the salt bridge and in each half-cell. (1 mark)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Construct" means to display information in a diagrammatic or logical form. Always start any electrochemical cell question by finding the half-equations. Once found, every other part of the cell can be identified. Despite how much information is in the question, it would be worth a maximum of 5 marks.
Step 2: Find the half-equations.	$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$ $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ (The coefficient of 2 in front of both iron ions is not in the half-equations but exists as a result of combining the half-equations into an overall equation.)
Step 3: Assign terminology based on the half-equations.	Sn(s) undergoes oxidation at the anode, which must be made of Sn(s). $Fe^{3+}(aq)$ undergoes reduction to form $Fe^{2+}(aq)$ at the cathode, which will be inert (graphite/carbon or platinum) as both the reactant and product are in solution.

Think	Do
Step 4: Determine electron movement and a suitable salt bridge solution.	Electrons in the outside circuit move from the anode to cathode. The salt bridge solution cannot precipitate with the solutions; as ions of group 1 metals and nitrates are always soluble, $KNO_3(aq)$ is a suitable solution.
Step 5: Describe the direction of ion movement in the salt bridge and in each half-cell.	Salt bridge: $K^+(aq)$ moves to the $Fe^{3+}\|Fe^{2+}$ half-cell to replace the positive charge lost when Fe^{3+} forms Fe^{2+}. $NO_3^-(aq)$ moves to the $Sn\|Sn^{2+}$ half-cell to balance the positive charge gained as Sn forms Sn^{2+} ions. Half-cell: In the $Sn\|Sn^{2+}$ half-cell, Sn(s) loses electrons to form Sn^{2+} ions, which migrate away from the electrode. In the $Fe^{3+}\|Fe^{2+}$ half-cell, Fe^{3+} migrates towards the electrode to pick up an electron and form Fe^{2+}, which then moves away from the electrode.
Step 6: Draw the information as a fully labelled galvanic cell.	 Oxidation half-reaction: $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$ (1 mark) Reduction half-reaction: $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ (1 mark) The diagram shows the • anode and cathode correctly named, together with the substance used for each and the + and – correctly assigned (1 mark) • direction of electron flow from the anode to cathode through the wire and a suitable, non-precipitating solution in the salt bridge (1 mark) • direction of all ion movement shown – positive ions moving away from the anode, negative ions moving from the salt bridge to the anode half-cell, positive ions moving from the salt bridge to the cathode half-cell. At the cathode, the correct directions are shown for both types of iron ions. (1 mark)

Your turn

Construct a fully labelled galvanic cell that has the overall redox equation of

$$Mg(s) + 2Cr^{3+}(aq) \rightarrow Mg^{2+}(aq) + 2Cr^{2+}(aq)$$

Your cell diagram must show the

- reduction and oxidation half-equations (2 marks)
- anode and cathode, polarity of electrodes and material that each electrode is made of (1 mark)
- electron movement and a suitable salt bridge solution (1 mark)
- direction of ion movement in the salt bridge and in each half-cell. (1 mark)

Real-world chemistry

Fuel cells in space shuttles

A limitation of batteries is that, eventually, the voltage that they produce decreases, and their cells stop functioning as their reactants are consumed and cannot produce a flow of electrons.

Fuel cells are an alternative way of producing an electrical current. Fuel cells are galvanic cells that have a constant supply of reactants and inert electrodes that cannot break down. The reactants and products are usually gaseous, which prevents the build-up of solid products that may block the flow of charge through the cell. A fuel cell can produce a current for as long as it has reactants.

A common fuel cell is an alkaline fuel cell or a hydrogen–oxygen fuel cell (Figure 5). Its reactants are hydrogen and oxygen gas, and it contains a basic electrolyte in place of a salt bridge, often potassium hydroxide (KOH). The electrodes are constructed from porous carbon. The pores increase the surface area of the electrodes, thus increasing the amount of reactant that makes contact with the electrodes. This increases the energy efficiency of the cell.

The half-equations are:

Anode: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

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

Overall: $O_2(g) + 2H_2(g) \rightarrow 2H_2O(l)$

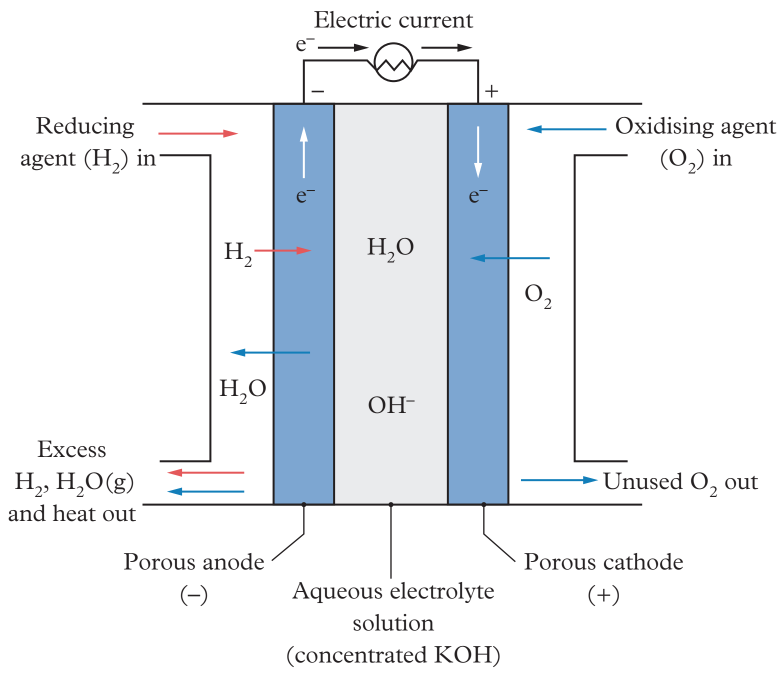


FIGURE 5 The set-up of an alkaline hydrogen–oxygen fuel cell

Alkaline fuel cells are 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 towards the shuttle's power systems.

The external tanks that launch a space shuttle into an orbit around Earth are filled with liquid hydrogen and liquid oxygen to keep the reactants separated in different half-cells or compartments (Figure 6). The hydrogen and oxygen react spontaneously, producing large quantities of heat energy in an exothermic reaction.

Approximately 8.5 minutes into launch, the fuel has 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.

FIGURE 6 The space shuttle attached to external fuel tanks

Apply your understanding

1 **Evaluate** the half- and overall reaction equation and **explain** why the alkaline fuel cell outlined above is considered carbon neutral. (2 marks)

2 **Explain** why the reactants must be kept separated and the consequences of having them come in contact. (2 marks)

3 **Justify** why a fuel cell is considered more energy efficient than a combustion reaction. (2 marks)

4 **Discuss** some of the ways that car manufacturers can overcome the design challenges in using a $H_2|O_2$ fuel cell. (3 marks)

Check your learning 7.1

Check your learning 7.1: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** how a galvanic cell can generate electricity. Refer to redox half-reactions and electron movement in your answer. (2 marks)

2 **Explain** the purpose of a salt bridge in a galvanic cell. (2 marks)

3 **Construct** a fully labelled galvanic cell with the following overall equations.

  a $Zn(s) + Mg^{2+}(aq) \rightarrow Zn^{2+}(aq) + Mg(s)$ (5 marks)

  b $2H^{+}(aq) + Co(s) \rightarrow H_2(g) + Co^{2+}(aq)$ (5 marks)

Analytical processes

4 **Determine** what material each electrode can be made of in a

  a zinc half-cell, where the electrode is the anode (1 mark)

  b copper half-cell, where the electrode is the cathode (1 mark)

  c half-cell containing a solution of HNO_3 in which the hydrogen ion undergoes reduction (1 mark)

  d half-cell in which hydrogen telluride (H_2Te) is bubbled through water to create an acidified solution. (1 mark)

Knowledge utilisation

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. (2 marks)

6 **Determine** why it is essential to separate a lithium/fluorine galvanic cell into two half-cells. **Discuss** the consequences if the reactants were kept in the same beaker. (2 marks)

Lesson 7.2

Standard electrode potentials

Key ideas

→ The voltage generated by a galvanic cell can be determined by using the electrochemical series.

→ The oxidation half-potential $E°$ is subtracted from the reduction half-potential $E°$ to calculate the cell potential difference (also called the EMF or voltage).

→ The calculation of $E°_{cell}$ can be used to determine whether a redox reaction is spontaneous or non-spontaneous.

What is the electrochemical series?

Learning intentions and success criteria

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 doesn'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 table of standard electrode potentials (Table 1) (also see page 11, QCAA *Formula and data book*), which are measured using an ion concentration of 1 mol L^{-1}, a gas pressure of 100 kPa (1 atm) and a temperature of 298 K – together these are called standard conditions.

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.

The half-equations on the table of standard electrode potentials 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 for each half-reaction written as a reduction. All are measured under standard conditions. The version of this table used by QCAA lists substances with the greatest negative reduction potentials at the top, and those with the greatest positive potentials at the bottom. Some versions of this table are listed in the reverse order to this, but you are still able to find and use $E°$ values in the same way.

TABLE 1 The electrochemical series: table of standard electrode potentials for half-reactions of 1 M solutions at 25°C (298 K)

Oxidised species $\rightleftharpoons$ reduced species	$E°$ (V)
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	–3.04
$K^+(aq) + e^- \rightleftharpoons K(s)$	–2.94
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	–2.91
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	–2.87
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	–2.71
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	–2.36
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	–1.68
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	–1.18
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	–0.83
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	–0.44
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	–0.24
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	–0.14
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	–0.13
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+0.16
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons SO_2(aq) + 2H_2O(l)$	+0.16
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	+0.52
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e \rightleftharpoons Ag(s)$	+0.80
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.08
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.89

Study tip

A copy of the electrochemical series can be found in the QCAA *Formula and data book*.

Study tip

A copy of the periodic table can be found in the appendix.

How do we measure 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:

  $$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

  Therefore, the hydrogen ion is the strongest oxidant, and the reduction potential of the other reactant has a positive value and sign.

  Bubbles of hydrogen will be produced at one electrode. Furthermore, $[H^+]$ will decrease as H^+ ions are consumed in the reaction. The cell will become less acidic, which you can observe by an increase in pH.

- If the hydrogen half-cell converts hydrogen gas into hydrogen ions, then it is the oxidation half-equation:

$$H_2(g) \rightarrow 2H^+(aq) + 2e^-$$

Therefore, hydrogen gas is the strongest reductant, and the reduction potential of the other reactant has a negative value and sign.

Hydrogen gas will be consumed by one electrode, meaning that the gas must be in contact with the electrode. Furthermore, $[H^+]$ will increase as H^+ ions are produced. The cell will become more acidic, which you can observe owing to a decrease in pH.

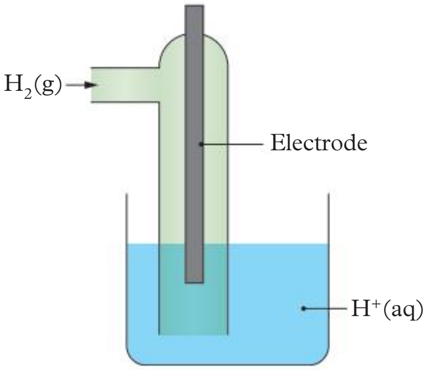


FIGURE 1 The standard hydrogen half-cell has an $E°$ of 0.0 V.

What are standard electrode potentials?

As well as observing the formation of hydrogen gas and measuring pH, you can measure the voltage that is generated by galvanic cells. **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 that will provide a suitable voltage to power the particular application as well as for other factors.

standard electrode potentials ($E°$) the electrical potential that an electrode generates under standard conditions

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. When 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.

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

To determine the EMF of a zinc–hydrogen galvanic cell, determine which half-reaction would be oxidation and which would be reduction. The one with a higher numerical value will undergo reduction. Consider the half-reactions shown below: –0.76 V is smaller than 0.00 V so this will proceed in the reverse direction as oxidation; 0.00 V is larger than –0.76 V, so this half-reaction is reduction.

$$Zn^{2+} + 2e^- \rightarrow \mathbf{Zn} \qquad E° = -0.76\,V$$

$$\mathbf{2H^+} + 2e^- \rightarrow H_2 \qquad E° = 0.00\,V$$

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:

$$\begin{aligned} EMF &= E°_{\text{reduction half-cell}} - E°_{\text{oxidation half-cell}} \\ &= 0.00\,V - (-0.76\,V) \\ &= 0.00\,V + 0.76\,V \\ &= 0.76\,V \end{aligned}$$

Therefore, the cell produces 0.76 V (Figure 2).

Study tip

When using the QCAA *Formula and data book*'s version of the table for galvanic cells, the reduction half-equation is lower on the electrochemical series. Therefore, to calculate EMF, subtract the top $E°$ from the bottom $E°$ (reduction – oxidation).

$EMF = E°_{\text{reduction half-cell}} - E°_{\text{oxidation half-cell}}$

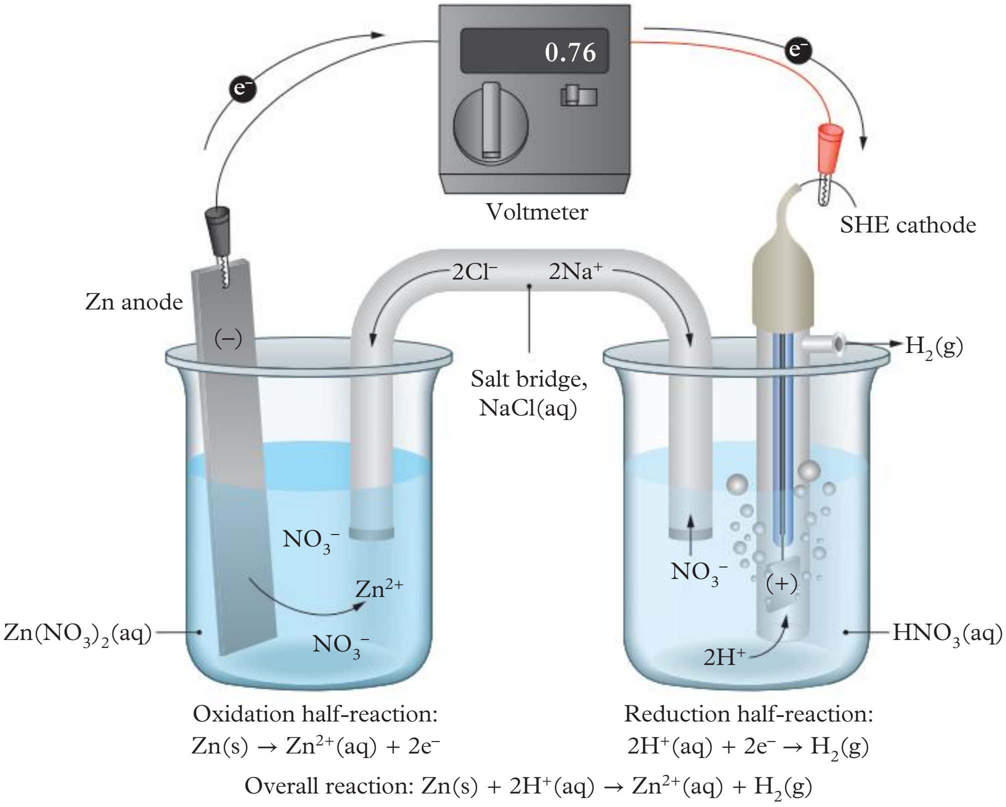


FIGURE 2 The zinc–hydrogen galvanic cell generates 0.76 V.

Worked example 7.2A demonstrates how to calculate the voltage from a galvanic cell.

Worked example 7.2A

Calculating the voltage of a galvanic cell

Calculate the voltage produced when a $Pb^{2+}|Pb$ half-cell is connected to an $Al^{3+}|Al$ half-cell. (1 mark)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to find the half-equations, identify oxidation and reduction *E*° values and then subtract the oxidation *E*° from the reduction *E*°.
Step 2: Find the half-equations and their *E*° values.	$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ $E° = -1.68\,V$ $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $E° = -0.13\,V$
Step 3: Identify which undergoes reduction and oxidation.	$Al^{3+}(aq) + 3e^- \rightarrow \mathbf{Al(s)}$ $E° = -1.68\,V$: oxidation $\mathbf{Pb^{2+}(aq)} + 2e^- \rightarrow Pb(s)$ $E° = -0.13\,V$: reduction
Step 4: Select the appropriate formula.	$EMF = E°_{\text{reduction half-cell}} - E°_{\text{oxidation half-cell}}$
Step 5: Substitute in the values and solve, remembering not to simplify until the end (show that you are subtracting a negative in your working out).	$EMF = E°_{\text{reduction half-cell}} - E°_{\text{oxidation half-cell}}$ $= -0.13\,V - (-1.68\,V)$ $= -0.13\,V + 1.68\,V$ $= 1.55\,V$ (1 mark)

Your turn

Calculate the voltage produced when a $Ni^{2+}|Ni$ half-cell is connected to a $Br_2|Br^-$ half-cell. (1 mark)

What are standard conditions?

It is essential to understand that standard electrode potentials are measured under **standard conditions** of 25°C (298 K), 100 kPa and 1 M.

standard conditions
the conditions under which all $E°$ values are measured: 25°C (298 K), 100 kPa and 1 M

When galvanic cells operate under non-standard conditions (i.e. a different temperature, pressure or concentration) the $E°$ values change and the "°" superscript is not used for non-standard conditions. 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. An example of this is the water and chlorine half-equations at +1.23 and +1.36 V.

How can we predict redox reactions from standard electrode potentials?

To determine whether two chemicals will react spontaneously in a redox reaction, follow the steps below.

1 Find the appropriate half-equations on the table of standard electrode potentials.

2 Identify the chemical species that are reacting and whether the half-equation would be oxidation or reduction.

3 Use $E°_{\text{cell}} = E°_{\text{reduction half-cell}} - E°_{\text{oxidation half-cell}}$ for the half equations and the chemicals you identified. Although it is not actually in a galvanic cell, the answer will tell you whether the reaction is spontaneous or not.

4 If the result obtained in step 3 is greater than 0 (positive), the reaction is energetically favourable and so is spontaneous. If the result is less than 0 (negative), the reaction is not be energetically favourable and so is not spontaneous.

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.

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E° = -0.76\text{V}$$
$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E° = +0.34\text{V}$$

2 Identify the chemical species that are reacting.

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E° = -0.76\text{V}$$

If Zn does form Zn ions, this would be oxidation.

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E° = +0.34\text{V}$$

If copper ions form metallic copper, this would be reduction.

3 $E°_{\text{cell}} = +0.34\text{ V} - (-0.76\text{ V}) = +1.10\text{ V}$

The answer is positive (greater than 0) so mixing these two reactants would be energetically favourable and result in a spontaneous reaction. 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) while some of the zinc turns into ions causing the mass of zinc remaining in the metal to decrease. The electrode is the site of the reaction

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.

where electrons are produced. The copper(II) sulfate solution starts to become colourless as the concentration of copper(II) ions in the solution decreases. If the copper deposit was then removed from the piece of zinc, the piece would appear damaged by the loss of zinc and look pitted or corroded.

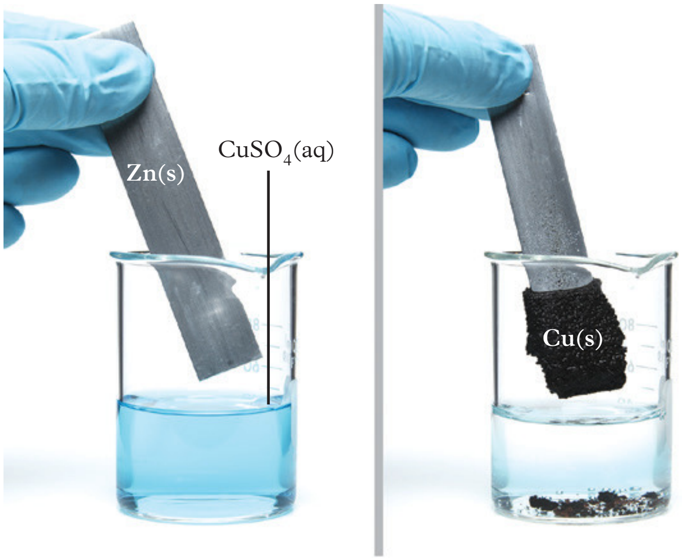


FIGURE 3 A solution of copper(II) sulfate and zinc metal. Copper metal precipitates out of solution.

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-hand side of the equation, so if it could react, it would undergo oxidation to form copper(II). This would make copper the reductant. Zinc(II) is on the left-hand side of the equation, so if it could react, it would undergo reduction to form Zn. A calculation will determine whether the reaction is spontaneous.

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E° = -0.76\,V \text{ (reduction)}$$
$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E° = +0.34\,V \text{ (Copper metal would have to undergo oxidation.)}$$
$$E° = E°_{reduction} - E°_{oxidation} = (-0.76\,V) - (+0.34\,V) = -1.10\,V$$

The answer is negative (less than 0), so mixing these two reactants would be energetically unfavourable, and the reaction would be non-spontaneous and therefore not occur.

Worked example 7.2B demonstrates the process of predicting whether a redox reaction occurs.

Worked example 7.2B

Predicting and justifying spontaneous redox reactions

Predict whether a reaction will occur between iron(II) nitrate ($Fe(NO_3)_2$) and the reactants below. **Justify** your answer using the standard electrode potentials

a magnesium metal (Mg) (2 marks)

b lead(II) nitrate ($Pb(NO_3)_2$). (4 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the questions are asking you to do.	“Predict” is to suggest what may happen based on available information, whereas “justify” is to give reasons or evidence to support an answer. We need to use the table of standard electrode potentials to predict whether a reaction will occur between $Fe^{2+}(aq)$ and the reactants in parts **a** and **b**, then use their strength to support the answer. Each question is worth 2 marks, one for the prediction and one for the justification.
Step 2: For part a, locate the half equations on the table of standard electrode potentials. Identify whether oxidation or reduction could occur.	**a** Iron(II) ions would need to be reduced and magnesium solid would need to be oxidised: $Mg^{+}(aq) + e^{-} \rightarrow Mg(s) \quad E^\circ = -2.36\text{ V}$ (oxidation) $Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s) \quad E^\circ = -0.44\text{ V}$ (reduction)
Step 3: Calculate the E° for the possible redox reaction. Use it to determine if the reaction is spontaneous.	$E^\circ = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}}$ $= (-0.44\text{ V}) - (-2.36\text{ V}) = +1.92\text{ V}$ (1 mark) E° is positive (greater than 0). Fe^{2+} and Mg will react spontaneously. (1 mark)
Step 4: For part b, locate the half equations on the table of standard electrode potentials	**b** Iron(II) ions are involved in two half-equations. Therefore, there are two possible sets of half-equations $\mathbf{Pb^{2+}(aq)} + 2e^{-} \rightarrow Pb(s) \quad E^\circ = -0.13\text{ V}$ (reduction) $Fe^{3+}(aq) + e^{-} \rightarrow \mathbf{Fe^{2+}(aq)} \quad E^\circ = +0.77\text{ V}$ (oxidation) or $\mathbf{Fe^{2+}(aq)} + 2e^{-} \rightarrow Fe(s) \quad E^\circ = -0.44\text{ V}$ (reduction) $\mathbf{Pb^{2+}(aq)} + 2e^{-} \rightarrow Pb(s) \quad E^\circ = -0.13\text{ V}$ (reduction)
Step 5: Calculate E° for the first possible redox reactions. Use it to determine if it will spontaneously react. Consider the result for the second possibility and provide a reason as to whether it could be spontaneous.	$E^\circ = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}}$ $= (-0.44\text{ V}) - (-2.36\text{ V})$ $= +1.92\text{ V}$ In the first option, neither iron(II) nor lead(II) is the strongest oxidant or reductant (1 mark), so they will not react (1 mark). In the second option, lead(II) is the strongest oxidant, but iron(II) is also an oxidant. Neither ion will donate electrons (1 mark) and so no reaction will occur (1 mark).

Your turn

Predict whether a reaction will occur between iodine ($I_2(s)$) and the reactants below. Justify your answer using the standard electrode potentials

a zinc metal (Zn) (2 marks)

b copper metal (Cu). (4 marks)

Challenge

Photochemical galvanic cells

A galvanic cell is set up with an aqueous solution of zinc nitrate and a graphite electrode at the cathode and an aqueous solution of aluminium nitrate and an aluminium electrode at the anode.

A student observed gas bubbles forming on one of the electrodes rather than metal plating onto the electrode.

a **Describe** a reason for this observation. (1 mark)

b **Identify** the half-equations and the overall reaction occurring in the cell. (2 marks)

c **Explain** a safety consideration for this galvanic cell, referring to your answer in part **b**. (2 marks)

Real-world chemistry

Pacemakers

The heart contains an electrical system that regulates 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 (Figure 4). A pacemaker is a small device that helps to control an irregular heartbeat. There are two parts to this device.

- A pulse generator contains a battery (a galvanic cell) and regulates the heartbeat.
- A set of small wires sends 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.

Initially, NiCd (nickel–cadmium) batteries were used in pacemakers. They operated under the principles of a galvanic cell:

$$Cd(s) + 2NiOOH(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$$

Although NiCd batteries could be recharged hundreds of times, they were heavy, which proved to be a problem for the people who had to carry them around all day, every day. Recharging the batteries was also problematic because they needed to be connected to an external power source.

Therefore, a lighter battery was developed that could maintain charge for tens of years. The LiI (lithium–iodide) battery operates according to the overall reaction equation:

$$2Li(s) + I_2(s) \rightarrow 2LiI(s)$$

Apply your understanding

1 **Construct** the oxidation and reduction half-equations for the NiCd battery. (2 marks)

2 **Identify** the strongest oxidant and reductant in the NiCd battery. (2 marks)

3 **Explain** some safety concerns with having this type of electrochemical device housed within the body. (3 marks)

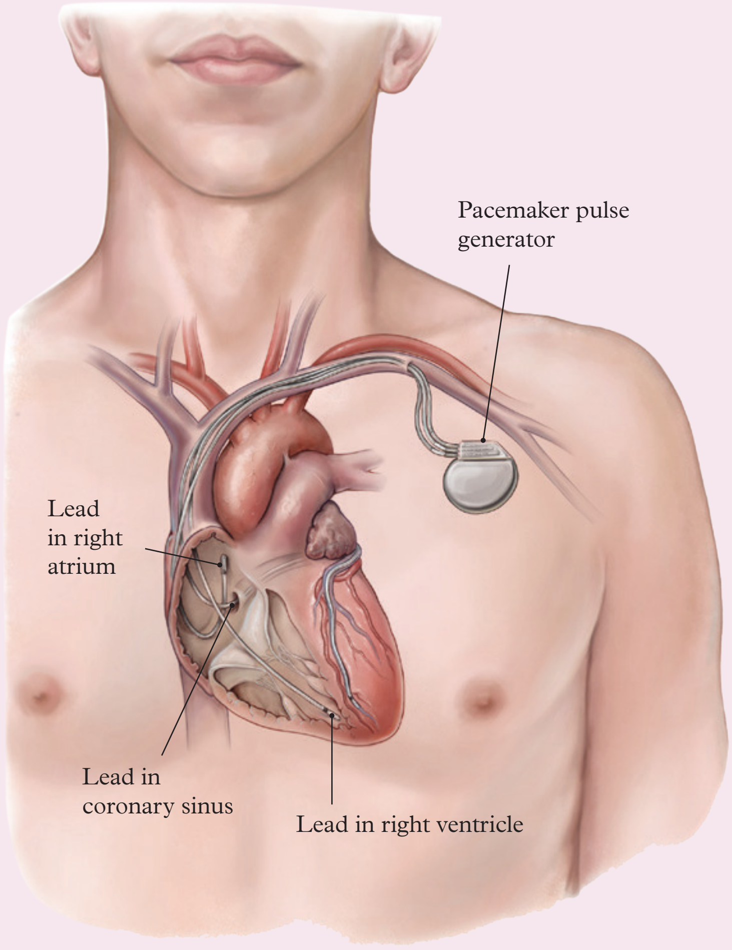


FIGURE 4 A pacemaker connected to an irregularly beating heart by three current-carrying leads

Skill drill

Analysing the accuracy of data

Science inquiry skill: Processing and analysing data (Lesson 1.7); Evaluating evidence (Lesson 1.8)

A student wishes to confirm the order of the half-equations on the table of standard electrode potentials. They prepared half-cells represented by the following half-equations to determine the EMF generated by each pair of half-cells. The data is represented in the table below.

$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $-2.36\,V$

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $-0.76\,V$

$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ $-0.44\,V$

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $+0.34\,V$

$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$ $+0.54\,V$

TABLE 2 Voltage data obtained from the experiment

Half-cell combinations	Voltage (V)				
	Mg^{2+}|Mg	Zn^{2+}|Zn	Fe^{2+}|Fe	Cu^{2+}|Cu	I_2|I^-
Mg^{2+}|Mg	0.00	1.31	1.62	2.55	2.50
Zn^{2+}|Zn		0.00	0.02	0.98	0.90
Fe^{2+}|Fe			0.00	0.60	0.51
Cu^{2+}|Cu				0.00	0.05
I_2|I^-					0.00

Some observations:

Copper was always the positive electrode; the solution decreased in intensity of the blue colour due to $Cu^{2+}(aq)$.

Magnesium was always the negative electrode; the electrode decreased in mass.

Practise your skills

1 **Construct** a hypothesis that outlines which half-cell should always undergo oxidation and reduction and a reason as to why. (2 marks)

2 **Comment** on the accuracy of the data and **justify** your answer with reference to the data. (2 marks)

3 **Evaluate** the observations and provide a reason for both observations. (4 marks)

4 **Construct** the overall reaction for the galvanic cell which produced the greatest voltage. Is this reaction what was predicted? **Justify** why. (2 marks)

5 If your predictions were different from the data, **explain** a reason for why this may have occurred. (2 marks)

Check your learning 7.2

Check your learning 7.2: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain** the purpose of the hydrogen half-cell in the electrochemical series. (1 mark)

2 **Describe** standard conditions. **Explain** what happens if a galvanic cell is not operated under standard conditions. (2 marks)

3 **Calculate** the $E°$ values of the following galvanic cells.

- **a** Cu^{2+}|Cu||Zn^{2+}|Zn (1 mark)
- **b** Mg^{2+}|Mg||Cu^{2+}|Cu (1 mark)
- **c** Fe^{2+}|Fe||Mg^{2+}|Mg (1 mark)
- **d** Cu^{2+}|Cu||Fe^{2+}|Fe (1 mark)
- **e** Mg^{2+}|Mg||Zn^{2+}|Zn (1 mark)
- **f** Zn^{2+}|Zn||Fe^{2+}|Fe (1 mark)

Analytical processes

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. (1 mark)
- **b** **Identify** the electrode required in each cell if it underwent oxidation. (1 mark)
- **c** **Calculate** the $E°$ values for each combination of half-cells (there should be three combinations). (1 mark)
- **d** **Sketch** and label three galvanic cells from part **c**. (12 marks)
- **e** **Determine** which chemical is the strongest oxidant and which is the strongest reductant. (1 mark)
- **f** **Determine** which combination of half-cells produces the highest voltage. (1 mark)

Knowledge utilisation

5 **Discuss** 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? (3 marks)

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. (3 marks)

Practical

Lesson 7.3

Constructing a galvanic cell

Learning intentions and success criteria

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

MODULE 7

Lesson 7.4

Review: Galvanic cells

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 from the salt bridge move towards the anode half-cell to balance the positive ions that move into the solution from the metal as it undergoes oxidation.
- Positive ions from the salt bridge move towards the positive cathode half-cell to replace the positive ions that plate as a metal onto the cathode as it undergoes 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).
- The calculation of $E°_{\text{cell}}$ can be used to determine whether a redox reaction is spontaneous or non-spontaneous.

7.3

- Practical: Constructing a galvanic cell

Key formulas

Voltage generated by a galvanic cell	$\text{EMF} = E°_{\text{reduction half-cell}} - E°_{\text{oxidation half-cell}}$

Review questions 7.4A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

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 Mg is the strongest oxidant and Cl_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 Cl^- is the strongest oxidant and Mg^{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:

$CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8H^+(aq) + 8e^-$

What is the reaction occurring at the cathode?

A $4H^+(aq) + O_2(g) \rightarrow 2H_2O(l)$
B $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$
C $4H^+(aq) + O_2(g) + 4e^- \rightarrow 2H_2O(l)$
D $2H_2O(l) + 4e^- \rightarrow 4H^+(aq) + O_2(g)$

4 The electrode where the metal is reduced is called the

A anode and has a positive charge.
B anode and has a negative charge.
C cathode and has a positive charge.
D cathode and has a negative charge.

5 The electrons in a galvanic cell flow from the

A positive anode to negative cathode.
B negative anode to positive cathode.
C positive cathode to negative anode.
D negative cathode to positive anode.

Use the following information to answer questions 6 and 7.

A galvanic cell is constructed from the following half-cells.

Half-cell 1: silver electrode and a colourless aqueous solution of $AgNO_3$

Half-cell 2: copper electrode in a blue aqueous solution of $CuCl_2$

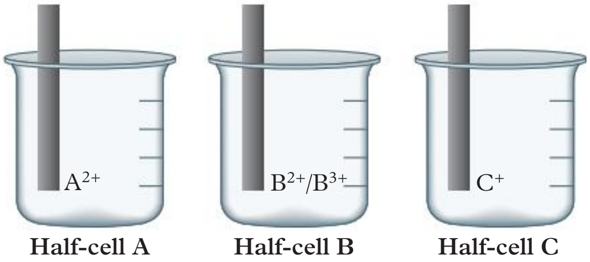
6 Identify which of the following is likely to occur.

A Chlorine gas forms at the anode.
B The blue solution becomes darker.
C The clear solution becomes cloudy.
D The silver electrode decreases in mass.

7 What would a suitable salt bridge solution contain?

A NaCl
B NaBr
C NaOH
D $NaNO_3$

8 Three half-cells A, B and C were constructed from unknown solutions according to the following diagram.



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.

What is the strongest reductant?

A A
B C
C C^+
D B^{2+}

9 Which of the following metals will not be oxidised by an aqueous 1.0 M H_3O^+ solution?

A Iron
B Zinc
C Copper
D Magnesium

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 steel hull acts as the anode.
B aluminium acts as the anode.
C aluminium acts as the cathode.
D aluminium gains electrons and acts as an oxidant or oxidising agent.

Review questions 7.4B Short response

Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

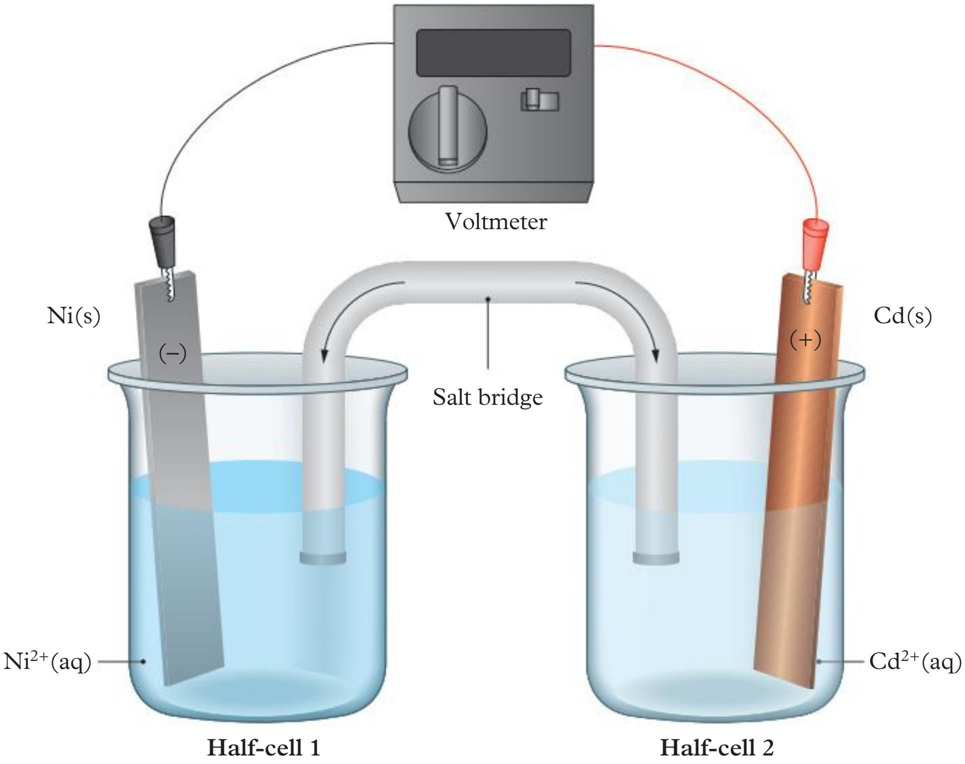
11 **Describe** the main purposes of separating the half-cells in a galvanic cell. (2 marks)

12 **Explain** why galvanic cell voltages are measured at standard conditions. (2 marks)

13 **Describe** the purpose of a salt bridge. (1 mark)

14 A nickel–cadmium galvanic cell is constructed as shown below, where:

$$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s) \quad E° = -0.40\ V$$



Copy the diagram and

- **a** **identify** the oxidation and reduction half-cells (1 mark)
- **b** **identify** the anode and cathode and polarity of each (1 mark)
- **c** **construct** the half-equations and overall equation (3 marks)
- **d** **identify** a suitable salt bridge substance and justify your choice (1 mark)
- **e** **clarify** the direction of ion and electron movement (1 mark)
- **f** **calculate** the $E°$ of the cell. (1 mark)

15 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, **identify** the

- **i** strongest reductant (1 mark)
- **ii** strongest oxidant (1 mark)
- **iii** oxidising agent (1 mark)
- **iv** reducing agent (1 mark)
- **v** two half-equations (2 marks)
- **vi** overall equation. (1 mark)

Analytical processes

16 **Compare** an internal circuit and an external circuit. (2 marks)

Knowledge utilisation

17 An iron nail is placed in an aqueous solution of

- I $AgNO_3$
- II $Mg(NO_3)_2$
- III $CuSO_4$
- IV $Pb(NO_3)_2$
- V $Zn(NO_3)_2$

- **a** **Justify** in which solution(s) you would expect a coating of another metal on the iron nail. (3 marks)
- **b** Use the electrochemical series to **explain** why some solutions would not result in the coating of another metal on the nail. (2 marks)
- **c** **Explain** the purpose of the SO_4^{2-} and NO_3^{-} ions in the solutions. (2 marks)

18 **Construct** fully labelled galvanic cells for the following half-cells.

- **a** For each of the following pairs of half-cells, draw a fully labelled galvanic cell diagram
  - **i** $Ag|Ag^{+}$ and $Cu^{2+}|Cu$ (5 marks)
  - **ii** $Cr_2O_7^{2-}|Cr^{3+}$ and $Fe^{2+}|Fe$ (5 marks)
  - **iii** $H_2O_2|H^{+}$ and $O_2|H_2O_2$ (5 marks)

  In each cell diagram, include
  - labels for the anode, cathode and polarity of the electrodes and which material the anode and cathode are made from
  - fully balanced half-equations, including states, and specify which is 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.
- **b** **Determine** the $E°$ values for each galvanic cell. (3 marks)

19 **Investigate** why blocks of zinc are attached to the steel supports on oil rigs in Bass Strait. Use chemical equations to support an argument of the strongest oxidant and reductant and therefore the overall chemical equation. (6 marks)

20 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. (3 marks)
- **b** **Determine** a possible identity for the metal and **justify** your choice, using the electrochemical series. (2 marks)

Data drill

Electrochemical cells

A student set up an electrochemical cell (Figure 1) to investigate the effect of temperature on the measured cell voltage. The student used 1.0 M solutions of the electrolytes in the experiment. The results of the experiment are given in Table 1.

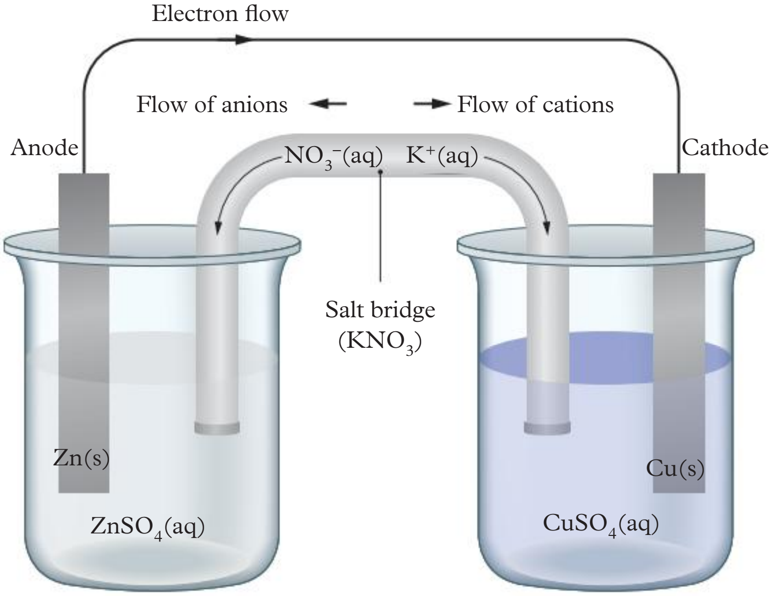


FIGURE 1 The electrochemical cell set-up for the temperature–voltage experiment

TABLE 1 Raw data recorded for the temperature–voltage experiment

Temperature (°C)	Voltage (V)					
	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Average
0	0.91	0.90	0.91	0.87	0.89	
3	0.91	0.94	0.90	0.95	0.93	
15	0.83	0.85	0.86	0.83	0.86	
22	0.84	0.85	0.82	0.86	0.85	
54	0.85	0.82	0.78	0.85	0.84	

Apply understanding

1 **Determine** the oxidation and reduction equations for the reactions occurring in the two half-cells. (2 marks)

2 **Calculate** the average voltages at each temperature. (2 marks)

3 **Identify** the independent and dependent variables. (2 marks)

Analyse data

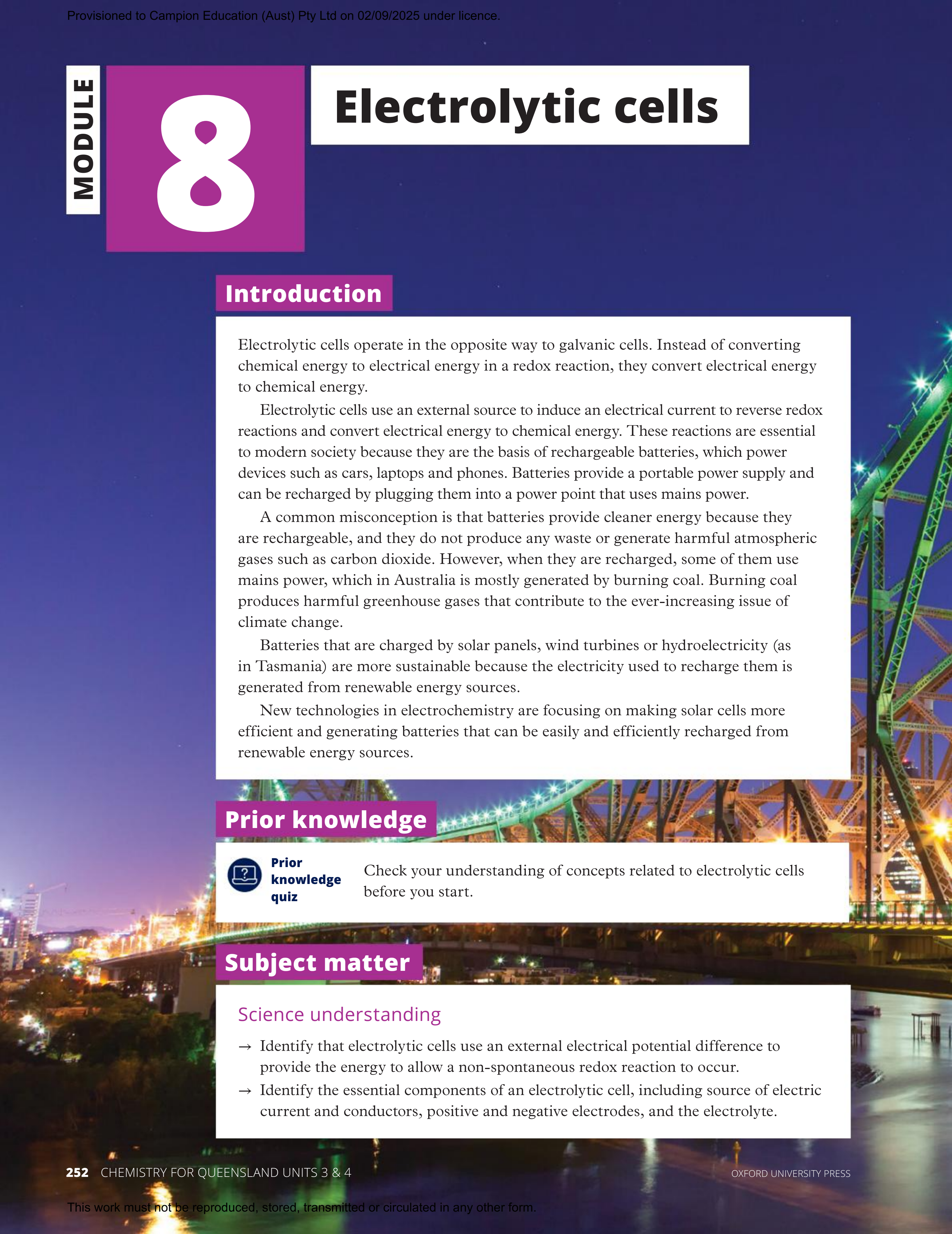
4 **Identify** the trend in the data by explicitly referring to the variables. (2 marks)

Interpret evidence

5 Is it possible to comment on the accuracy of the data? **Justify** your answer using the conditions of the experiment. (2 marks)

6 **Draw a conclusion** about the impact of non-standard conditions on $E°$ values. (3 marks)

Module 7 checklist: Galvanic cells



MODULE 8

Electrolytic cells

Introduction

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 use an external source to induce an electrical current to reverse redox reactions and convert 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 into 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, some of them 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.

Prior knowledge

Prior knowledge quiz

Check your understanding of concepts related to electrolytic cells before you start.

Subject matter

Science understanding

→ Identify that electrolytic cells use an external electrical potential difference to provide the energy to allow a non-spontaneous redox reaction to occur.

→ Identify the essential components of an electrolytic cell, including source of electric current and conductors, positive and negative electrodes, and the electrolyte.

- → State the factors that affect the products in electrolysis.
- → Determine the products of the electrolysis of a molten salt.
- → Explain the products of the electrolysis of aqueous solutions, e.g. dilute and concentrated sodium chloride(aq) and copper sulfate(aq).
- → Describe the electrolytic cells can be used in small-scale and industrial situations, including metal plating and the purification of copper.
- → Calculate moles of electrons, current, time, mass of substance or volume of gas produced or used during electrolysis. (Formula: $q = n(e^-) \times F$ or $q = I \times t$)
- → Analyse data to determine the relative amounts of product produced at each electrode in electrolysis.

Science as a human endeavour

- → Appreciate that electrochemistry has a wide range of uses, ranging from industrial scale metal extraction to personal cosmetic treatments.
- → Explore the desalination process to produce fresh water.

Science inquiry

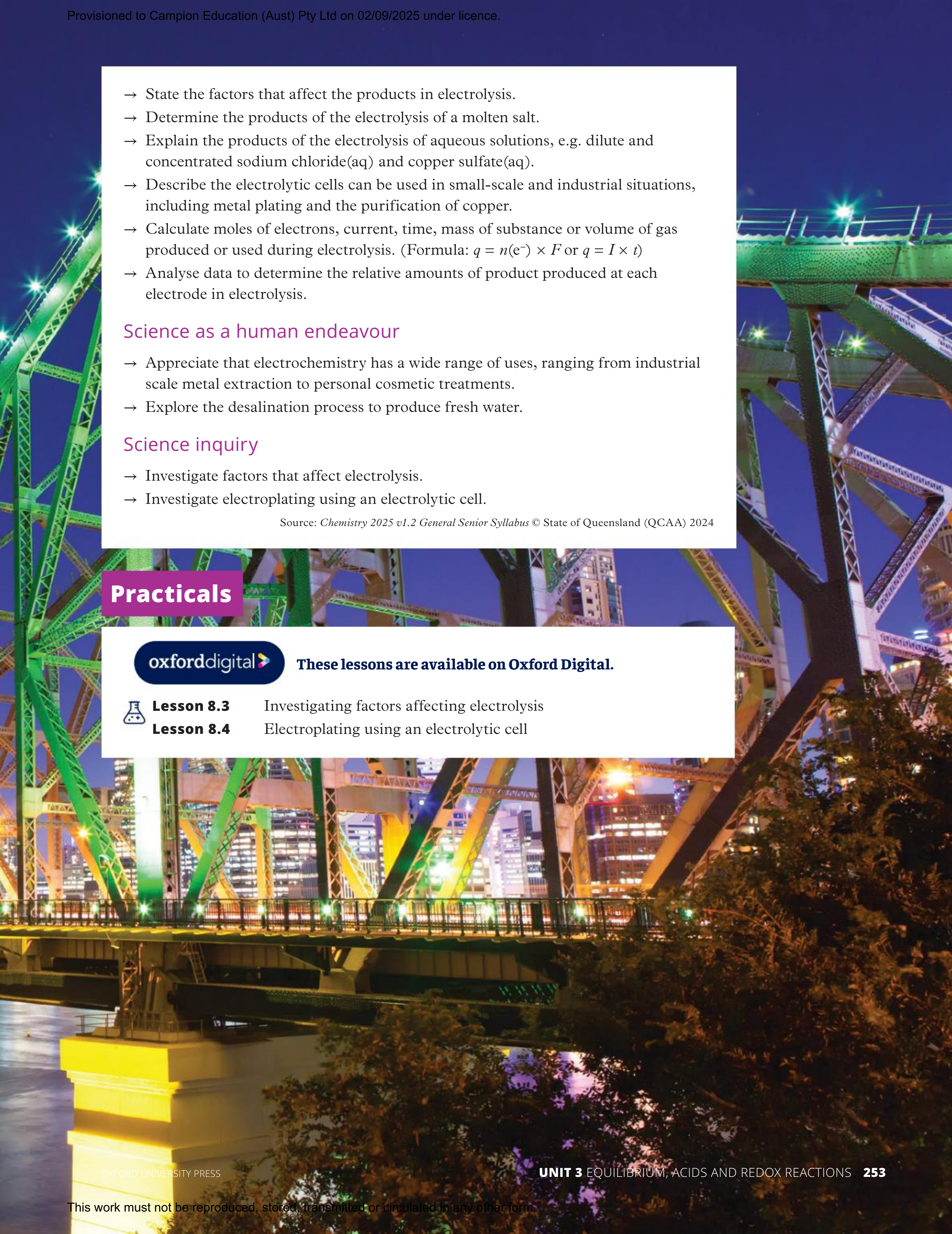
- → Investigate factors that affect electrolysis.
- → Investigate electroplating using an electrolytic cell.

Source: *Chemistry 2025 v1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

Practicals

These lessons are available on Oxford Digital.

Lesson 8.3	Investigating factors affecting electrolysis
Lesson 8.4	Electroplating using an electrolytic cell



Lesson 8.1
Electrolytic cells

Key ideas

→ The process of electrolysis involves reversing spontaneous reactions and converting electrical energy into chemical energy. For this process, an electric charge must be applied. It is the opposite of a galvanic cell.

→ The electrolysis of molten liquids occurs in the absence of water, but the electrolysis of aqueous solutions occurs in solutions where salts are dissolved in water.

Learning intentions and success criteria

electrolysis
the process by which electrical energy is passed into a cell, using a power source, resulting in the reversal of spontaneous redox reactions

What is electrolysis?

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 (Module 7) are reversed. In reversing these equations, electrolysis allows for the cell to recharge so that it can then be used again on discharge. An example of this process is a rechargeable battery, otherwise known as a secondary cell – it can both discharge and recharge.

How do you recharge a battery?

In a galvanic cell, chemical energy is converted to electrical energy in a redox reaction. Recharging a battery is the opposite of this process and is one form of electrolysis. The recharging process 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. Rechargeable batteries typically have a porous divider down the middle, although other electrolytic cells do not. 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 may use just one electrolyte in which both the anode and the cathode are placed, whereas a galvanic cell typically has three different electrolyte solutions: one in each half-cell and the third in the 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 an external power source to push electrons onto one of the electrodes. This is labelled 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 labelled positive.)

- 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.

Note that, similarly to galvanic cells, ions carry the charge within the cell; electrons are able to carry current in the external circuit but not through the electrolyte.

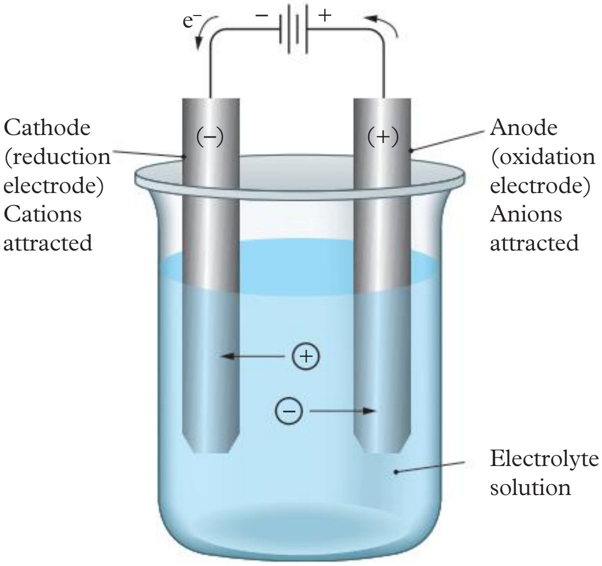


FIGURE 1 A basic diagram of an electrolytic cell

Reversing a galvanic cell

Consider a galvanic cell with $Ni^{2+}|Ni$ and $Cu^{2+}|Cu$ half-cells (Figure 2):

$$E°_{Ni} = -0.24\,V, E°_{Cu} = +0.34\,V$$

- 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.
- Nickel is the strongest reductant. Therefore, nickel is oxidised at the anode, which is negative because electrons are produced when Ni^{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 calculating the $E°_{cell}$ (Figure 2):

$$\begin{aligned} \text{EMF} &= E°_{\text{reduction half-cell}} - E°_{\text{oxidation half-cell}} \\ &= 0.34\,V - (-0.24\,V) \\ &= 0.34\,V + 0.24\,V \\ &= 0.58\,V \end{aligned}$$

This value is positive (>0) so the reaction is spontaneous, and the galvanic cell will operate as described above.

Consider the corresponding electrolytic cell.

- The power supply must be set up so that electrons are pushed onto the negative electrode, reversing the reaction that produced electrons to instead now consume them. A voltage greater than 0.58 V is required to do this. The negative electrode in a galvanic cell remains negative in an electrolytic cell for recharging batteries.
- Positive nickel ions are attracted to the negative electrode, forming nickel 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.
- Ni^{2+} is the strongest oxidant because it causes the copper to undergo oxidation.
- Copper metal is the strongest reductant because it causes Ni^{2+} to undergo reduction.

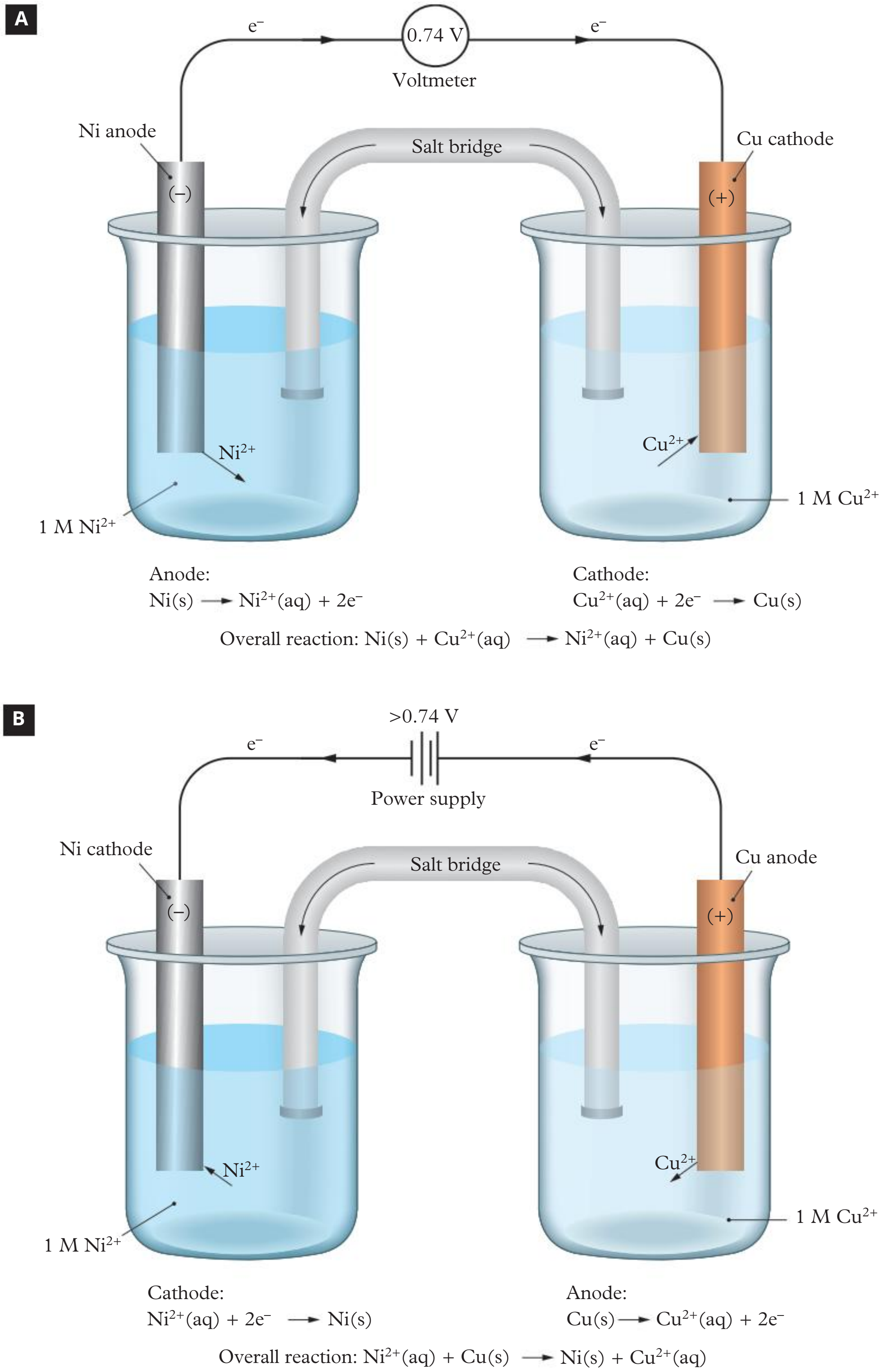


FIGURE 2 The reaction in the (A) copper/nickel galvanic cell can be reversed by (B) using the power supply to push electrons onto the negative electrode.

Study tip

Reduction always occurs at the cathode. RED CAT always applies.

Electrolysis of molten salts

molten
melted or liquefied

The electrolysis of **molten** salts occurs at very high temperatures because the salts must be liquids. 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. By mixing two salts, the melting temperature and energy requirements are lower. Any metal ions with a reduction potential less than −0.83 V can only be obtained by electrolysing the molten salt rather than a solution. Electrolysis of a solution of these salts would reduce water to form hydrogen by:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83\,V$$

Similarly, fluoride ions, which have a reduction potential much greater than +1.23 V, cannot be reduced in aqueous solution. This is a little more complicated because ions such as chloride ions can be reduced from aqueous solution at high concentrations, but not at low concentrations.

Consider a molten sodium chloride electrolytic cell (Figure 3) known as a Downs cell. A Downs cell contains the molten sodium chloride or other salts in a single cell, with a central carbon anode, and a donut-shaped iron cathode near the perimeter. Between the cathode and the anode, a stainless-steel mesh in a thin donut shape keeps both products separate so that they do not spontaneously react again.

- The power source pushes electrons onto the negative electrode (the cathode). The calculated $E°$ for the reaction between sodium metal and chlorine gas is (1.36 V – (–2.71 V)) = 4.07 V, so a voltage greater than this is required.
- Positive ions in the liquid (Na^+) are attracted to the negative electrode (the cathode), 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):

$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

- The two electrodes are placed within the molten salt but not at the bottom of the Downs cell. This enables each ion to move to the oppositely charged electrode for reaction. The mesh screen allows for this movement of ions. The carbon anode is within an inverted funnel shape made of metal. As chlorine gas bubbles off the anode, it rises and is collected. The circular cathode is made of iron and is outside the mesh screen. As liquid sodium is less dense than sodium chloride, it rises to the top of the molten liquid and is able to be drained off.
- The overall reaction equation for this process is:

$$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$$

Figure 3 illustrates the molten sodium chloride electrolytic cell.

The Downs cell is used not only to extract sodium but also for some other molten salts. Other electrolysis cells are used for some of the other more reactive metals. The molten electrolyte contains ions of the molten salt and sometimes additional ions.

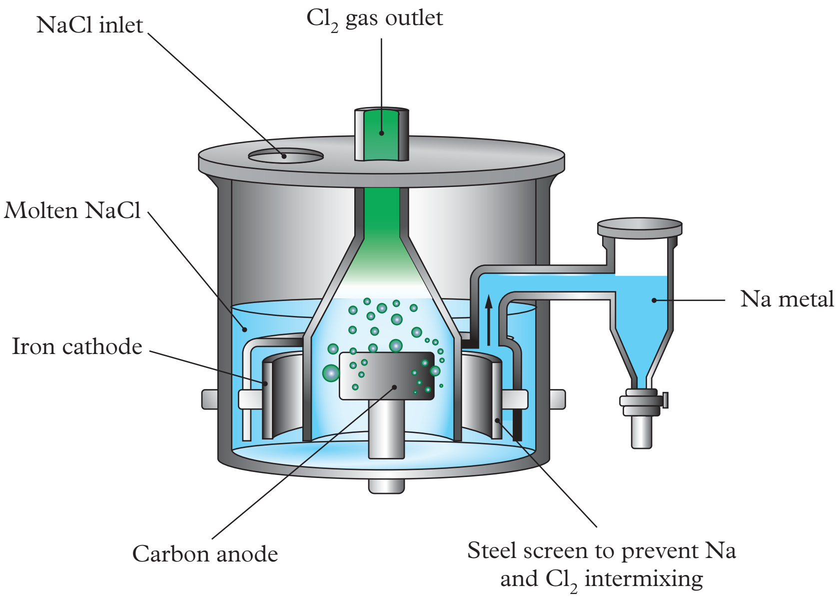


FIGURE 3 The electrolysis of molten sodium chloride

If asked to identify components of an electrolytic cell, remember that electrons are being pushed onto the cathode by the external power source, and the cathode is labelled as negative. Positive ions are attracted to it and reduced there. The negative ions move towards the anode, which is labelled as positive. Oxidation occurs there. The power source may be drawn as parallel lines; the shorter line would be the one electrons flow from towards the cathode.

Sometimes, the negative ion is being oxidised, such as Cl^-, which forms chlorine. However, in the case of the electrolysis of aluminium oxide (alumina), the carbon anode itself reacts with the negative oxygen ions to form carbon dioxide. As a result, the carbon anodes need to be replaced.

Electrolysis of aqueous solutions

Some ions can only be oxidised or reduced from their molten liquid forms. However, for other ions, electrolysis of an aqueous solution can be used. In the electrolysis of aqueous solutions, water can also be a reactant. The water half-equations that are used in electrolysis are:

$$2H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq) + H_2(g) \qquad E° = -0.83\,V$$
$$\tfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O(l) \qquad E° = +1.23\,V$$

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:

$$Na^+(aq) + e^- \rightleftharpoons Na(s) \qquad E° = -2.71\,V$$
$$2H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq) + H_2(g) \qquad E° = -0.83\,V$$
$$\tfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O(l) \qquad E° = +1.23\,V$$
$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E° = +1.36\,V$$

Chloride and water can both undergo oxidation, but you would expect the strongest reductant to be more likely to react at standard conditions. The reduction of oxygen to form water has a lower reduction potential, which means that water is a stronger reductant than chloride ions and will be more easily oxidised.

$$\tfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O(l) \qquad E^\circ = +1.23\,V$$
$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E^\circ = +1.36\,V$$

Sodium ions and water can undergo reduction, but only the strongest oxidant will react. Because the strongest oxidant on the electrochemical series has a higher reduction potential, water is more reactive than sodium ions and will undergo electrolysis. (Note: –0.83 is a higher, less negative value than –2.71.)

$$Na^+(aq) + e^- \rightleftharpoons Na(s) \qquad E^\circ = -2.71\,V$$
$$2H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq) + H_2(g) \qquad E^\circ = -0.83\,V$$

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: $H_2O(l) \rightarrow \tfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$
- the overall reaction equation is: $3H_2O(l) \rightarrow 2OH^-(aq) + H_2(g) + \tfrac{1}{2}O_2(g) + 2H^+(aq)$

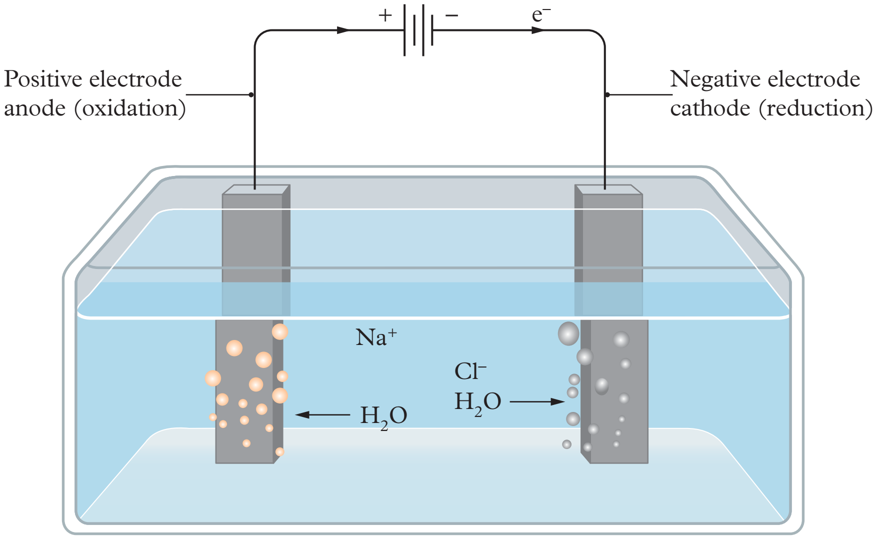
The $2OH^-(aq)$ and $2H^+(aq)$ form $2H_2O(l)$, so the equation can be further simplified to:

$$H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

or

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

Figure 4 illustrates the components of an aqueous sodium chloride electrolytic cell.



$$H_2O(l) \longrightarrow \tfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \qquad 2H_2O(l) + 2e^- \longrightarrow 2OH^-(aq) + H_2(g)$$
$$\text{Overall: } 2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$

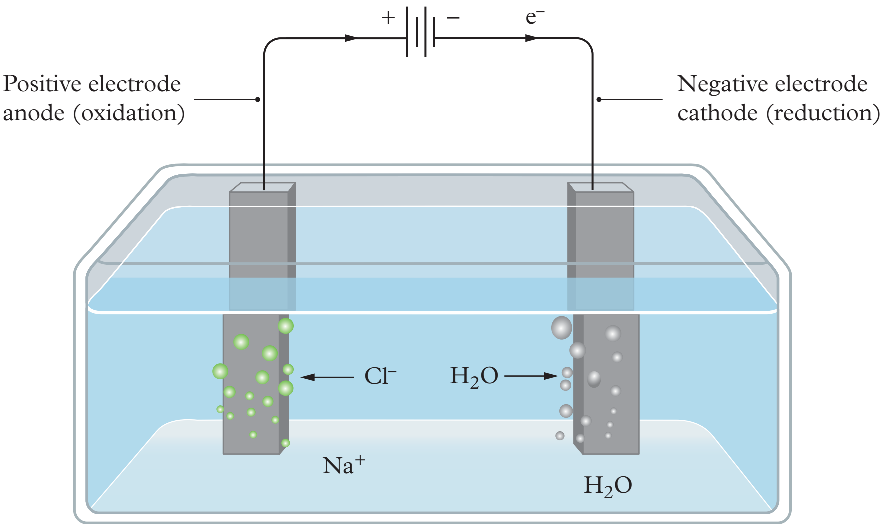
FIGURE 4 The aqueous sodium chloride electrolytic cell under standard conditions produces oxygen gas at the anode (left) and hydrogen gas at the cathode (right).

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 (Figure 5).

$$\tfrac{1}{2}O_2(g) + 2H^+(aq) + e^- \rightleftharpoons H_2O(l) \qquad E^\circ = +1.23V$$
$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E^\circ = +1.36V$$

Under non-standard conditions (conditions other than 1 M, 100 kPa and 25°C), the electrode potentials of each half-equation change. When the concentration of chlorine is increased, the electrode potential changes, and chloride ions are able to be oxidised to form chlorine gas. At intermediate concentrations of sodium chloride, the chloride ions and the water compete at the anode, and each of them undergoes oxidation. A mixture of chlorine and oxygen is formed. Chlorine is slightly water soluble, and in small amounts will remain dissolved in the water. This is the basis of the electrolyser used to produce chlorine in a saltwater pool. If brine, which is a concentrated or saturated solution of sodium chloride, is used, the electrolytic cell produces chlorine gas, rather than oxygen. The chloride ion becomes the strongest reductant and reacts before water does.



$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$ $\qquad 2H_2O(l) + 2e^- \longrightarrow 2OH^-(aq) + H_2(g)$

Overall: $2H_2O(l) + 2Cl^-(aq) \longrightarrow 2OH^-(aq) + H_2(g) + Cl_2(g)$

FIGURE 5 The aqueous sodium chloride electrolytic cell produces chlorine gas at the anode (left) rather than oxygen at very high concentrations of sodium chloride. Hydrogen is still produced at the cathode (right).

Purification of blister copper

Blister copper is impure (98–99.5%) copper that is contaminated with bubbles of sulfur dioxide and other metals. Blister copper can be purified by electrolysis.

In modern refineries, the anode is impure copper and the cathode is made of stainless steel (although it used to be made of pure copper). 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 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.

$$\begin{array}{ll}
\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O(l) & E° = +1.23\,V \\
Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) & E° = +0.34\,V \\
Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) & E° = +0.34\,V \\
2H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq) + H_2(g) & E° = -0.83\,V
\end{array}$$

The impurities in the blister copper are also affected by the electrolysis process. Silver and gold present in the impure anodes are more difficult to oxidise than copper, based on the electrochemical series (Module 7). Therefore, they will remain as solids and gather at the base of the container as so-called "anode mud" (Figure 6). Any metal that is more easily oxidised than copper on the electrochemical series will become an ion and move into the solution. Typically, lead and zinc are found in copper deposits and both of these will be oxidised and remain in the solution.

If the copper(II) sulfate solution contains sulfuric acid (H_2SO_4), two extra half-equations apply:

$$SO_4^{2-}(aq) + 2H^+(aq) + 2e^- \rightleftharpoons SO_2(g) + 2H_2O(l) \qquad E° = +0.17\,V$$
$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \qquad E° = 0.00\,V$$

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.

$$\tfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O(l) \qquad E° = +1.23\,V$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E° = +0.34\,V$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E° = +0.34\,V$$
$$SO_4^{2-}(aq) + 2H^+(aq) + 2e^- \rightleftharpoons SO_2(g) + 2H_2O(l) \qquad E° = +0.16\,V$$
$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \qquad E° = 0.00\,V$$
$$2H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq) + H_2(g) \qquad E° = -0.83\,V$$

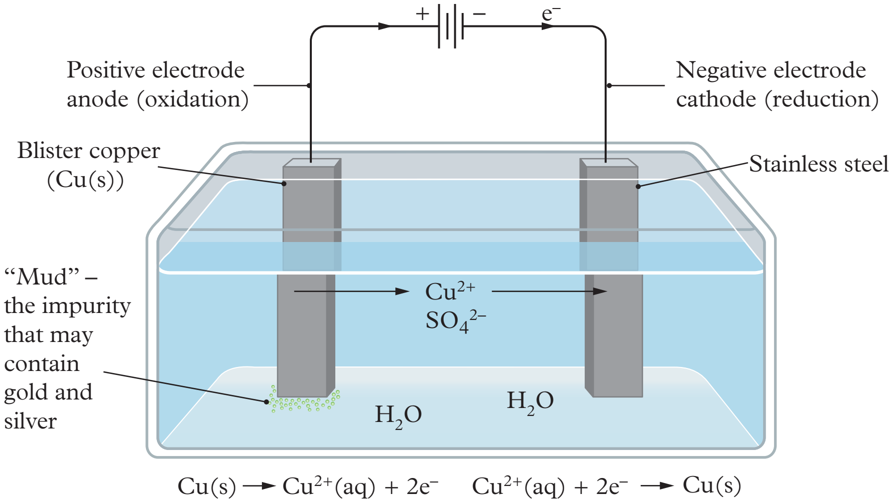


FIGURE 6 The electrolytic cell for purifying blister copper. The modern use of stainless steel electrodes, developed at the refinery in Queensland, enables copper of a much higher purity to be obtained than when a copper cathode was used.

Study tip

Don't forget that spectator ions are not included in the half-reaction and overall redox reactions.

Study tip

The positive electrode attracts anions (negative ions). The negative electrode attracts cations (positive ions).

Worked example 8.1A

Determining the products of the electrolysis of a molten salt

Molten potassium bromide undergoes electrolysis. **Determine** the

a anode product of this reaction (1 mark)

b cathode product of this reaction (1 mark)

c voltage that must be exceeded for this reaction to occur. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the questions are asking you to do.	"Determine" means establish, conclude or ascertain after consideration, observation, investigation or calculation. We need to consider the ions in the melt and which electrode the react at. We need to use the standard reduction potentials to calculate the voltage that must be exceeded for this reaction to happen. Parts **a** and **b** are each worth 1 mark, so we must express the formula and the state of each product. Part **c** is worth 2 marks, so we need to identify the standard reduction potentials and calculate an answer, expressed in volts.
Step 2: Recognise the ions present in the molten electrolyte.	Molten KBr contains K^+ and Cl^- ions.
Step 3: For part **a**, determine which ion moves towards the anode and its product.	**a** Oxidation occurs at the anode. Br^- ions will be oxidised to form $Br_2(g)$. (Note: Br_2 is a liquid at room temperature but will be a gas at the high temperatures used in electrolysis.) (1 mark)
Step 4: For part **b**, determine which ion moves towards the cathode and its product.	**b** Reduction occurs at the cathode. K^+ ions will be reduced to form K(l). (Note: K is a solid at room temperature but will be a liquid at the high temperatures used in electrolysis.) (1 mark)
Step 5: For part **c**, identify the $E°$ values for oxidation and reduction, to be used in the calculation.	**c** $E°$ for oxidation of Br^- is +1.08 V $E°$ for reduction of K^+ is –2.94 V (1 mark) $E°$ (overall) = $E_{red} - E_{ox}$ = –2.94 – (+1.08) = –4.04 V (non-spontaneous, so negative)
Step 6: Finalise your answer by rounding the numbers to an appropriate number of significant figures and include the units.	The cell voltage must exceed 4.04 V for electrolysis to occur. (1 mark)

Your turn

Molten calcium chloride undergoes electrolysis. **Determine** the

a anode product of this reaction (1 mark)

b cathode product of this reaction (1 mark)

c voltage that must be exceeded for this reaction to occur. (2 marks)

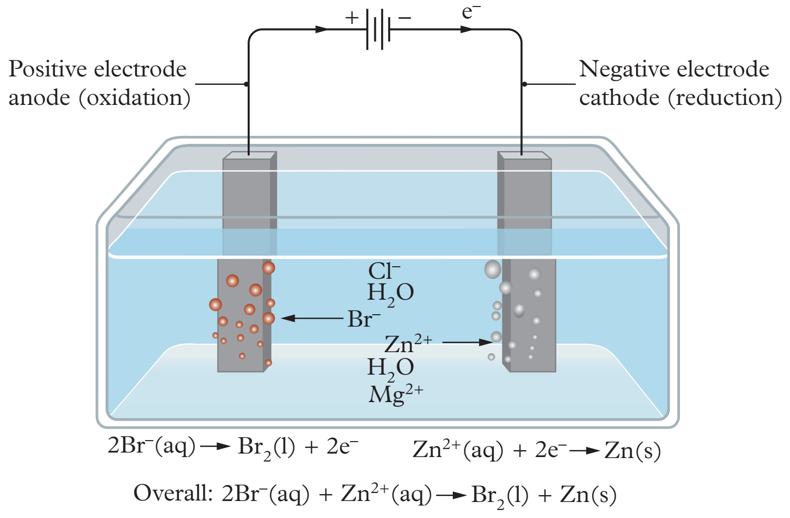
Worked example 8.1B

Constructing electrolytic cells in aqueous solution

Construct a fully labelled electrolytic cell that is made from an aqueous solution of both magnesium bromide and zinc chloride. Standard conditions are used. (5 marks)

Your cell diagram must show

- reduction and oxidation half-equations (2 marks)
- anode and cathode, polarity of electrodes (1 mark)
- direction of electron and ion movement (1 mark)
- the cell voltage required by the cell. (1 mark)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	“Construct” means to display information in a diagrammatical or logical form. Always start any electrochemical cell question by finding the half-equations. Once found, every other part of the cell can be identified. Despite how much information is in the question, it would be worth a maximum of 5 marks.
Step 2: Find the possible half-equations and identify the reactant present in the solution. Use the reduction potentials to determine which is most likely to occur.	$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ −2.36 V $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ −0.83 V $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ −0.76 V $Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$ +1.08 V $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ +1.23 V $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ +1.36 V (Note: States are aqueous where possible.) Most easily reduced is Zn^{2+} and most easily oxidised is Br^-. Half-equations: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ (1 mark) $2Br^-(aq) \rightarrow Br_2(l) + 2e^-$ (1 mark)
Step 3: Assign terminology based on the half-equations.	$Zn^{2+}(aq)$: undergoes reduction at the cathode, which is positive. $Br^-(aq)$: undergoes oxidation at the anode, which is negative. (1 mark)
Step 4: Determine the direction of electron and ion movement.	Electrons move from anode to cathode. In the electrolyte, Zn^{2+} ions migrate towards the negative electrode (cathode) and Br^- ions migrate towards the positive electrode (anode). (1 mark)
Step 5: Calculate the cell voltage.	EMF in galvanic/discharge $= E°_{reduction} - E°_{oxidation}$ $= +1.08 - (-0.76) = 1.84\text{ V}$ Therefore, to operate the cell in electrolysis, greater than 1.84 V is required. (1 mark)
Step 6: Draw the information into a fully labelled galvanic cell.	 Diagram should show: • reduction and oxidation half-equations • labels for anode, cathode and positive and negative electrodes (polarity) • electrons in external circuit moving from anode to cathode, zinc ions in electrolyte moving to cathode, bromine ions in electrolyte moving to anode.

Your turn

Construct a fully labelled electrolytic cell electrolytic cell that is made from an aqueous solution of sodium fluoride and calcium bromide. (5 marks)

Your cell diagram must show

- reduction and oxidation half-equations (2 marks)
- anode and cathode, polarity of electrodes (1 mark)
- direction of electron and ion movement (1 mark)
- the cell voltage required by the cell. (1 mark)

How do we use electrolysis to coat a more reactive metal with a less reactive one?

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 another metal to improve their appearance or to provide protection against corrosion. 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 coated with more reactive metals, typically zinc and this is called galvanising. Galvanising can be done using electrolysis. For example, when galvanised iron is used in roofs, the zinc is preferentially oxidised, protecting the iron. Zinc is reactive but forms an impervious oxide layer, which resists corrosion, whereas iron oxide is flaky and exposes fresh surfaces for corrosion.

Electroplating is also used to plate cheaper metal objects with more attractive and valuable metals. Cutlery and other fine tableware were often made using brass or pewter as the base metal, then silver-plated by electrolysis to produce a more affordable silver item. Chromium is a very attractive shiny metal and is electroplated onto items made of iron or steel to improve their appearance; for example, the bumper bars and other decorative items on older cars. Gold is often electroplated onto silver jewellery rather than using solid gold, which is much more expensive. In all of these instances, the metal item to be plated serves as the cathode. The metal to be plated onto the cathode is present as a positive ion in the electrolyte. Reduction causes it to form a fine layer of solid metal on the item.

FIGURE 7 A U-tube used in the electrolysis of potassium iodide with a phenolphthalein indicator

Testing electrolytic cells

In a laboratory, a U-tube can be used as an electrolytic cell (Figure 7). 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 (avoid breathing any fumes of gas produced such as chlorine due to its high toxicity), acids and bases are indicated by colour changes of the indicator, and metals are indicated by the plating of another metal. In Figure 7, the electrolyte is aqueous potassium iodide. At the cathode on the left, potassium ions cannot be reduced due to having a reduction potential of –2.94 V. Instead, water is reduced, forming hydroxide ions. This causes the phenolphthalein in the solution to turn pink. At the anode on the right, oxidation of bromine occurs. Bromine is a reddish-brown liquid and is soluble in water.

Comparing galvanic and electrolytic cells

Table 1 summarises the differences between galvanic cells and electrolytic cells.

TABLE 1 A summary 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) Usually three electrolytes, solutions in both half cells and in the salt bridge	One cell: products are separated, and one electrolyte is used
Anode	Negative (electrons are produced and flow into the circuit) 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	Strongest oxidant is reduced Strongest reductant is oxidised	Strongest oxidant is reduced at standard conditions Strongest reductant is oxidised at standard conditions

Skill drill

Using evidence to justify the predicted outcomes of an experiment

Science inquiry skills: Understanding the scientific method (Lesson 1.3), Evaluating evidence (Lesson 1.8) and Planning investigations (Lesson 1.4)

A student constructs the following aqueous electrolytic cells using a U-tube:

Experiment 1: NaCl(aq)
Experiment 2: Zinc sulfate(aq)
Experiment 3: Hydrochloric acid(aq)

Practise your skills

1 For each of the above reactions, **generate** a hypothesis for the observations that you would predict. (2 marks each)

2 **Justify** the expected observations for the three reactions if they were conducted under non-standard conditions. (3 marks)

3 Is the experiment valid? **Explain** your justification. (2 marks)

Real-world chemistry

Electrolysis of hair follicles

Galvanic electrolysis was first used in 1869 by Dr Charles Michael, an ophthalmologist from St Louis, USA. Dr Michael used an electrified needle to treat trichiasis, a condition where the eyelashes become ingrown.

An electric current is applied with a very fine needle-shaped electrode, or metal probe, into each hair follicle to destroy the root. The water and sodium chloride salt, which is naturally contained within the skin, act as the reactants:

Anode (+): $Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Cathode (–): $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$

If enough hydroxide is produced, it can damage the cells that cause hair growth and prevent it from growing in the future.

Apply your understanding

1 **Explain** the purpose of the sodium in the sodium chloride salt solution. (1 mark)

2 **Construct** the overall equation for the redox reaction. (1 mark)

3 **Evaluate** the concerns with the products of these reactions if they are not separated. (2 marks)

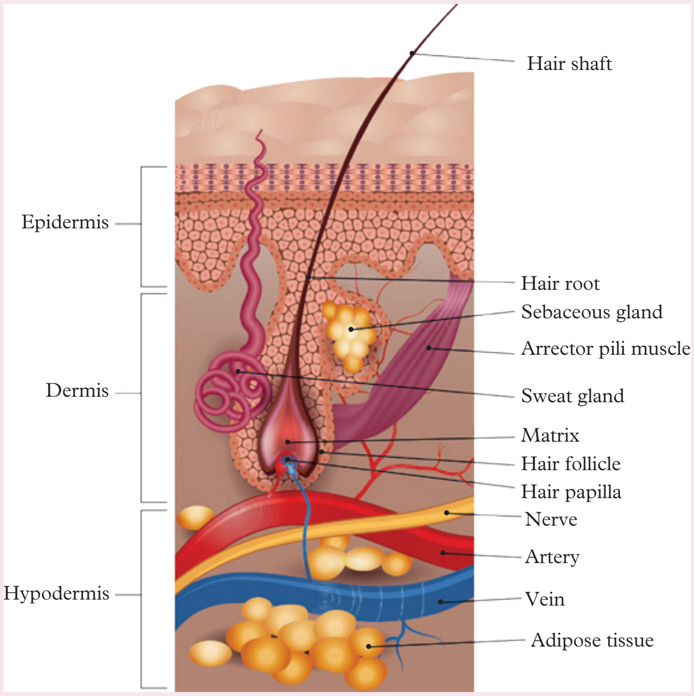


FIGURE 8 The anatomy of a hair follicle

Check your learning 8.1

Check your learning 8.1: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** the structural differences between a galvanic cell and an electrolytic cell. (2 marks)

2 **Describe** the differences between the electrodes of galvanic cells and electrolytic cells. (2 marks)

3 **Construct** a diagram of an electrolytic cell for

  a aqueous magnesium chloride

  b aqueous cobalt iodide

  c aqueous acidified potassium permanganate.

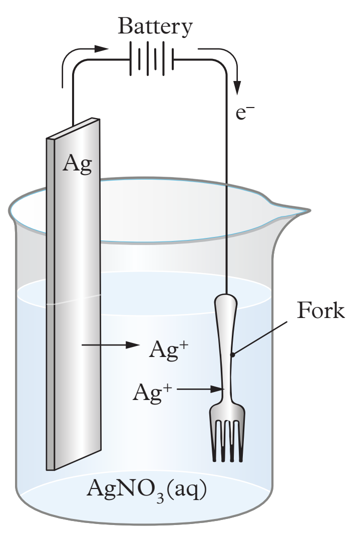
Your cell diagram must show

- reduction and oxidation half-equations (2 marks)
- anode and cathode, polarity of electrodes (1 mark)
- direction of electron and ion movement (1 mark)
- the cell voltage required by the cell. (1 mark)

Knowledge utilisation

4 A scientist needed to use chlorine gas in a reaction and decided to use electrolysis to generate the gas. **Create** a methodology to produce a supply of pure chlorine gas by electrolysis of a solution. (3 marks)

5 The experiment shown in the following diagram was set up to plate silver metal onto a brass 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 negative terminal of the battery was connected to the fork and the positive terminal to the silver electrode. The battery was turned to 4 V and run for 10 min.

- **a** **Predict** the outcome of the experiment based on the method. (2 marks)
- **b** **Evaluate** the method and **explain** anything that may affect the ability to plate silver onto the fork. (2 marks)
- **c** **Construct** an improved method. (2 marks)

6 **Predict** the products at the anode and at the cathode for the electrolysis of

- **a** molten potassium bromide (2 marks)
- **b** a molten mixture of lithium fluoride and magnesium chloride (2 marks)
- **c** molten aluminium fluoride. (2 marks)

Lesson 8.2

Faraday’s laws

Key ideas

→ Faraday’s laws can be used to predict the quantity of reactant and product or the amount of current or time required to consume a certain quantity of reactant or produce a certain quantity of product.

→ Faraday’s first law states that the charge of a cell is proportional to the mass plated at the cathode: $Q \propto m$.

→ Faraday’s second law states that in order to produce 1 mol of a metal, 1, 2, 3 or another whole number of moles of electrons must be consumed: $Q = n(e^-) \times F$.

Learning intentions and success criteria

How did Faraday conduct his experiments?

Faraday's laws of electrolysis were first developed using electrolytic cells. In the development of his laws, Faraday ran an electrical current through various solutions that contained indicators. In his experiments (Figure 1), he used a glass plate with two tin foil squares attached. To these squares, he attached copper wires that led to a power source, and platinum electrodes that connected the circuit to a piece of filter paper at the centre of the glass plate. The purpose of the platinum electrodes was not only to conduct the electrical current through a solution on the filter paper, but also to hold the filter paper in place.

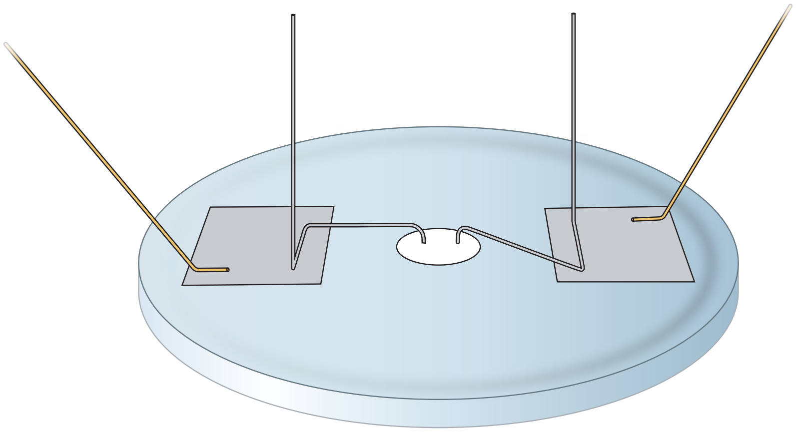
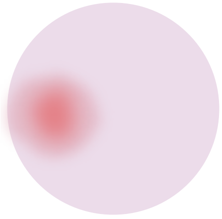
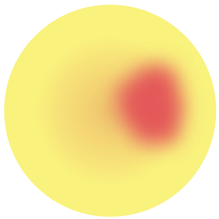
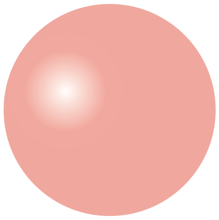


FIGURE 1 Faraday's apparatus for investigating electrolysis

Faraday repeated his experiment using four different solutions with indicators, as shown in Table 1.

TABLE 1 Experimental solutions and indicators used by Faraday

	Experiment 1	Experiment 2	Experiment 3	Experiment 4
Solution	Potassium iodide (KI)	Sodium chloride (NaCl)	Sodium sulfate (Na_2SO_4)	Hydrochloric acid (HCl)
Indicator	Starch	Litmus solution	Turmeric	Litmus solution
How the indicator works	Starch turns blue in the presence of iodine (I_2).	Litmus solution turns red in acidic conditions (H^+).	Turmeric is yellow in acidic or neutral conditions but red in alkaline conditions (OH^-).	Litmus solution starts red in acidic conditions (H^+) and turns blue in alkaline conditions (OH^-).
Results				

The results of Faraday's experiment can be explained with an understanding of electrolysis.

The results of solution 1

Oxidation occurs at the positive anode: $2I^-(aq) \rightarrow I_2(s) + 2e^-$

Reduction occurs at the negative cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Although Faraday may not have known what was happening at the cathode, the blue dot on the left of the filter paper can be observed. This was due to the iodide undergoing oxidation to form iodine at the positive anode.

The results of solution 2

Oxidation occurs at the positive anode: $2H_2O(l) \rightarrow O(g) + 4H^+(aq) + 4e^-$

Reduction occurs at the negative cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

The red dot on the left of the filter paper can be observed. This was due to the oxidation of water into oxygen gas and protons. The litmus paper turned red on the formation of the protons as the solution at the anode became acidic.

The results of solution 3

Oxidation occurs at the positive anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Reduction occurs at the negative cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

The red dot on the right of the filter paper can be observed. This was due to the reduction of water into hydrogen gas and hydroxide ions. The turmeric turned red on the formation of the hydroxide as the solution at the cathode became alkali.

The results of solution 4

Oxidation occurs at the positive anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Reduction occurs at the negative cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

The white dot on the left of the filter paper can be observed. This was unexpected because the litmus solution should remain red at the anode due to the formation of protons. As the experiment was conducted under non-standard conditions, Faraday was observing the chloride and water half-equations (at +1.36 and +1.23 V) swap, and chloride become a stronger reductant than water. The chlorine that is forming at the anode is bleaching the paper from its red colour to white, resulting in the white spot.

How can Faraday's work be used to quantify electrochemistry?

In an electroplating cell, a metal will be deposited onto the cathode of the cell. Faraday's laws investigate the relationship between the mass of the metal that is deposited and the amount of charge that is applied to the cell.

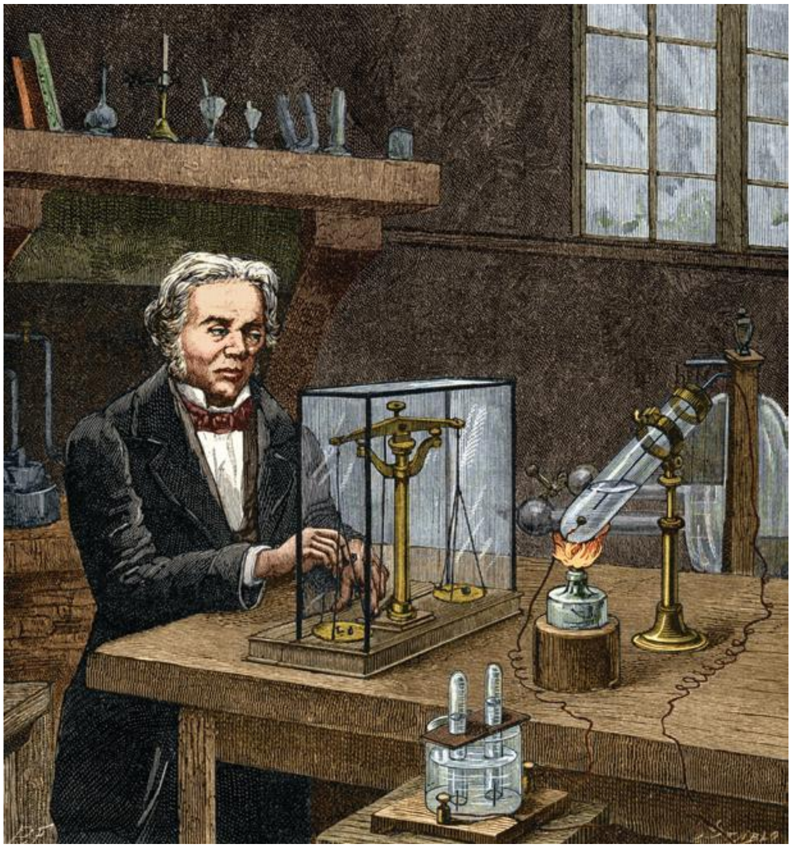


FIGURE 2 Faraday's laboratory

Faraday's first law

Current is a flow of **charge**. Charge is a property possessed by subatomic particles such as electrons and protons. Any particle with an excess or a deficiency of electrons will be charged. In chemistry, both monatomic and polyatomic ions, must be considered. Within an external circuit, the charge-carrying particle is the electron; within electrolytes, both molten and solution form, ions carry charge. In electrochemistry, the total charge used is measured by considering the current and the time the current was applied for. To measure the amount of current flowing through an electrochemical cell, an ammeter must be attached in the external circuit, which measures the current of the cell in amperes, often referred to as amps (A). A timer is also required to determine the length of time (in seconds) that the current is flowing for.

current
the flow of electrons generated by a power source; the number of coulombs of charge per second, measured in amps (A); symbol for current is *I*

charge
a property of subatomic particles, for example each electron has a 1– charge; measured in coulombs (C) and represented by *Q*

The amount of electric charge (Q) (in **coulombs**) that passes through a cell can be calculated as the product of current (I) (in amps) and time (t) (in seconds):

$$Q = I \times t$$

$$\text{coulombs (C)} = \text{amps (A)} \times \text{seconds(s)}$$

coulomb
the unit used to measure charge, 1 coulomb (C) of charge is the amount of charge carried by a current of 1 amp (A) flowing for a time of 1 second

Faraday found that increasing the charge increased the mass of the metal that plated onto the cathode. Basically, the higher the current and the longer it runs, the larger the mass of metal, or the volume of gas, produced at the cathode.

Figure 3 demonstrates this linear relationship between the mass of metals and the charge applied to the cell.

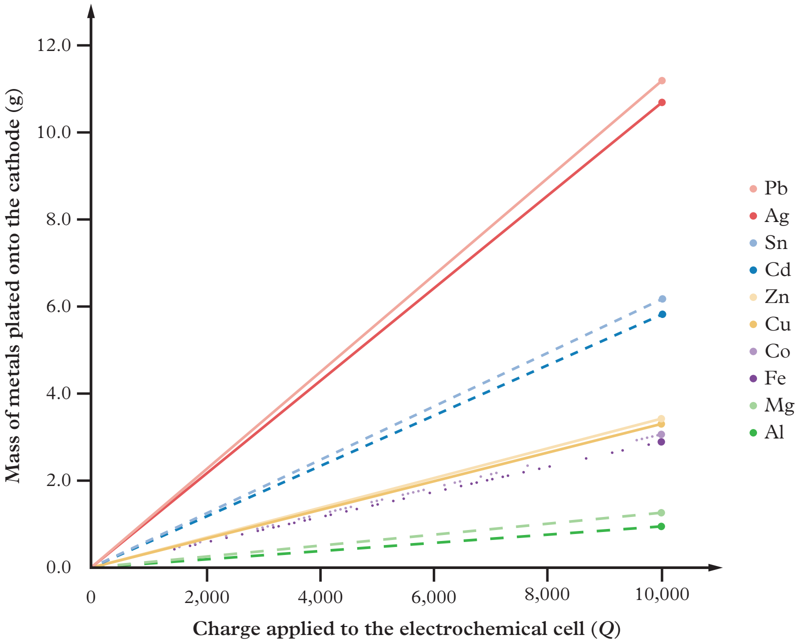


FIGURE 3 The mass of various metals plated at the cathode of an electrolysis cell when up to 10,000 C of charge is applied

Faraday determined that, the mass of the metal plated onto the cathode is proportional to the charge applied to the cell. This is **Faraday's first law**.

$$Q \propto m$$

Faraday's first law
the mass of the metal plated at the cathode is proportional to the charge applied to the cell: $Q \propto m$

Faraday's second law

Although Faraday identified the relationship between mass and charge, there was no other relationship that could be identified until he converted the mass of each metal into number of moles by dividing each by their molar masses.

He then plotted the data; the amount in moles of each metal plated at the cathode against the charge applied to the cell. A similar graph can be observed in Figure 4.

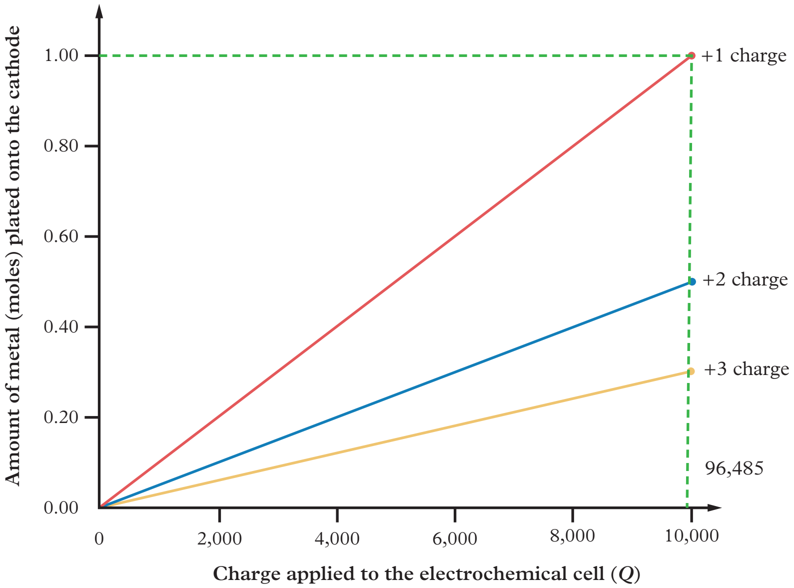


FIGURE 4 The amount in moles of various metals plated at the cathode of an electrolysis cell when charge is applied. All metal ions with a 1+ charge have the same linear trend. The same is true of metal ions with 2+ and 3+ charges.

Upon analysis of Figure 4, significant trends can be observed.

1. All metals with a 1+ charge experience the same linear trend (red trendline).
2. All metals with 2+ charges experience the same linear trend (blue trendline).
3. Although only one 3+ ion was investigated, it has its own linear trendline (yellow trendline).

Data trends could also be observed from Figure 4.

1. All 1+ metals required 96,485 C of charge to plate 1 mol of metal onto the cathode.
2. All 2+ metals required 2 × 96,485 C of charge to plate 1 mol of metal onto the cathode. Therefore, 0.5 mol of metal was plated using 96,485 C.
3. All 3+ metals required 3 × 96,485 C of charge to plate 1 mol of metal onto the cathode. Therefore, 0.33 mol of metal was plated using 96,485 C.

Faraday concluded that the charge on 1 mol of electrons must be 96,485 C. This is known as **Faraday's constant**, F, where $F = 96{,}485\ \text{C mol}^{-1}$.

Faraday's constant
1 $F = 96{,}485\ \text{C mol}^{-1}$; states that the charge of 1 mole of electrons is 96,485 C

The mathematical relationship that represents this relationship is:

$$Q = n(\text{e}^-) \times F$$

where Q is the charge of a cell (C), n is the number of moles and F is Faraday's constant (96,485 C mol^{-1}).

It can also be represented as:

$$Q = n(\text{e}^-) \times 96{,}485$$

Assuming that all of the following examples use 1 mol of electrons, the charge required to plate 1 mol of the metal can be calculated as:

- 1+ ions, which have $1e^-$, require 96,485 C of charge to plate 1 mol of the metal:

$$\text{e.g. } Na^+(aq) + e^- \rightleftharpoons Na(s)$$

$$Q = n(e^-) \times F = 1 \times 96{,}485 = 96{,}485\,C$$

- 2+ ions, which have $2e^-$, require 193,000 C of charge to plate 1 mol of the metal:

$$\text{e.g. } Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$$

$$Q = n(e^-) \times F = 2 \times 96{,}485 = 192{,}970\,C$$

- 3+ ions, which have $3e^-$, require 289,500 C of charge to plate 1 mol of the metal:

$$\text{e.g. } Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$$

$$Q = n(e^-) \times F = 3 \times 96{,}485 = 289{,}455\,C$$

Gases can also be produced at the anode by oxidation and sometimes at the cathode by reduction, as seen in Lesson 8.1. The relationships also apply for gases. Gases are not plated onto an electrode but rise and can be captured. Use the number of moles of electrons and use the half-equation to determine the mole ratio between electrons and 1 mole of gas to determine the number of moles of gas produced. The volume at a given pressure and temperature can then be calculated. $PV = nRT$ is used, where n is the number of moles of gas produced.

For example, to produce chlorine at the anode when pure chlorine is being produced, the reduction half-equation is:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

The half-equation ratios show that to produce 1 mole of chlorine gas from 2 moles of chloride ions, 2 moles of electrons would need to be removed from the ions. Therefore, $n(e^-)$ is 2, even though the ionic charge is -1. The same ratio between molecular chlorine and electrons exists in cells where a molten salt is used and chlorine is produced.

Faraday's second law
to produce 1 mole of a metal, 1, 2, 3 or another whole number of moles of electrons must be consumed

Oxygen gas can be produced by the oxidation of water and the reduction half-equation is:

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

In order to produce one mole of oxygen gas at the anode, 4 moles of electrons need to be removed from water. Therefore, $n(e^-)$ is 4, even though each oxygen atom had an oxidation state of –2 in water.

Study tip

Remember to use a ratio statement when connecting the number of moles of electron to the number of moles of the substance at the anode or cathode. The ratio can be seen by the number of electrons per mole of substance in the half-equation.

Faraday's second law states that in order to produce 1 mol of a metal or a gas, 1, 2, 3 or another whole number of moles of electrons must be consumed.

Charge on one electron

The charge on 1 mol of electrons is 96,485 C. If you consider that 1 mol of electrons is 6.02×10^{23} electrons, then the charge on one electron can be calculated as:

$$\frac{96{,}485}{6.02 \times 10^{23}} = 1.60008 \times 10^{-19}\ C$$

Because electrons are negatively charged, this number is typically represented as -1.60×10^{-19} C.

Worked example 8.2A

Calculating the mass of an electrode

An aqueous copper sulfate electroplating cell was made using 1.0 M $CuSO_4$ and two 1.50 g copper electrodes. A voltage of 8.0 V was applied, creating a current of 0.500 A for 5.00 min.

Calculate the mass of the cathode after the 5.00-minute time period. (4 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to calculate the final answer to the correct number of significant figures, showing all working throughout the process for 4 marks.
Step 2: Calculate the charge.	$Q = I \times t = 0.5\text{ A} \times (5\text{ min} \times 60\text{ s min}^{-1}) = 1500\text{ C}$ (Note: $1\text{ A} = 1\text{ C s}^{-1}$) (1 mark)
Step 3: Calculate the number of moles of electrons.	$n(\text{e}^-) = \frac{Q}{F} = \frac{1500\text{ C}}{96{,}485\text{ mol}^{-1}} = 0.0155\text{ mol}$ (1 mark)
Step 4: Determine the half-equation.	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Step 5: Calculate the number of moles of the metal deposited onto the electrode.	$n(\text{Cu}) = n(\text{e}^-) \div 2$ $= 0.0155\text{ mol} \div 2 = 7.77 \times 10^{-3}\text{ mol}$ (1 mark)
Step 6: Calculate the mass of the metal deposited onto the electrode.	$m(\text{Cu}) = n \times M$ $= 7.77 \times 10^{-3}\text{mol} \times 63.55\text{ g mol}^{-1} = 0.49\text{ g}$
Step 7: Calculate the mass of the electrode to 3 s.f.	Add the mass of the copper to the mass of the cathode. $1.5\text{ g} + 0.49\text{ g} = 1.99\text{ g}$ (1 mark)

Your turn

An aqueous nickel sulfate electroplating cell was made using 1.0 M $NiSO_4$, a 0.9 g nickel cathode and 1.2 g nickel anode. A voltage of 10.0 V is applied, creating a current of 7.52 A for 15.00 min.

Calculate the mass of the cathode after the 15.00-minute time period. (4 marks)

Worked example 8.2B

Calculating volume of gas produced during electrolysis

A solution acidified with sulfuric acid to make it conductive is added to a Hoffman's voltameter, which is a piece of equipment used to electrolyse water. Electrolysis is carried out. The oxygen and hydrogen produced at the platinum electrodes are collected separately. A sufficiently high voltage and a current of 0.020 A are used for 15.0 min. The gas produced at each electrode is measured at 23.0°C and 100.8 kPa.

a **Determine** which gas is produced at each electrode. (2 marks)

b **Calculate** the volume of hydrogen produced. (4 marks)

c **Calculate** the volume of oxygen produced. (2 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Determine" means establish, conclude or ascertain after consideration, observation, investigation or calculation. We need to consider the half-equations for the oxidation and reduction of water to match each gas to the electrode that produces it. We must also express the names of the gases and their electrodes. "Calculate" means to determine or find a number or answer by using mathematical processes. We need to show all the logical steps to calculate the volume of each gas, and express the volume with the appropriate units. All logical steps need to be shown for part marks.

▶

Think	Do
Step 2: Select the appropriate formulas and gather the required data.	Half-equations required $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ (–0.83 V) $O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 2H_2O(l)$ (+1.23 V) $Q = I \times t$ $Q = n(e^-) \times F$
Step 3: For part **a**, consider the half-equations and determine what happens at each electrode in a non-spontaneous reaction.	**a** Electrons will be pushed onto the cathode, causing reduction of water, which produces hydrogen, as in the first half-equation. (1 mark) Electrons will be removed from the anode, causing oxidation of water, which produces oxygen, as in the second half-equation when reversed. (1 mark)
Step 4: For part **b**, calculate *Q*, the quantity of charge.	**b** $Q = I \times t = 0.020\ \text{A} \times (15\,\text{min} \times 60\,\text{s}\,\text{min}^{-1}) = 180\,\text{C}$ (1 mark)
Step 5: Calculate *n*(e⁻) the number of moles of electrons.	$n(e^-) = \frac{Q}{F} = \frac{180\ \text{C}}{96{,}485\ \text{C mol}^{-1}} = 1.866 \times 10^{-3}$ mol (1 mark)
Step 6: Use the ratio of electrons to hydrogen to determine the number of moles of hydrogen gas.	(From the first half-equation) 2 mol of e^- produces 1 mol of H_2 $n(H_2) = \frac{1.866 \times 10^{-3}\ \text{mol}}{2} = 9.33 \times 10^{-4}$ mol (1 mark)
Step 7: Use the ideal gas law to calculate the volume of hydrogen. R can be found in the QCAA *Formula and data book*. Remember to change temperature to kelvin. Finalise by recording your answer to 2 s.f. and include units of L.	$PV = nRT$ So $V = \frac{nRT}{P}$ $= \frac{9.33 \times 10^{-4}\ \text{mol} \times 8.31\ \text{J K}^{-1}\text{mol}^{-1} \times (23 + 273)\text{K}}{100.8\ \text{kPa}}$ $= 0.0228$ L 0.023 L of hydrogen is produced. (1 mark)
Step 8: For part **c**, use *n*(e⁻) from step 5 for this step as the amount of electrons pushed onto the cathode will be the same as the amount of electrons removed from the anode. Use the ratio of electrons to oxygen to determine the number of moles of oxygen gas.	**c** (From the second half-equation) Removing 4 mol of e^- produces 1 mol of O_2 $n(O_2) = \frac{1.866 \times 10^{-3}\,\text{mol}}{4}$ $= 4.664 \times 10^{-4}$ mol (1 mark)
Step 9: Use the ideal gas law to calculate the volume of hydrogen. *R* can be found in the QCAA *Formula and data book*. Remember to change temperature to kelvin. Finalise by recording your answer to 2 s.f. and include units of L. (Notice that the volume of oxygen is half the volume of hydrogen reflecting the ratio of oxygen and hydrogen in water.)	$PV = nRT$ So $V = \frac{nRT}{P}$ $= \frac{4.664 \times 10^{-4} \times 8.31 \times (23 + 273)}{100.8}$ $= 0.0114$ L 0.011 L of hydrogen is produced. (1 mark)

Your turn

A saturated solution of NaCl (brine) is electrolysed. The chlorine and hydrogen produced at the platinum electrodes are collected separately. A current of 0.10 A is used for 10.0 min. The gas produced at each electrode is measured at 21°C and 101 kPa.

a **Determine** which gas is produced at each electrode. (2 marks)

b **Calculate** the volume of chlorine produced. (4 marks)

c **Calculate** the volume of hydrogen produced. (2 marks)

Worked example 8.2C

Calculating time

A modern aluminium refinery uses a current of 300,000 A to extract aluminium from molten aluminium oxide. **Calculate** how long (hours) the cell has to operate for it to produce 202 kg of molten aluminium at the cathode. (4 marks)

$$Al^{3+}(l) + e^- \rightarrow Al(s)$$

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to calculate the final answer to the correct number of significant figures, showing all working throughout the process.
Step 2: Calculate the amount in moles of the aluminium metal.	$n(\mathrm{Al}) = \frac{m}{M} = \frac{202\,\mathrm{kg} \times 1{,}000\ \mathrm{g\ kg^{-1}}}{26.98\ \mathrm{g\ mol^{-1}}} = 7{,}487\ \mathrm{mol}$ (1 mark)
Step 3: Calculate the amount in moles of electrons, using a ratio statement from the half-equation. Remember, because the half-equation has been given to you, you do not need to rewrite it.	$n(e^-) = n(\mathrm{Al}) \times 3$ $= 22{,}461\,\mathrm{mol}$ (1 mark)
Step 4: Calculate the charge used in the cell.	$Q = n(e^-) \times F$ $= 22{,}461\ \mathrm{mol} \times 96{,}485\ \mathrm{C\ mol^{-1}}$ $= 2.167 \times 10^{-9}\,\mathrm{C}$ (1 mark)
Step 5: Calculate the time that the cell has to run for and then convert this to hours.	$t = \frac{Q}{I} = \frac{2.167 \times 10^{-9}\ \mathrm{C}}{300{,}000\ \mathrm{A}} = 7{,}224\ \mathrm{s}$ $\frac{7224\ \mathrm{s}}{60\ \mathrm{s\ min^{-1}}} = 120\ \mathrm{min}$ $\frac{120\ \mathrm{min}}{60\ \mathrm{h\ min^{-1}}} = 2.00\ \mathrm{h}$
Step 6: Calculate the time to 3 s.f.	Final answer: 2.00 h (3 s.f.) (1 mark)

Your turn

To plate 10.0 g of iron onto the cathode of a cell, a current of 12.0 A is applied. **Calculate** how long (hours) the cell has to operate for it to deposit this mass onto the electrode. (4 marks)

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

Worked example 8.2D

Calculating the charge on a metal ion

To determine the charge on a metal ion, a current of 1.465 A is run for 9,500 s to plate a mass of 2.5 g of chromium at the cathode of a cell. **Calculate** the charge on the chromium ion. (4 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to calculate the final answer to the correct number of significant figures, showing all working throughout the process.
Step 2: Determine the charge.	$Q = I \times t = 1.465\ \mathrm{A} \times 9{,}500\ \mathrm{s} = 13{,}917.5\,\mathrm{C}$ (1 mark)

Think	Do
Step 3: Determine the number of moles of electrons from the charge.	$n(e^-) = \frac{Q}{F} = \frac{13{,}917.5\ \text{C}}{96{,}485\ \text{C mol}^{-1}} = 0.144$ mol (1 mark)
Step 4: Determine the number of moles of the metal from its mass.	$n(\text{Cr}) = \frac{m}{M} = \frac{2.50\ \text{g}}{52.0\ \text{g mol}^{-1}} = 0.048$ mol (1 mark)
Step 5: Construct a ratio statement to determine the ratio of electrons to the metal.	$\text{Cr(s)} + xe^- \rightleftharpoons \text{Cr}^{x+}$ $n(e^-){:}\ n(\text{Cr}) = 0.144{:}0.048$ $\therefore x = \frac{0.144}{0.048} = 3$
Step 6: Calculate the charge, no significant figures necessary.	Final answer: The charge on the chromium ion is 3+, Cr^{3+}. (1 mark)

Your turn

To determine the charge on a metal ion, a current of 1.434 A is run for 5 h to plate a mass of 8.5 g of copper at the cathode of a cell. **Calculate** the charge on the copper ion. (4 marks)

Challenge

Thickness of plating on an electrode

A tin mug is being used as an award. Before being presented, it must be plated with silver. The mug has a surface area of 280 cm^2, and the density of silver is 10.49 g cm^{-3}. Assuming that there is only 1.00 h to plate the silver onto the mug and that a current of 5.0 A can be generated, **calculate** the thickness of silver that can be plated onto the mug.

$$\text{Thickness of the metal (cm)} = \frac{\text{volume (cm}^3)}{\text{surface area (cm}^2)}$$

1 **Calculate** the mass of the silver that is plated. (2 marks)
2 **Calculate** the volume of silver based on its mass and density. (1 mark)
3 **Calculate** the thickness of the silver as volume divided by surface area. (1 mark)

Skill drill

Analysing the effect of voltage on electrolysis

Science inquiry skill: Processing and analysing data (Lesson 1.7)

A student designs an experiment to determine the effect of an increase in voltage on the charge running through a cell and therefore the mass plated at the cathode in a 1 M aqueous copper(II) sulfate electrolytic cell.

They measure the mass of the cathode before and after each experiment to calculate the mass gained. They apply 4, 6 and 10 V to the cell for 5 min each experiment and repeat each voltage three times. For each voltage, they obtain a current of 1.5, 3.0 and 4.5 A.

Practise your skills

1 **Calculate** the theoretical charge and mass expected in the experiment. (6 marks)
2 **Sketch** a graph to represent the trend in the theoretical data. (2 marks)
3 As they conduct the experiment, the student observes that the temperature of the copper sulfate solution increases. **Propose** a reason why this would occur. (2 marks)

How can Faraday's laws be applied in everyday situations?

Although Faraday's laws were developed using electroplating cells, which require electrical energy, they can equally be applied to galvanic and fuel cells, which generate it.

In these cases, it is essential to understand that the current (A) is determined by the resistance of the device that the battery/cell is powering, and voltage (V) is the push of electrons supplied by the battery/cell.

Therefore, these calculations may be used to determine the life of a battery or the length of time that it takes for the cell to consume all its reactants. Alternatively, it may be used to calculate the amount of reactant required to ensure that a cell lasts for a desired period of time.

Calculating the amount of reactants in a battery

The amount of reactant in a battery or cell will decrease over time as the amount of product increases. This can be calculated as a decrease in mass of reactants or an electrode or a decrease in concentration of aqueous reactants. Alternatively, it can be the increase in mass of an electrode when the electrolyte plates onto it.

Worked example 8.2E

Calculate the mass loss of a copper electrode

A copper–silver galvanic cell consisting of Cu|Cu^{2+} (1 M) and Ag|Ag^{+} (1 M), is connected to a small 40 W light bulb for 75.0 min. During that time, the average current drawn by the bulb is 0.36 A. **Calculate** the mass of copper that will dissolve from the anode during this time. (4 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to calculate the final answer to the correct number of significant figures, showing all working throughout the process.
Step 2: Calculate the charge.	$Q = I \times t$ $= 0.36\text{ A} \times (75.0\text{ min} \times 60\text{ s min}^{-1}) = 1{,}620\text{ C}$ (1 mark)
Step 3: Calculate the number of moles of electrons.	$n(e^-) = \frac{Q}{F}$ $= \frac{1{,}620\text{ C}}{96{,}485\text{ C mol}^{-1}} = 0.0168\text{ mol}$ (1 mark)
Step 4: Write a half-equation.	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Step 5: Complete the ratio statement.	$n(Cu) = n(e^-) \div 2$ $= 0.0168\text{ mol} \div 2 = 0.0084\text{ mol}$ (1 mark)
Step 6: Calculate the mass of the copper electrode that is dissolved in the battery.	$m(Cu) = n \times M$ $= 0.0084\text{ mol} \times 63.55\text{ g mol}^{-1} = 0.53\text{ g}$
Step 7: Calculate the mass to 2 s.f.	Final answer: 0.53 g (2 s.f.) (1 mark)

Your turn

An zinc–nickel galvanic cell consisting of 1 M concentrations of reactants, is connected to a small 60 W light bulb for 45.0 min. During that time, the average current drawn by the bulb is 0.54 A. **Calculate** the mass of metal that will dissolve from the anode during this time. (4 marks)

Worked example 8.2F

Calculate the mass of lead formed in a car battery

A car battery is often called a lead–acid battery because of the nature of the reactants and the electrolyte. The reactions occurring at each electrode are

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$
$$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$

A car is left in the driveway of a house, turned off with the lights and radio on. The battery runs using a current of 1.20 A for 1.00 h.

Calculate the mass of lead that is oxidised per hour. (4 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to calculate the final answer to the correct number of significant figures, showing all working throughout the process.
Step 2: Calculate the charge	$Q = I \times t$ $= 1.20 \times (1 \times 60 \times 60) = 4{,}320\,C$ (1 mark)
Step 3: Calculate the number of moles of electrons.	$n(e^-) = \frac{Q}{F}$ $= \frac{4{,}320}{96{,}485} = 0.13$ mol (1 mark)
Step 4: Complete a ratio statement using the oxidation half-equation to determine the number of moles of electrons.	$n(Pb) = n(e^-) \div 2$ $= 0.045 \div 2 = 0.022$ mol (1 mark)
Step 5: Calculate the mass of lead that is oxidised in the battery.	$m(Pb) = n \times M$ $= 0.022 \times 207.2 = 4.64$ g
Step 6: Calculate the mass per hour to 3 s.f.	Final answer: 4.64 g (3 s.f.) (1 mark)

Your turn

An electric vehicle's lithium battery is highly dangerous because lithium catches fire when it reacts with water. The reactions occurring at each electrode are

$$LiC_6(s) \rightarrow C_6(s) + Li^+(aq) + e^-$$
$$Li^+(aq) + CoO_2(s) + e^- \rightarrow LiCoO_2(s)$$

An EV driving on a hot day, using the radio, air conditioner and various electronic equipment, will run using a current of 40.0 A for 3.00 h.

Calculate the mass of $LiC_6(s)$ oxidised per hour. (4 marks)

Study tip

If a half-equation is not given in the question, it should be included in your answer with the ratio statement. If it is given in the question, there is no need to rewrite it in your answer; just write the ratio statement.

How do you calculate the life of a battery?

When calculating the life of a cell, the amount of time it will take to consume the reactants, it is essential to know how much reactant is present, and the current that is produced. In practice, most galvanic cells stop working well before all of the reactants are consumed, due to reaching concentrations insufficient to power an external circuit. We then say they are flat. A fuel cell which has a supply of fuel will be able to continue consuming the fuel until it is used.

Worked example 8.2G

Calculate the time to consume a tank of hydrogen gas

A hydrogen–oxygen fuel cell uses an acidic electrolyte. 5.00 kg of H_2 can be stored in a 125 L tank to power the fuel cell, and the car it is connected to requires a current of 75.0 A. **Calculate** the time (in days) that it would take to consume the H_2 in the tank. (4 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Calculate" means to determine or find a number or answer by using mathematical processes. We need to calculate the final answer to the correct number of significant figures, showing all working throughout the process.
Step 2: Calculate the number of moles of hydrogen.	$n(H_2) = \frac{m}{M}$ $= \frac{5{,}000\text{ g}}{2.02\text{ g mol}^{-1}} = 2{,}475\text{ mol}$ (1 mark)
Step 3: Write a balanced half-equation for hydrogen in acidic conditions.	$2H^+(aq) + 2e^- \rightarrow H_2(g)$
Step 4: Complete a ratio statement to determine the number of moles.	$n(e^-) = n(H_2) = 2{,}475\text{ mol}$ (1 mark)
Step 5: Calculate the charge.	$Q = n(e^-) \times F = 2{,}475\text{ mol} \times 96{,}485\text{ C mol}^{-1} = 2.388 \times 10^8\text{ C}$ (1 mark)
Step 6: Calculate the time.	$t = \frac{Q}{I} = \frac{2.388 \times 10^8\text{ C}}{75\text{ A}} = 3.18 \times 10^6\text{ s}$ $3.18 \times 10^6\text{ s} \div 60\text{ s min}^{-1} = 5.31 \times 10^4\text{ min}$ $5.31 \times 10^4\text{ min} \div 60\text{ min h}^{-1} = 884.5\text{h}$ $884.5\text{ h} \div 24\text{ h day}^{-1} = 36.86\text{ days}$
Step 7: Calculate the time to an appropriate number of significant figures	Final answer: 36.9 days (3 s.f.) (1 mark)

Your turn

A hydrogen–oxygen fuel cell uses an acidic electrolyte. 100.0 L of H_2 can be stored in a tank at SLC to power the fuel cell, and the bus it is connected to requires a current of 125.0 A. **Calculate** the time (in days) that it would take to consume the H_2 in the tank. (4 marks)

Skill drill

Determining the aim, hypothesis and variables

Science inquiry skill: Understanding the scientific method (Lesson 1.3)

A student designs an experiment to verify Faraday's second law of electrolysis. The student compares each of the following half-cells to the standard hydrogen half-cell ($H_2|H^+$):

$Ag|Ag^+$
$Au|Au^+$
$Cu|Cu^{2+}$
$Mg|Mg^{2+}$

He applies 6 V to each electrochemical cell for 5.0 min and generates a current of 0.25 A in each cell.

Practise your skills

1 **Identify** the independent and dependent variables. (2 marks)
2 **Generate** a hypothesis for the experiment. (2 marks)
3 **Identify** the aim of the experiment. (2 marks)

Challenge

Percentage of fuel remaining

An ethanol fuel cell uses an acidic electrolyte. 5.000 L of ethanol (density of 0.789 g mL^{-1}) is combusted into carbon dioxide when pumped through the cell over the course of 16.50 h. The half-equation for this reaction has an $E°$ value of –0.33 V. The cell is capable of producing current of 100.0 A.

a **Calculate** the volume of ethanol that is consumed in 16.5 hours. (5 marks)

b **Calculate** the percentage of ethanol remaining for future use. (2 marks)

Real-world chemistry

What is a watt?

The watt (W) was named after James Watt, an eighteenth century Scottish inventor. His most famous work was first developed from his observation of a kettle. When it boiled, the steam pushed the cap of the kettle, which led to his fascination with the potential of steam to push more objects. At this time, the steam engine had already been invented; however, Watt's work led to significant improvements on the design.

Due to the significance of his work, the watt was named after him. A watt is the SI unit of power or work. It is measured in joules per second (J s^{-1}) and can be calculated as

$$P = V \times I$$

where P is power in watts (W), V is voltage in volts (V) and I is current in amps (A).

In Chemistry, we often use the formula:

$$E = V \times I \times t$$

to calculate the energy involved in a galvanic, primary, fuel or electrolytic cell. This is a variation on power and watts.

Most electrical equipment has a sticker that states the electrical requirements of the appliance. This will often include a voltage and a wattage value.

To calculate your daily energy consumption, in kilowatt hours (kWh), you must multiply the wattage (W) by the number of hours (h) used per day and then divide this by 1,000 to convert it into kilowatt hours:

$$\text{Daily energy consumption} = \frac{\text{watts} \times \text{ hours of used per day}}{1{,}000}$$

$$= \text{kWh}$$

Electricity bills detail your total energy consumption as the number of days that electricity has been consumed, the amount consumed (in kWh), the rate, which represents the cost of the electricity, and the supply charge (service charge). It may also break this down into light/power and heating/hot water. The kWh value is measured from your electricity meter, which is connected to the electrical system of your house.

Apply your understanding

1 If an electrical appliance states that it requires 720 W and 230 V, **calculate** the current supplied to the device. Assuming that it is used for 5 min, **calculate** the charge applied to the appliance. (2 marks)

2 A device requires 0.5 A and 3.75 W. Assuming a single dry cell (commonly referred to as a battery in daily usage) creates a voltage of 1.5 V, **determine** how many dry cells are required to power the device. (2 marks)

3 A battery-powered LED desk lamp contains a 3 V cell and requires a current of 1.67 A. Assuming the lamp operates for 3 h, **calculate** the energy usage in kWh. (2 marks)

Check your learning 8.2

Check your learning 8.2: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** what 1 faraday represents. (1 mark)

2 **Explain** what charge is and how it can be calculated. (2 marks)

3 **Calculate** the mass of metal plated onto the cathode in a molten cell consisting of CaF and KBr salts, when run for 10 h at a current of 5.5 A. (4 marks)

4 **Calculate** the mass of gas that evolves at the anode of an aqueous NaF(aq) cell when run for 30.0 min at 0.90 A. (4 marks)

5 In a tin plating cell the half-equation occurring at the cathode is:

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

Calculate the mass of tin plating at the cathode with a current of 8.00 A for 15.0 min. (4 marks)

6 In a silverplating cell, the half-equation occurring at the cathode is:

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

Calculate how long, in hours, it would take to deposit 10.0 g of silver at the cathode of an aqueous silver-plating cell that runs at a current of 5.10 A. (4 marks)

Practical

Lesson 8.3

Investigating factors affecting electrolysis

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Learning intentions and success criteria

Practical

Lesson 8.4

Electroplating using an electrolytic cell

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Learning intentions and success criteria

MODULE 8

Lesson 8.5

Review: Electrolytic cells

Summary

8.1
- The process of electrolysis involves reversing spontaneous reactions and converting electrical energy into chemical energy. For this process, an electric charge must be applied. It is the opposite of a galvanic cell.
- The electrolysis of molten liquids occurs in the absence of water, but the electrolysis of aqueous solutions occurs in solutions where salts are dissolved in water.

8.2
- Faraday's laws can be used to predict the quantity of reactant and product or the amount of current or time required to consume a certain quantity of reactant or produce a certain quantity of product.
- Faraday's first law states that the charge of a cell is proportional to the mass plated at the cathode: $Q \propto m$.
- Faraday's second law states that in order to produce 1 mol of a metal, 1, 2, 3 or another whole number of moles of electrons must be consumed: $Q = n(e^-) \times F$.

8.3
- Practical: Investigating factors affecting electrolysis

8.4
- Practical: Electroplating using an electrolytic 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	$\text{EMF} = E^\circ_{\text{reduction half-cell}} - E^\circ_{\text{oxidation half-cell}}$
Charge (Q)	$Q = It$
Charge (Q)	$n(e^-) = \frac{Q}{F}$
1 faraday	96,485 C mol^{-1}

Review questions 8.5A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

1 In an electrolytic cell
- **A** reduction occurs at the positive electrode, which is connected to the negative terminal of the power source.
- **B** reduction occurs at the negative electrode, which is connected to the negative terminal of the power source.
- **C** oxidation occurs at the positive electrode, which is connected to the negative terminal of the power source.
- **D** oxidation occurs at the negative electrode, which is connected to the negative terminal of the power source.

2 In an electrolytic cell, the
- **A** electrolyte allows for the movement of ions in the internal circuit.
- **B** salt bridge allows for the movement of ions in the internal circuit.
- **C** electrolyte allows for the movement of electrons in the internal circuit.
- **D** salt bridge allows for the movement of electrons in the internal circuit.

3 The voltage used to recharge a cell in electrolysis is
- **A** equal to the voltage produced in the galvanic process.
- **B** less than 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 Rechargeable batteries work because
- **A** the reaction during discharge is non-spontaneous and can be reversed.
- **B** during charging, more electrons are stored inside the battery for later use.
- **C** they can produce electrical energy from chemical energy when an external current is applied.
- **D** the cell reaction during discharge can be reversed by applying a current in the opposite direction.

5 During the electrolysis of molten lead bromide ($PbBr_2$), which half-equation correctly represents the reaction occurring at the anode?
- **A** $2H^+ + 2e^- \rightarrow H_2$
- **B** $Pb^{2+} \rightarrow Pb + 2e^-$
- **C** $Pb^{2+} + 2e^- \rightarrow Pb$
- **D** $2Br^+ \rightarrow Br_2 + 2e^-$

6 During the electrolysis of an aqueous solution of sodium chloride, which of the following is produced at the cathode?
- **A** Oxygen gas
- **B** Chlorine gas
- **C** Sodium metal
- **D** Hydrogen gas

Use the following information to answer questions 7 and 8.

A molten electrolytic cell was set up using inert electrodes and a mixture of sodium chloride and barium bromide.

7 Which half-equation occurs at the anode?
- **A** $2Br^-(l) \rightarrow Br_2(g) + 2e^-$
- **B** $Br_2(g) + 2e^- \rightarrow 2Br^-(l)$
- **C** $Cl_2(g) + 2e^- \rightarrow 2Cl^-(l)$
- **D** $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

8 Which half-equation occurs at the cathode?
- **A** $Na(l) \rightarrow Na^+(l) + e^-$
- **B** $Na^+(l) + e^- \rightarrow Na(l)$
- **C** $Ba(l) \rightarrow Ba^{2+}(l) + 2e^-$
- **D** $Ba^{2+}(l) + 2e^- \rightarrow Ba(l)$

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** The electrolyte solution becomes darker in colour.
- **C** A colourless and odourless gas is produced at the positive electrode.
- **D** A colourless and odourless gas is produced at the negative electrode.

10 During the electrolysis of a tin(II) nitrate solution, nitrate ions are
- **A** attracted to the anode, where they undergo oxidation.
- **B** attracted to the cathode, where they undergo reduction.
- **C** attracted to one electrode but are neither oxidised nor reduced.
- **D** not attracted to either electrode because they are spectator ions only.

Review questions 8.5B Short response

Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

11 **Explain** whether electrons can move through a solution. (2 marks)

12 **Explain** why the polarity assigned to electrodes is reversed in an electrolytic cell, compared to a galvanic cell. (2 marks)

13 **Explain** why reactants are kept in the same vessel in an electrolytic cell but must be separated in a galvanic cell. (2 marks)

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
- oxidation and reduction half-equations (2 marks)
- anode and cathode, electrode polarity (1 mark)
- overall equation (1 mark)
- strongest oxidant and strongest reductant (1 mark)
- movement of ions in the cell and the movement of electrons. (1 mark)

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 (2 marks)
- the strongest oxidant and reductant (1 mark)
- the oxidising and reducing agent (1 mark)
- a balanced overall equation. (1 mark)

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 For the following electrolytic cells, **identify** the

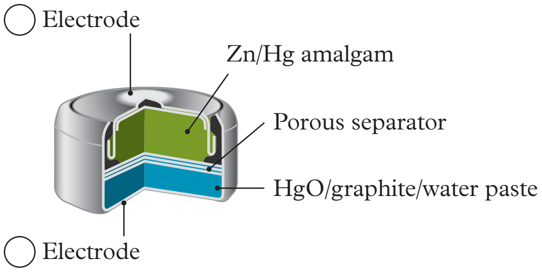
- anode and cathode and electrode polarity (1 mark)
- the material the electrodes are made from (1 mark)
- oxidation and reduction half-equations, including states, and labelled as oxidation or reduction (2 marks)
- electrolyte (demonstrating ion movement within the cell) and direction of electron flow (1 mark)
- the minimum voltage required for the cell to recharge (1 mark)
- overall balanced chemical equation including states. (1 mark)

a A mixture of molten lithium chloride and molten calcium iodide

b A mixture of aqueous calcium nitrate, aqueous nickel bromide and aqueous potassium chloride

c An aqueous solution of potassium fluoride (KF)

17 A zinc–mercury button cell battery is shown in the following diagram.



Cell reaction:
$Zn(s) + HgO(s) \rightarrow Hg(l) + ZnO(s)$

a **Identify** the positive and negative electrodes of the cell. (1 mark)

b **Construct** the half-equation for the reaction that occurs at the anode in discharge. (1 mark)

c Assume that this button cell is alkaline and rechargeable. **Construct** the half-equation for the reaction that occurs at the cathode in recharge. (2 marks)

18 In Faraday's first experiment, there was no solid made at the cathode. **Explain** why potassium metal was not seen being deposited onto the cathode. (2 marks)

19 In solution 3 of Faraday's experiments, he used a turmeric indicator. **Identify** what alternative indicator he could have used and what results you would expect to have been observed. (2 marks)

20 A rechargeable battery uses the following half-equations.

$Fe(s) + 2OH^-(aq) \rightarrow Fe(OH)_2(s) + 2e^-$
$E°$ is positive

$Ni(OH)_2(s) + OH^-(aq) \rightarrow Ni(OH)_3(s) + e^-$
$E°$ is negative

a **Identify** the anode and cathode half-equations in both discharge and recharge and **identify** the polarity of electrodes that would result. (6 marks)

b **Identify** the overall equations in discharge and recharge. (2 marks)

c **Identify** the electrolyte in this cell. (1 mark)

21 An aqueous nickel chloride electroplating cell was made using 1.0 M $NiCl_2$. Both electrodes are made of silver. A voltage of 12.0 V is applied, creating a current of 2.50 A for 23.50 min.

a **Calculate** the mass of product generated at the cathode after the 23.50 min time period. (3 marks)

b The gas generated at the anode is collected and the volume measured at a temperature of 20.0°C and a pressure of 101 kPa. **Calculate** the volume of gas. (3 marks)

22 In an electrolytic cell, 150.0 mL of a 2.0 M lead(II) nitrate ($Pb(NO_3)_2$) solution undergoes electrolysis with a current of 3.60 A for 12.00 min. Both electrodes are made of graphite.

a **Calculate** the mass of product deposited at the cathode. (5 marks)

b **Calculate** the new concentration of the Pb^{2+} ions in the solution. (3 marks)

23 An aqueous magnesium fluoride electrolytic cell was made using 1.00 M MgF_2. Both electrodes are made of graphite. A voltage of 7.50 V is applied, creating a current of 4.5 A for 15.50 min.

- **a** **Calculate** the mass of product generated at the cathode after the 15.50 min time period if the cell is run at SLC. (3 marks)
- **b** **Calculate** the volume of gas generated at the anode after the 15.50 min time period if the cell is run at SLC. (3 marks)

Analytical processes

24 To plate 2.50 g of zinc onto the cathode of a cell, a current of 18.0 A is applied.

- **a** **Determine** how long (hours) the cell has to operate for to deposit this mass onto the electrode. (5 marks)
- **b** Consider the values of the reduction potentials of zinc ions and of water. If bubbles of gas were observed at the cathode, **identify** the gas and **deduce** the effect this will have on the mass of zinc plated in the time calculated in part **a**. (2 marks)

25 To determine the charge on a metal ion, a current of 17.19 A is run for 10 min to plate a mass of 5.128 g of molybdenum at the cathode of a cell. **Determine** the charge on the molybdenum ions used. (4 marks)

Knowledge utilisation

26 **Evaluate** the products, in terms of half-equations and overall equation, that would result from electrolytic cells where the electrolyte is

- **a** molten NaCl (3 marks)
- **b** concentrated NaCl(aq) (3 marks)
- **c** dilute NaCl(aq). (3 marks)

27 **Develop** a mind map to communicate the links and ideas between the following concepts: redox, oxidation, reduction, oxidant, reductant, oxidising agent, reducing agent, galvanic cell, battery, electrolytic cell, recharge, discharge, salt bridge, electrolyte, anode, cathode, polarity, $E°$ and power source. (6 marks)

28 **Develop** a summary of Modules 7 and 8, outlining the similarities and differences between galvanic cells and batteries. Your summary must include

- structural and chemical differences (2 marks)
- structural and chemical similarities (2 marks)
- advantages (2 marks)
- disadvantages (2 marks)
- applications. (2 marks)

29 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 (2 marks)
- **b** **construct** the overall reaction equation in discharge (2 marks)
- **c** use these equations to **evaluate** the battery, specifically explaining why it was banned in 1991 (2 marks)
- **d** **investigate** the health effects of this type of battery (2 marks)
- **e** **discuss** what battery was introduced as a substitute for the HgO battery (2 marks)
- **f** **construct** the cathode and anode half-equations in discharge for the substitute battery, labelling them as oxidation or reduction (2 marks)
- **g** **construct** the overall reaction equation for the substitute battery in discharge (1 mark)
- **h** use these equations to **evaluate** the substitute battery, specifically why it is safer than the HgO battery. (2 marks)

30 A student is given a sample of vanadium nitrate salt in a laboratory. They are given to task to determine the formula of the chemical compound, but know that vanadium can form a V^{5+}, V^{4+}, V^{3+} and V^{2+} ion.

- **a** **Design** an experiment that the student can use to determine the charge on the vanadium ion. (4 marks)
- **b** Assuming that the ion being analysed is the V^{3+} ion, based on the current and voltage that you used for part **a, calculate** the mass of vanadium that you would expect to measure. (4 marks)

Data drill

The effect of voltage on mass plated on the cathode

A student conducts a practical investigation to determine the effect of increasing the voltage in an aqueous $CuSO_4$ cell on the mass of copper plated on the cathode.

The student runs all of the trials for 3.00 min and records the current with an ammeter, the change in temperature of the cell and the change in mass of the cathode (Table 1).

Apply understanding

1 **Identify** the independent and dependent variables. (2 marks)

2 **Use** the variables to write a hypothesis for the investigation. (1 mark)

Analyse data

3 **Identify** the trend in the data by referring to the variables. (2 marks)

4 **Identify** whether the experiment is repeatable. Use the data to support your response. (2 marks)

TABLE 1 A summary of data from the experiment

Trial	Voltage (V)	Current (A)	Change in temp. (°C)	Change in mass (g)
1	4	0.42	2	0.04
2		0.63	2	0.05
3		0.65	2	0.05
4	6	0.83	2.5	0.05
5		0.97	2.5	0.06
6		0.93	2	0.06
7	8	0.77	5	0.08
8		0.93	5.5	0.06
9		1.26	6	0.07

Interpret evidence

5 Use the data to **justify** one error in the experiment. (2 marks)

6 **Determine** how the error that you identified in question **5** can be avoided. (2 marks)

Module 8 checklist: Electrolytic cells

UNIT 3 Topic 2 review

Multiple choice

(1 mark each)

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 $CH_3CH_2OH(aq) + HCOOH(aq) \rightarrow CH_3COOCH_3(aq) + H_2O(l)$

2 In a galvanic cell, the most important purpose of the salt bridge is to

A connect the two half-cells to ensure that the cell is a complete circuit.

B transfer electrons between cells and therefore carry the electricity that is generated by the cell.

C control the flow of current in the cell so that the cell does not produce excessive amounts of energy.

D transfer ions that carry charge between cells in order to balance the build-up of positive and negative charges in half-cells.

3 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:

$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$ $E° = -0.36\,V$

$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$ $E° = 1.69\,V$

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 $PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$

D $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

4 In the following reaction, what is the oxidising agent?

$$2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl^-$$

A Cl^-

B Cl_2

C Fe^{2+}

D Fe^{3+}

5 In the following reaction, what is the change in oxidation state of sulfur (S)?

$$H_2SO_4 + 8HI \rightarrow H_2S + 4I_2 + 4H_2O$$

A +4 to 0

B +6 to 0

C –2 to +6

D +6 to –2

6 Which of the following statements is true about oxidation and reduction?

A Oxidation and reduction always involve oxygen.

B Oxidation and reduction always occur separately.

C Oxidation is the gain of electrons, and reduction is the loss of electrons.

D Oxidation is the loss of electrons, and reduction is the gain of electrons.

7 In the reaction:

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

which species is oxidised?

A Cu

B Zn

C Cu^{2+}

D Zn^{2+}

8 What is the oxidation state of Mn in $KMnO_4$?

A +2

B +4

C +5

D +7

9 In a galvanic cell, the anode is the electrode where

A oxidation occurs.
B reduction occurs.
C electrons are gained.
D the solution remains neutral.

10 In a galvanic cell with Zn and Cu electrodes, electrons flow

A through the salt bridge.
B from the cathode to the anode.
C from Cu to Zn through the wire.
D from Zn to Cu through the wire.

11 Which of the following is true for an electrolytic cell?

I It converts chemical energy into electrical energy.
II It requires an external power source to drive a non-spontaneous reaction.
III The anode is positively charged.

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

12 In the electrolysis of molten NaCl, what is produced at the cathode?

A NaCl
B H_2 gas
C Cl_2 gas
D Na metal

13 In the electrolysis of water, which gas is produced at the anode?

A Oxygen
B Nitrogen
C Hydrogen
D Carbon dioxide

14 The following redox reaction occurs in a rechargeable flow cell during discharge. Which statement is correct?

$$Zn(s) + 2Ce(CH_3SO_3)_4(aq) \rightarrow 2Ce(CH_3SO_3)_3(aq) + Zn(CH_3SO_3)_2(aq)$$

A Zn is oxidised at the cathode.
B $Ce(CH_3CO_3)_4$ is oxidised at the anode.
C Zn is the oxidant and $Ce(CH_3CO_3)_4$ is the reductant.
D $Ce(CH_3CO_3)_4$ is the oxidant and Zn is the reductant.

15 Which of the following pairs of reactants will generate the highest voltage in a galvanic cell at SLC?

A Cl^-/Cl_2 and H^+/H_2
B Fe^{2+}/Fe and Ag^+/Ag
C Fe^{2+}/Fe^{3+} and H^+/H_2
D Zn^{2+}/Zn and Ni^{2+}/Ni

Short response

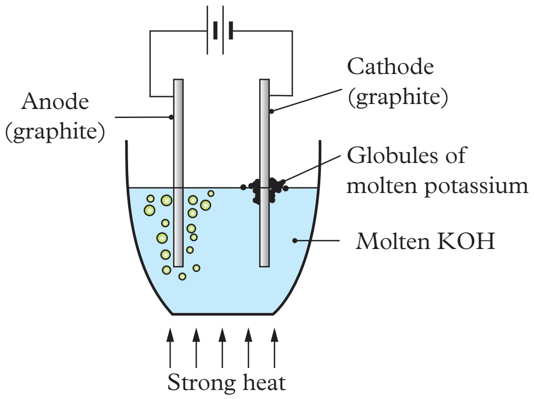
16 **Sketch** a diagram of a galvanic cell that can be used to generate a voltage of as close to 1.5 V as possible, under standard conditions. Your choice of materials must be safe enough to use in a high school laboratory.

a **Determine** and label the:
  i solutions used in the two half-cells (1 mark)
  ii two half-equations and the balanced overall equation, all must include appropriate states (3 marks)
  iii materials used as the anode and cathode and the polarity of each electrode (2 marks)
  iv salt bridge and a suitable chemical, identifying the movement of ions in the bridge (2 marks)
  v direction of electron flow (1 mark)
  vi voltage of the cell. (1 mark)

b **Justify** your choice of material for each electrode, using the electrochemical series and your knowledge of oxidants and reductants. (4 marks)

c **Justify** your choice of chemical for the salt bridge. (2 marks)

17 Potassium was discovered in 1807 by English scientist Sir Humphrey Davy. Davy passed a current through molten 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.



a **Identify** the missing components in the table. (4 marks)

	Polarity of electrode	Half-equation
Anode		
Cathode		

b **Construct** the overall reaction equation. (1 mark)

c **Determine** what minimum voltage is required to run the cell. (1 mark)

d **Deduce** what issue is involved with not including a porous membrane between the electrodes. (2 marks)

18 The cell from question **17** was recreated using a 1 M aqueous solution of KOH at 25°C and 100 kPa.

a **Identify** the missing components in the table. (4 marks)

	Polarity of electrode	Half-equation
Anode		
Cathode		

b **Construct** the overall reaction equation. (1 mark)

c **Determine** what minimum voltage is required to run the cell. (1 mark)

d **Determine** how 2 M concentrations would differ from 1 M. **Justify** your answer using the electrochemical series. (2 marks)

e A student suggests that it is not possible to produce solid potassium by aqueous electrolysis. **Justify** whether their statement is correct. (2 marks)

19 Methane is a biogas that can be extracted from the biodegradation of plants and animal matter. It combusts according to the following, unbalanced, half-equation:

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

a Using oxidation numbers, **determine** which chemical species acts as the oxidant. (2 marks)

b **Construct** the oxidation half-equation. (1 mark)

c **Construct** the reduction half-equation. (1 mark)

d **Construct** the balanced overall equation. (1 mark)

20 Iron metal reacts with oxygen in the atmosphere to produce iron oxide (Fe_2O_3), which is commonly identified as red rust.

a **Construct** the balanced overall equation. (1 mark)

b **Construct** the oxidation half-equation. (1 mark)

21 An aqueous solution of aluminium sulfate and copper bromide is added to an electrolytic cell with two inert electrodes.

a **Construct** the oxidation half-equation. (1 mark)

b **Construct** the reduction half-equation. (1 mark)

c **Construct** an overall reaction equation for the cell. (1 mark)

d **Calculate** the minimum voltage that is required by the cell. (1 mark)

e **Explain** an observation that you would make when the cell was running at SLC. (2 marks)

22 An aqueous solution of nickel chloride and zinc nitrate is added to an electrolytic cell with two inert electrodes.

a **Construct** the oxidation half-equation. (1 mark)

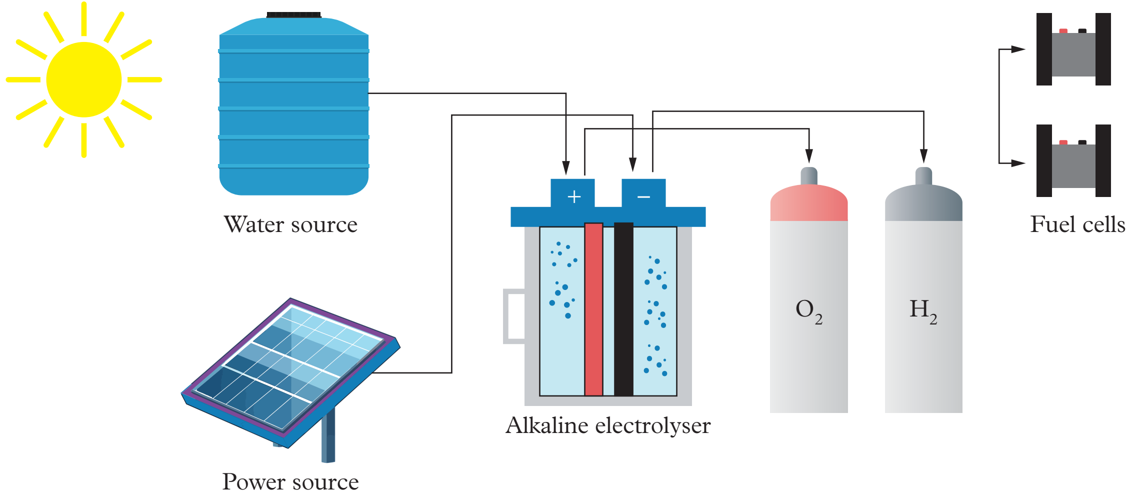
b **Construct** the reduction half-equation. (1 mark)

c **Construct** an overall reaction equation for the cell. (1 mark)

d **Calculate** the minimum voltage that is required by the cell. (1 mark)

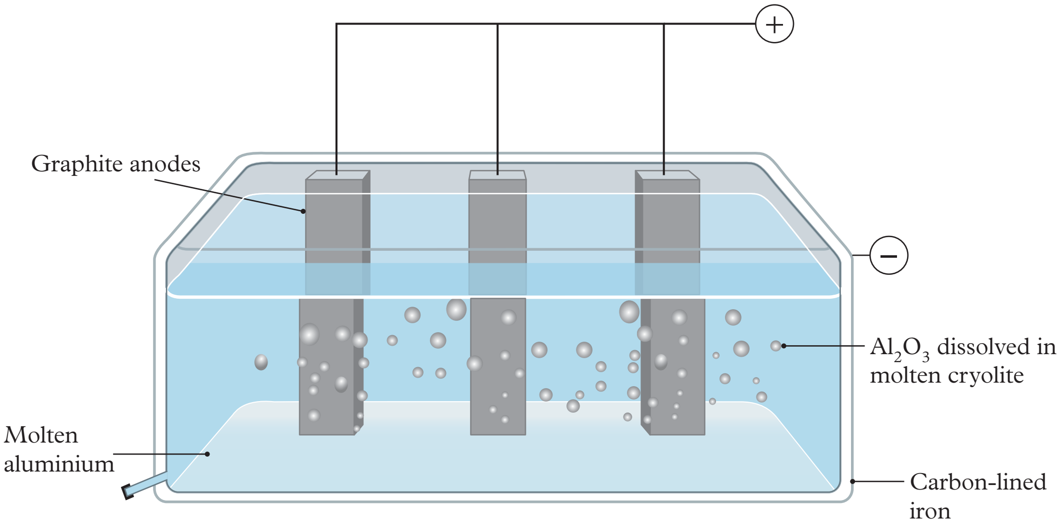
e **Explain** an observation that you would make when the cell was running at SLC. (2 marks)

23 Photovoltaic cells are being considered as an alternative for hydrogen production for use in fuel cells. The following diagram outlines the use of a solar cell to provide electricity which powers the alkaline electrolyser, then stores the hydrogen and oxygen produced and uses them in the fuel cells.



- **a** **Identify** the energy transformation occurring in the electrolytic cell. (1 mark)
- **b** **Construct** the reduction half-equation. (1 mark)
- **c** **Identify** the polarity of the anode in the electrolytic cell. (1 mark)
- **d** If the cell runs for 10 hours with a current of 5.5 A at SLC, **calculate** the volume of hydrogen gas generated by the cell. (4 marks)
- **e** **Outline** one safety consideration with this process. (2 marks)

24 Aluminium is a low-density, light metal used in the production of lightweight machinery and transport vehicles. To purify aluminium, it must first be extracted from the ground as a mineral called bauxite. The bauxite is converted to pure aluminium oxide (Al_2O_3), which is then mixed with molten cryolite (Na_3AlF_6) and melted at 1,012°C. The carbon graphite electrodes react during the process, rather than being inert, and produce CO_2(g).



- **a** **Construct** the half-equation occurring at the graphite anodes. (1 mark)
- **b** **Calculate** the mass of Al produced if the cell runs at 500,000 A and 4 V for 8 hours. (4 marks)
- **c** In a review of the process, chemists investigated why only 483.4 kg of Al was being obtained rather than the mass calculated in part **a**. **Calculate** the percentage efficiency of the process. (2 marks)
- **d** **Deduce** why aluminium is extracted from the base of the cell. (1 mark)

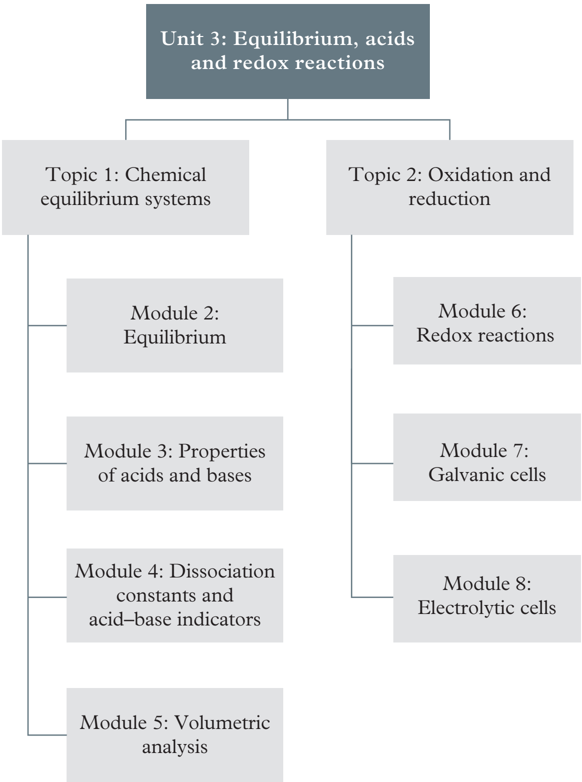
TOTAL MARKS

/85

UNIT 3 Review

PART A – Revisit and revise

Part A of the Unit review asks you to reflect on your learning and identify areas in which you need more work.



PART B – Exam essentials

Now that you've completed your revision for Unit 3, it's time to learn and practise some of the skills you will need to answer exam questions like a pro! Our expert authors have created the following advice and tips to help you maximise your results on the end-of-year examination.

Exam tip 1: Use the mark allocation to indicate the minimum number of points required in a response

Look at the number of marks awarded to a question as a guide to the number of aspects or points required to be made in the desired response. This specifically pertains to questions with the cognitive verbs "identify", "explain" and "justify". For these types of questions, it is always advisable to be explicit and sequential in your response. For example, a 3-mark question with the cognitive verb "explain" should have a response that contains a minimum of three points or aspects within it answering the question.

See it in action

Read the real exam question below and see how the tip has made a difference between a response that has scored full marks and a response where marks have been lost.

QUESTION 25 (5 marks)

Three unknown gases are combined in a sealed flask and allowed to reach equilibrium as shown by the equation.

$$3A_2(g) + X_2(g) \rightleftharpoons 2XA_3(g)$$

(a) Determine whether the gases reach a state of dynamic equilibrium. Explain your reasoning. *[3 marks]*

Source: *QCAA 2022 Chemistry External Examination Paper 1* © State of Queensland (QCAA)

Complete response

The question indicates that the three gases are contained in a sealed flask, indicating that the system is closed. This assumes there is no reaction with the external surroundings with reaction species neither entering nor leaving the system. This allows the reactants to form into products. Since the reaction is indicated to be reversible, when there is sufficient production of the product species XA_3, it will begin to decompose back into its reactants A_2 and X_2, causing a state where all three gases are present. Equilibrium will then be reached when the rate of XA_3 product formation is equal to its decomposition, reaching a steady state. In other words, the rate of the forward reaction equals that of the reverse reaction, which remains constant over time.

Explains that a closed system means that matter is not exchanged with the surroundings as opposed to just stating that it is a closed system [1 mark]

Explains further what dynamic equilibrium is – that it occurs only with reversible reactions in closed systems because all particles are present [1 mark]

Identifies that the characteristic feature of equilibrium states is the equal rates of the forward and reverse reactions [1 mark]

Incomplete response

Has identified the system is closed, which is a requirement for dynamic equilibrium, but has not justified with an explanation as to why closed systems are necessary [0 marks]

All three gases are in a closed system; hence, over time when the rate of the forward reaction equals the rate of the reverse decomposition reaction, a state of dynamic equilibrium is reached. This means that the rate of formation of product XA_3 will be equal to the rate of its decomposition into the reactants A_2 and X_2 because of the presence of all three gases remaining constant over time. Despite both reactions occurring simultaneously, because the concentration of each of the species remains constant over time but macroscopically nothing appears to change, the state is termed dynamic to indicate changes occurring at the molecular level.

Explains that equilibrium is characterised by the rate of the forward reaction being equal to the rate of the reverse reaction [1 mark]

Identifies that the three gases reach dynamic equilibrium by the characteristic feature of constantly reacting over time with each species' concentration remaining constant overtime [1 mark]

Has explained further the characteristic features of dynamic equilibrium, but still has not made reference to reactions occurring only with the species in the reaction because of the closed system [0 marks]

Think like an assessor

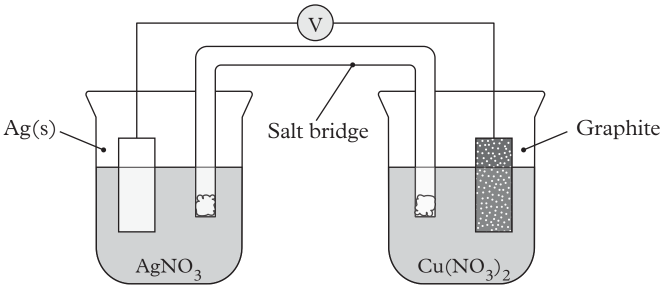
To maximise your marks on an exam, it can help to think like a QCAA assessor. Consider how many marks each question is worth and what information the assessor is looking for.

A student has given the following response in a practice exam. Imagine you are a QCAA assessor and use the marking guide below to mark the response.

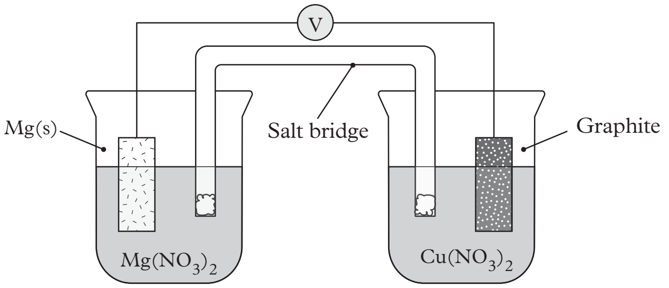
QUESTION 3 (7 marks)

An experiment was conducted at standard state conditions to investigate the potential difference (V) produced by different galvanic cells. The three cells used in the experiment are shown.

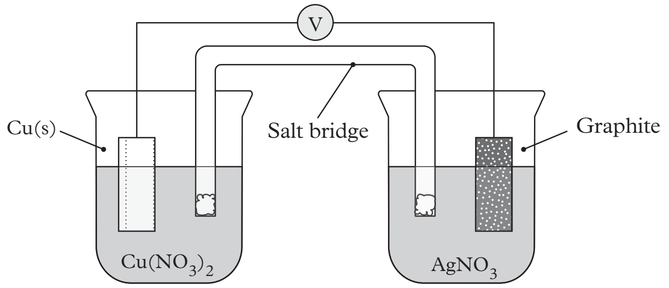
Cell 1



Cell 2



Cell 3



(a) Predict which cell produced the highest voltage. Explain your reasoning. *[3 marks]*

Source: *QCAA 2023 Chemistry External Examination Paper 2* © State of Queensland (QCAA)

Cell 2 would produce the highest voltage of 2.02 V because cell 1 and cell 3 both have a negative voltage of −1.14 V and −1.18 V respectively.

Marking guide

Question 3a	• determines that cell 1 is not spontaneous [1 mark] • determines voltage of cells 2 and 3 [1 mark] • predicts which cell produces maximum voltage [1 mark]

Source: *QCAA 2023 Chemistry marking guide and response* © State of Queensland (QCAA)

Fix the response

Consider where you did and did not award marks in the above response. How could the response be improved? Write your own response to the same question to receive full marks from a QCAA assessor.

Exam tip 2: Focus on showing all steps and using correct units when applying stoichiometry.

The most common mistakes when completing acid–base and equilibrium stoichiometry-based questions include:

- not providing a balanced acid–base equation to begin with to establish the reacting mole ratio. Frequently, students try to omit steps by incorrectly applying the formula used for dilutions rather than calculating amounts in moles and using the mole ratio.

- not ensuring that equations are correctly annotated (see QCAA *Formula and data book* for $n = cV$ rearranged from molarity/concentration $(c) = \frac{\text{moles of solute } (n)}{\text{volume of solution } (V)}$ and $\text{pH} = -\log_{10} [\text{H}^+]$ and equations such as number of moles $(n) = \frac{\text{mass } (m)}{\text{molar mass } (M)}$)
- not ensuring that equilibrium dissociation equations are correctly expressed to reflect the equation or reaction as provided from left (reactants) to right (products)
- not expressing the volume in litres (L) rather than millilitres (mL) and not expressing molarity (M) or concentration in mol/L or mol L^{-1}.

See it in action

Read the real exam question below and see how the tip has made a difference between a response that has scored full marks and a response where marks have been lost.

QUESTION 22 (2 marks)

Calculate the concentration of HF (hydrogen fluoride) in an aqueous solution with a pH of 4.00 ($K_a = 7.2 \times 10^{-4}$). Show your working.

Concentration = ______________ mol L^{-1} (to two significant figures)

Source: *QCAA 2022 Chemistry External Examination Paper 1* © State of Queensland (QCAA)

Complete response

$HF(aq)(WA) \rightleftharpoons H^+(aq) + F^-(aq)$

$K_a = \frac{[H^+][F^-]}{[HF]}$ Since HF WA doesn't completely dissociate

Since $pH = 4 \therefore [H^+] = 10^{-4}$ mol L^{-1}

Since $[H^+] = [F^-] \therefore [F^-] = 10^{-4}$ mol L^{-1} (1:1 ratio)

$\therefore 7.2 \times 10^{-4} = \frac{(10^{-4})(10^{-4})}{[HF]}$

$\therefore [HF] = \frac{(10^{-4})^2}{7.2 \times 10^{-4}}$

Uses correct substitution of concentrations into the rearranged K_a equation [1 mark]

$[HF] = 1.4 \times 10^{-5}$ mol L^{-1}

Correctly calculates [HF] = 0.00014 mol L^{-1} or 1.4×10^{-5} M [1 mark]

Incomplete response

Correctly calculates $[H^+]$= 0.0004 M [0 marks]

$pH = 4 \rightarrow [H^+] = 10^{-pH}$

$= 10^{-4}$ M

$[HF] = [H^+] = 10^{-4}$ M

Incorrectly assumes HF to be a strong acid and equates [HF] to $[H^+]$ and does not use K_a dissociation formula for weak acids [0 marks]

Think like an assessor

To maximise your marks on an exam, it can help to think like a QCAA assessor. Consider how many marks each question is worth and what information the assessor is looking for.

A student has given the following response in a practice exam. Imagine you are a QCAA assessor and use the marking guide below to mark the response.

QUESTION 25 (5 marks)

Three unknown gases are combined in a sealed flask and allowed to reach equilibrium as shown by the equation.

$3A_2\,(g) + X_2\,(g) \rightleftharpoons 2XA_3\,(g)$

(b) Determine if the relative position of equilibrium lies towards the products or reactants, if the molar concentrations at equilibrium are 3.4 mol L^{-1} for A_2, 1.8 mol L^{-1} for X_2 and 4.2 mol L^{-1} for XA_3. Explain your reasoning. *[2 marks]*

Source: *QCAA 2022 Chemistry External Examination Paper 1* © State of Queensland (QCAA)

$$K_c = \frac{[P]}{[R]} = \frac{[XA_3]}{[A_2][X_2]}$$

$$K_c = \frac{(4.2)}{(3.4)(1.8)}$$

$= 0.68$

Because K_c is small, at equilibrium there are more reactants than products.

Marking guide

Question 25b	• determines $K_c = 0.25$ [1 mark] • indicates that since $K_c < 1$, equilibrium lies towards the reactants [1 mark]

Source: *QCAA 2022 Chemistry marking guide and response* © State of Queensland (QCAA)

Fix the response

Consider where you did and did not award marks in the above response. How could the response be improved? Write your own response to the same question to receive full marks from a QCAA assessor.

Exam tip 3: Use data to justify explanations.

Questions where data is provided in the stimulus often contain the cognitive verbs “determine”, “predict”, “discuss”, “explain”, “evaluate” and “justify”. For these questions, it is important that the given data is used in the response as a means of the justification or explanation provided. If information appears to be missing, then check the QCAA *Formula and data book* for additional relevant details that can prove useful in answering the question.

See it in action

Read the real exam question below and see how the tip has made a difference between a response that has scored full marks and a response where marks have been lost.

QUESTION 24 (5 marks)

R and Q are unknown transition metals from period 4 of the periodic table. Pieces of R and Q were placed separately into four 0.1 M aqueous solutions. The results are shown.

Unknown metal	0.1 M aqueous solution			
	$Zn(NO_3)_2$	$Mg(NO_3)_2$	$Cu(NO_3)_2$	$AgNO_3$
R	Coating	No coating	Coating	Coating
Q	No coating	No coating	Coating	Coating

A second experiment was conducted to determine the potential difference produced by electrochemical cells constructed using metals R and Q as the electrodes.

Electrochemical cell	Cathode	Anode	Voltage (V)
1	Q	R	+0.94
2	R	Q	–0.94

Determine the identity of metals R and Q. Explain your reasoning.

Source: *QCAA 2023 Chemistry External Examination Paper 1* © State of Queensland (QCAA)

Complete response

Realises that there is missing information that can be obtained from the QCAA *Formula and data book* regarding the standard potential values for various elements to enable an actual identification of Mn based on reactivity series.

Uses the reactivity data to identify the relative reactivity level of metals Q and R. This leads to an explanation that metal R is more reactive than Zn and less reactive than Mg [1 mark]

R reacts with 3 out of the 4 solutions, which means that as a metal it is able to undergo oxidation with the metal solutions undergoing reduction. Since R(s) is able to displace zinc, copper and silver ions in solution, it is a more reactive metal and more likely to undergo oxidation than the above-mentioned metal ions in solution. Since metal R was not able to displace Mg ions in solution, it is less reactive than Mg metal. Looking at the standard reduction potential table – metal R must be manganese, which is the only element in period 4 less reactive than Mg but more reactive than zinc, copper and silver. Likewise, metal Q displaces copper and silver ions from solution but not zinc ions; hence, zinc metal is considered a more reactive metal than metal Q. This means that metal Q could be nickel, cobalt, iron or chromium based on the standard reduction potential table.

Identifies metal R as manganese based on standard reduction potential table in the QCAA *Formula and data book* [1 mark]

Uses the data to explain that metal Q must be Ni, Co, Fe or Cr [1 mark]

Given that $E_{cell} = E_{reduction} - E_{oxidation}$

Using cell 1: $+0.94 = E_Q - -1.18$

Therefore $E_Q = 0.94 - 1.18$

$-0.24\ V = E_Q$

Therefore, nickel with $E^\circ = -0.24$ must be metal Q.

Uses the electrochemical data to determine that the $E_Q = -0.24$ V [1 mark]

Identifies that metal Q is nickel [1 mark]

Incomplete response

Uses data to explain reactivity of metal R being more reactive than Zn but less reactive than Mg [1 mark]

Metal R reacts with 3 out of the 4 solutions, which means it can undergo oxidation while the metal ions in solution are reduced. Since R(s) displaces zinc, copper and silver ions, it is more reactive than these metals and more likely to oxidise. However, R does not displace magnesium ions, so it is less reactive than magnesium. From the standard reduction potential table, metal R is likely to be a metal less reactive than magnesium but more reactive than zinc, copper and silver. This suggests that R could be manganese or silver. Since silver is not a period 4 element, it was omitted. For metal Q, it displaces copper and silver ions but not zinc ions, which indicates zinc is more reactive than Q. Possible options for Q are nickel, cobalt, iron or chromium based on standard reduction potentials of elements in period 4.

Uses the data to explain that metal Q must be Ni, Cr, Co or Fe [1 mark]

Identifies metal R correctly [1 mark]

Hence using $E_{cell} = E_{reduction} - E_{oxidation}$

Using cell 1: $+0.94 = E_Q - -1.18$

Therefore $E_Q = 0.94 - 1.18$

$-2.12\ V = E_Q$

Therefore, metal Q must be cobalt or chromium, which do not appear on the reduction potential table and there is no element with +2.12 V reduction potential provided, whereas Fe, Ni are both provided and do not match the values calculated.

Uses electrochemical data incorrectly to identify the reduction potential for metal Q [0 marks]

Incorrectly identifies metal Q [0 marks]

Think like an assessor

To maximise your marks on an exam, it can help to think like a QCAA assessor. Consider how many marks each question is worth and what information the assessor is looking for.

A student has given the following response in a practice exam. Imagine you are a QCAA assessor and use the marking guide below to mark the response.

QUESTION 24 (5 marks)

This table shows the effect of temperature on the pH of pure water.

Temperature (°C)	pH
10	7.27
15	7.17
20	7.08
25	7.00
30	6.92
50	6.63

(a) Analyse the data to explain whether the self-ionisation of water is endothermic or exothermic. Explain your reasoning. *[3 marks]*

Source: *QCAA 2020 Chemistry External Examination Paper 1* © State of Queensland (QCAA)

As the temperature increases, $[H_3O^+]$ increases. This occurs because increases in temperature cause a decrease in pH, which means an increase in acidity. Given that the dissociation of water follows the equation $H_2O \rightarrow H^+ + OH^-$, and since increases in temperature favours the exothermic reaction according to LCP, then the self-ionisation of water must be exothermic.

Marking guide

Question 24a	• identifies that $[H_3O^+]$ increases as the temperature increases [1 mark] • identifies that equilibrium shifts towards the products and the endothermic direction [1 mark] • determines that self-ionisation of water is endothermic [1 mark].

Source: *QCAA 2020 Chemistry marking guide and solution* © State of Queensland (QCAA)

Fix the response

Consider where you did and did not award marks in the above response. How could the response be improved? Write your own response to the same question to receive full marks from a QCAA assessor.

Practice makes perfect

Now that you know all these tips, it's time for you to move on to Part C – Practice exam questions to put them into practice.

Part C – Practice exam questions

Now it's time to put the tips and advice you've learnt into practice while you complete these exam-style questions!

Multiple choice

(1 mark each)

1 Which of the following best defines a reversible reaction?

A A reaction in which products can react to reform reactants

B A reaction in which the reactants are completely converted into products

C A reaction that does not occur to completion

D A reaction that requires a catalyst to proceed

2 What is the expression for the equilibrium constant for the following reaction?

$4H_2(g) + CS_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$

A $[CH_4][H_2S]^2$

B $\frac{[CH_4][H_2S]^2}{[H_2]^4[CS_2]}$

C $\frac{[H_2][CS_2]}{[CH_4][H_2S]}$

D $\frac{[H_2]^4[CS_2]}{[CH_4][H_2S]^2}$

3 Identify the solubility product expression for NiS.

A $[Ni^{2+}][S^{2-}]$

B $\frac{[NiS]}{[Ni^{2+}][S^{2-}]}$

C $\frac{[Ni^{2+}][S^{2-}]}{[NiS]}$

D $\frac{[Ni^{2+}][S_2]}{[NiS]^2}$

4 Given that the equilibrium constant for the formation of hydrogen fluoride gas from its elements is 7.8×10^{14}, determine the statement that best reflects the probability of product formation in the reaction between hydrogen gas and fluorine gas to form hydrogen fluoride.

A Definite

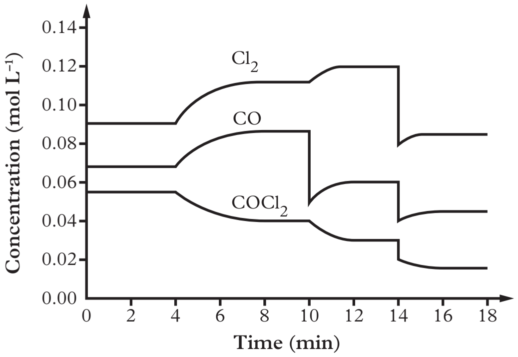
B Improbable

C Likely

D Unlikely

Use the following information to answer questions 5 to 7.

$COCl_2(g) \rightleftharpoons Cl_2(g) + CO(g) \quad \Delta H = +108\text{ kJ}$



5 What change has been made to the system at the 4-minute mark?

A A decrease in temperature

B A decrease in volume

C An increase in temperature

D An increase in volume

6 What change has been made to the system at the 14-minute mark?

A An increase in volume

B The addition of a catalyst

C The addition of an inert gas

D A decrease in volume

7 Identify the impact on the K value if the reaction is reversed and the coefficients are doubled.

A $\frac{1}{K^2}$

B $\frac{1}{2K}$

C K^2

D $K^{\frac{1}{2}}$

8 Determine which of the following options contains a list of strong Brønsted–Lowry acids or bases.

A HCl, HNO_3, NH_3, H_2SO_4

B HCl, NaOH, H_2SO_4, KOH

C KOH, HNO_3, NaOH, H_3PO_4

D NaOH, HCl, H_2CO_3, KOH

9 Identify the acid of the conjugate base $H_2PO_4^-$.

A HPO_4^-

B HPO_4^{2-}

C H_3PO_4

D PO_4^{2-}

10 For an aqueous solution with pH 6, determine the expected concentration of the hydroxide ion at 25°C.

A 10^{-2} mol L^{-1}

B 10^{-4} mol L^{-1}

C 10^{-6} mol L^{-1}

D 10^{-8} mol L^{-1}

11 What is a possible pH of the equivalence point for a titration between hydrochloric acid and ammonia?

A 7

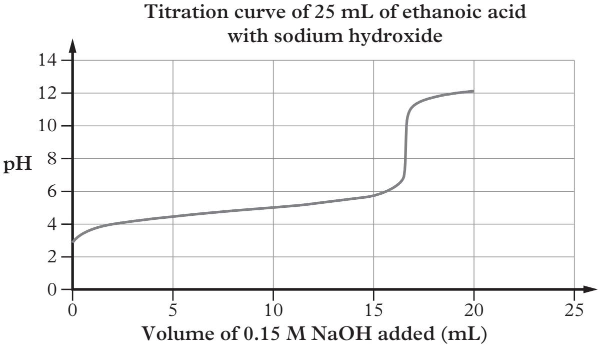
B 9

C 5

D 8

Use the following information to answer questions 12 and 13.

The following data is collected from a titration of 25 mL of ethanoic acid (CH_3COOH) of unknown concentration with 0.15 M NaOH.



12 What is the pH and the volume at the equivalence point of the titration?

A 8.9, 16.67 mL

B 11.1, 17.00 mL

C 6.5, 16.34 mL

D 4.8, 8.33 mL

13 What is a suitable indicator to identify the end point?

A Bromothymol blue

B Methyl orange

C Methyl red

D Phenolphthalein

14 The concentration of carbonic acid (H_2CO_3, $pK_a = 6.35$) in a solution is approximately 0.10 M. What is the resulting pH of the solution?

A 6.49

B 3.75

C 4.40

D 8.57

15 Lactic acid ($pK_a = 3.88$), malic acid ($pK_a = 3.40$), citric acid ($pK_a = 3.13$) and formic acid ($pK_a = 3.75$) are weak acids commonly found in nature. Categorise the acids from strongest to weakest.

A Citric acid > formic acid > malic acid > lactic acid

B Citric acid > malic acid > formic acid > lactic acid

C Formic acid > citric acid > malic acid > lactic acid

D Malic acid > citric acid > lactic acid > formic acid

16 Determine the oxidation number of nitrogen in ammonium sulfide ($(NH_4)_2S$).

A +3

B –3

C +1

D –2

17 Identify which of the following represents a redox reaction.

A $NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$

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

C $CuO(s) + 2HCl(aq) \rightarrow CuCl_2(aq) + H_2O(l)$

D $MgCO_3(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + H_2O(l) + CO_2(g)$

18 Identify the oxidising agent in the redox reaction in question **17**.

A Zn(s)

B $HNO_3(aq)$

C $H^+(aq)$

D $N^+(aq)$

19 Silver, zinc, magnesium, copper, nickel and sodium are all extracted or refined using electrolysis. Which of them cannot be extracted from an aqueous solution in this way?

A Silver and copper

B Zinc, magnesium, nickel and sodium

C Zinc, magnesium and sodium

D Magnesium and sodium

20 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:

$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq) \quad E^o = -0.36\,V$

$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l) \quad E^o = 1.69\,V$

What is the half-equation that occurs at the anode during discharge?

A $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

B $PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$

C $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

D $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$

Short response

21 A 25 L sample of a mixture at equilibrium at 500°C contains 552 mol N_2, 800 mol H_2 and 200 mol NH_3. The balanced equation is:

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

Determine the value of K_{eq} and **identify** whether at equilibrium the reactants or products are favoured. (4 marks)

22 **Determine** the concentration of silver ions in a saturated solution of Ag_3PO_4, given that the K_{sp} of the salt is 1.8×10^{-18}. (3 marks)

23 The K_{sp} of silver carbonate is 8.1×10^{-12}. **Determine** the equilibrium concentration of silver ion in a solution of 0.25 M K_2CO_3. (4 marks)

24 **Predict** the effect on the equilibrium position if the temperature was decreased and a catalyst added to the reaction:

$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2 + 2H_2O(g)$

$\Delta H = -114.4\,kJ\,mol^{-1}$

(3 marks)

25 The yellow chromate ion CrO_4^{2-} and the orange dichromate $Cr_2O_7^{2-}$ ion exist in a pH-dependent equilibrium, as shown:

$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons 2Cr_2O_7^{2-}(aq) + H_2O(l)$

- **a** **Describe** the colour change expected in the equilibrium mixture if NaOH was added and dissolved. **Justify** your reasoning. (3 marks)
- **b** **Identify** whether the reaction is a redox reaction. **Justify** your reasoning. (2 marks)

26 The hydrogen carbonate ion–carbonic acid system works as a buffer in the human circulatory system. The blood buffer system is represented by the following equation:

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$

Explain how slow, shallow breathing leads to respiratory acidosis. (3 marks)

27 **Determine** the pH of 0.050 M solution of sodium cyanide (NaCN), given that K_b of CN^- is 2.1×10^{-5}. (5 marks)

28 For the following voltaic cell:

$Mg|Mg^{2+}\ (1\,M)\ ||\ Cu^+\ (1\,M)|Cu$

- **a** **determine** the cell potential obtained (1 mark)
- **b** **determine** the direction of electron flow in the external circuit (1 mark)
- **c** **determine** which half-cell the two ions in the salt bridge move into. The salt bridge contains a solution of potassium nitrate. (1 mark)

29 Using the information provided in the QCAA *Formula and data book*, **identify** which of the below reactions will proceed spontaneously.

- **a** $Na + Cl_2$ (2 marks)
- **b** $Ag + Cu^{2+}$ (2 marks)
- **c** $H_2 + Cu$ (2 marks)

30 In the process of producing aluminium metal, the ore bauxite is treated to extract the mineral, aluminium oxide. Next, molten aluminium oxide is electrolysed, with the carbon anode undergoing oxidation itself.

- **a** **Determine** the products at each electrode. (2 marks)
- **b** **Calculate** the minimum voltage required for each of the electrolytic cells used in the extraction process if the half-reaction $2O_{2-} \rightarrow O_2 + 4e^-$ has $E° = +0.20\,V$. (2 marks)

31 Ethyl ethanoate is a common solvent and flavour enhancement in foods and pharmaceuticals. Ethyl ethanoate and water are produced in a reversible esterification reaction of ethanol and ethanoic acid:

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l) \quad \Delta H = -25\,kJ\,mol^{-1}$

(Given: $M(CH_3COOH) = 44.06\,g\,mol^{-1}$, $M(CH_3CH_2OH) = 46.08\,g\,mol^{-1}$)

- **a** **Construct** an equilibrium expression for the reaction if its equilibrium constant is 4.80. (1 mark)

b Initially, 5 mL of ethanol with a density of 0.789 g mL^{-1} and 5 mL of ethanoic acid with a density of 1.05 g mL^{-1} were mixed with a very small amount of concentrated H_2SO_4 added as a catalyst. Assuming that the overall volume is the sum of the two volumes of reactants, **calculate** the mass, the number of moles and the initial concentration of each reactant. (6 marks)

c After 15 minutes, the concentration of ethyl ethanoate in the reaction mixture is found to be 4 mol L^{-1}. **Calculate** Q_c of the reaction. Assume that the overall volume of the mixture has not changed. (3 marks)

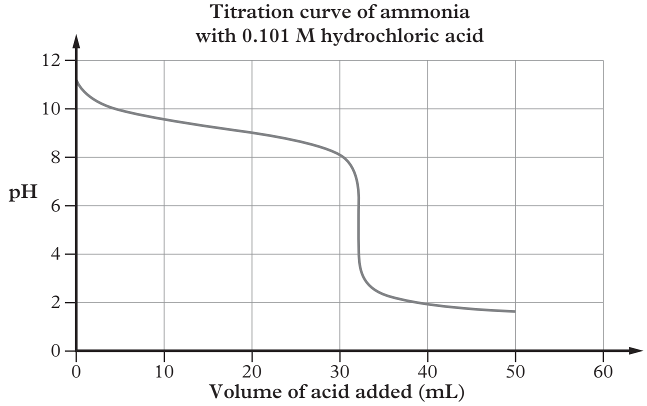
d **Determine** if the reaction mixture has reached equilibrium. (1 mark)

e **Predict** the impact that an increase in temperature will have on the yield of ethyl ethanoate and the overall K_c value. (3 marks)

f **Predict** the impact of conducting this reaction using aqueous solutions rather than pure liquids. (2 marks)

32 **Determine** the volume of acidified 0.010 M $KMnO_4$ solution that needs to be added to oxidise all of the Fe^{2+} ions in a test tube containing 1.0 mL of 0.050 M $FeSO_4$. (4 marks)

33 A 25.00 mL solution of a cleaner containing $NH_4OH(aq)$ is titrated with a standardised solution of HCl with a concentration of 0.101 mol L^{-1}. The following graph is obtained.



a **Determine** the pH at the equivalence point. (1 mark)

b **Calculate** the initial concentration of the weak base. (3 marks)

c **Determine** the dissociation constant, K_b, of the weak base. (2 marks)

d **Propose** an appropriate indicator for this titration and the colour expected to be seen at the end point. (2 marks)

e Between 8 and 24 mL on the graph, 16 mL of strong acid is added. **Identify** the chemical species present in the solution at this time and **explain** how each of them contribute to the appearance of the curve as acid is added. (3 marks)

f **Sketch** the appearance of the graph of a conductometric titration using the same volumes and quantities, showing from 0 to 50 mL of added acid. (3 marks)

34 Magnesium can be produced from the electrolysis of molten magnesium chloride ($MgCl_2$).

a **Explain** how molten magnesium chloride is able to conduct an electric current. (2 marks)

b **Identify** the missing components below. (4 marks)

	Polarity of electrode	Half-equation
Anode		
Cathode		

c **Determine** the minimum voltage required to run the electrolysis. (2 marks)

d **Explain** why magnesium is not formed during electrolysis of aqueous magnesium chloride solution. (2 marks)

e **Deduce** what issue is involved with not including a porous membrane between the electrodes. (1 mark)

35 In an electrolytic cell, 150.0 mL of a 0.20 M lead(II) nitrate ($Pb(NO_3)_2$) solution is electrolysed using a current of 0.360 A for 12 minutes. Both electrodes are made of graphite.

a **Calculate** the mass of product deposited at the cathode. (3 marks)

b **Calculate** the new concentration of the lead(II) nitrate solution. (2 marks)

TOTAL MARKS

/110

UNIT 4

Structure, synthesis and design

Unit 4 overview

In Unit 4, students explore the ways in which models and theories relate to chemical synthesis, structure and design, and associated applications; and the ways in which chemistry contributes to contemporary debate about current and future uses of local, regional and international resources. Students focus on the principles and application of chemical synthesis, particularly in organic chemistry, and consider where and how functional groups can be incorporated into already existing carbon compounds in order to generate new substances with properties that allow them to be used in a range of contexts. Current and future applications of chemistry include the development of specialised techniques to create or synthesise new substances to meet the specific needs of society, such as pharmaceuticals, fuels, polymers and nanomaterials. Participation in a range of experiments and investigations will allow students to progressively develop their range of science inquiry skills while gaining an enhanced appreciation of organic structure, reactions and syntheses. Collaborative experimental work also helps students to develop communication, interaction, character and management skills. Throughout the unit, students develop skills in experimental methodology, qualitative and quantitative data analysis and current organic developments to describe and explain the importance of this branch of chemistry to society.

Unit 4 objectives

1. Describe ideas and findings about properties and structure of organic materials and chemical synthesis and design.
2. Apply understanding of properties and structure of organic materials and chemical synthesis and design.
3. Analyse data about properties and structure of organic materials and chemical synthesis and design.
4. Interpret evidence about properties and structure of organic materials and chemical synthesis and design.
5. Evaluate processes, claims and conclusions about properties and structure of organic materials and chemical synthesis and design.
6. Investigate phenomena associated with properties and structure of organic materials and chemical synthesis and design.

Source: *Chemistry 2025 v1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

Unit 4 Topics

Topic	Module	
Topic 1 Properties and structure of organic materials	**Module 9**	Structure of organic compounds
	Module 10	Organic reactions and reaction pathways
	Module 11	Organic materials: structure and function
	Module 12	Analytical techniques
Topic 2 Chemical synthesis and design	**Module 13**	Chemical synthesis
	Module 14	Macromolecules

MODULE 9

Structure of organic compounds

Introduction

Organic chemistry is based on the carbon-containing compounds that make up all living organisms and that have been synthesised by organic chemists for a wide range of purposes. Carbon is an element with four valence electrons. Each carbon atom can form four single covalent bonds. Carbon is also capable of forming double and triple bonds. It covalently bonds with other atoms such as hydrogen, nitrogen, oxygen, sulfur, halogens and itself. Because of this, there is a vast number of organic compounds in existence, some natural and some synthetic. Organic compounds include fossil fuels (methane gas, butane gas and petroleum), medications (paracetamol, penicillin and amphetamine), harmful compounds (mustard gas and strychnine 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.

Prior knowledge

Prior knowledge quiz

Check your understanding of concepts related to the structure of organic compounds before you start.

Subject matter

Science understanding

→ Identify organic molecules including alkanes, alkenes, alkynes, alcohols, aldehydes, ketones, carboxylic acids, haloalkanes, esters, amines and amides.

→ Discriminate between class and functional groups, e.g. for OH, hydroxyl is the functional group and alcohol is the class.

→ Describe the features of a homologous series.

→ Discriminate between saturated and unsaturated organic molecules.

→ Discriminate between empirical, molecular and structural formulas.

→ Determine molecular and structural formulas for organic compounds, up to C10, including simple methyl and ethyl branched chains, for
  - alkanes, alkenes and alkynes
  - alcohols (primary, secondary and tertiary)
  - aldehydes and ketones
  - carboxylic acids

  - amines and amides
  - haloalkanes (primary, secondary and tertiary)
  - esters.
- → Apply IUPAC rules in the nomenclature of organic compounds, up to C10, including simple methyl and ethyl branched chains, for
  - alkanes, alkenes and alkynes
  - alcohols (primary, secondary and tertiary)
  - aldehydes and ketones
  - carboxylic acids
  - haloalkanes (primary, secondary and tertiary)
  - esters.
- → Identify structural and stereoisomers, including geometrical (*cis* and *trans*) and optical isomers.
- → Deduce the structural formula of geometrical (*cis* and *trans*) isomers (non-cyclic alkenes), optical isomers and isomers of the non-cyclic alkanes up to C_6.
- → Sketch the structural formula and apply IUPAC rules in the nomenclature for isomers of alkanes (non-cyclic) and alkenes (straight chain) up to C_6, and for the geometrical (*cis* and *trans*) isomers of simple alkenes (non-cyclic).
- → Determine the structural formula of optical isomers for simple organic compounds.
- → Identify chiral carbon atoms.
- → Analyse data to determine the structural, molecular and empirical formula of organic compound and the percentage composition of elements in organic compounds.
- → Explain the trends (melting point, boiling point, volatility, solubility in water and organic solvents) within and between homologous series (alkanes, alkenes, alcohols, carboxylic acids) in terms of intermolecular and intramolecular bonding, e.g. dispersion forces, dipole-dipole interactions and hydrogen bonds.
- → Analyse data to determine the physical properties of an homologous series, trends in melting point, boiling point, volatility and the solubility alkanes, alkenes, alcohols and carboxylic acids.

Science as a human endeavour

- → Consider that triglycerides (lipids) are esters, and that saturated and unsaturated fatty acids have different structures and properties.
- → Appreciate that the developments in computer modelling enabled more accurate visualisation and prediction of three-dimensional organic structures, such as proteins, which is critical in drug design and biotechnology.

Science inquiry

Investigate:

- → properties of homologous series*
- → 3D models of organic molecules.

***Note:** Simulations may be used.

Source: *Chemistry 2025 v1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

Practicals

These lessons are available on Oxford Digital.

Lesson 9.6 Modelling isomers of organic molecules
Lesson 9.8 Investigating properties of homologous series

Lesson 9.1
Hydrocarbons

Key ideas

→ Simple hydrocarbons contain carbon and hydrogen only and are named according to IUPAC rules of nomenclature.

→ Hydrocarbons can contain single, double or triple bonds, which are named according to IUPAC rules and described as saturated or unsaturated.

→ Groups of compounds with similar structures and differing only in the length of their carbon chain are described as a homologous series.

→ Branched hydrocarbons are named according to IUPAC rules, including the locant and the prefix for the branch.

Learning intentions and success criteria

What are hydrocarbons?

Hydrocarbons are the simplest form of organic compounds, consisting only of the elements carbon and hydrogen. Hydrocarbons contain a **main chain** of carbon atoms bonded together. Each carbon is also bonded to hydrogen atoms and so reaches a stable octet of valence electrons. Because each carbon atom can form up to four single covalent bonds, carbon has the ability to form molecules with chains of carbon atoms of varying length, which may be a continuous chain (called straight) or branched. In addition, the ability of carbon to form double and triple bonds with itself increases the number and variety of hydrocarbons.

The **nomenclature** of hydrocarbons is determined by the number of carbon atoms in the main chain, and the bonding 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 for naming organic compounds, e.g. the IUPAC rules of organic nomenclature

FIGURE 1 Oil and gas (sourced from under the seafloor) are examples of simple hydrocarbons.

How is the number of carbons in the main chain used in naming?

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 indicates 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 to 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

prefix
a group of letters added to the beginning of a word; the first part of an organic compound's name

Study tip

The prefixes for 5 to 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.

How is the type of bonding between carbons in the main chain used in naming?

The name of a hydrocarbon also indicates the type of bonding between carbons. If the hydrocarbon contains only single covalent bonds (involving two electrons), the name ends with the **suffix** "ane" and the hydrocarbon is an alkane (e.g. hexane).

Alkanes have the general formula of C_nH_{2n+2}. Every carbon atom in the middle section of the chain is bonded to two hydrogen atoms and the neighbouring two carbon atoms. The carbon atoms at either end are bonded to one carbon atom and three hydrogen atoms.

Worked example 9.1A shows you how to name an **alkane**.

If the hydrocarbon contains one or more double bonds, then the name includes the suffix "ene" and the hydrocarbon is an **alkene** (e.g. hexene). The double bond is represented by two lines in the structural formula. For alkenes with one double bond, the general formula is C_nH_{2n}. Due to the double bond between two carbon atoms, there are two fewer hydrogen atoms than in the corresponding alkane. The smallest alkene is ethene.

If the hydrocarbon contains a triple bond, then the name includes the suffix "yne" and the hydrocarbon is an **alkyne** (e.g. hexyne). The triple bond is represented by three lines in the structural formula. For alkynes with one triple bond, the general formula is C_nH_{2n-2}. Due to the triple bond between two carbon atoms, there are four fewer hydrogen atoms than in the corresponding alkane. The smallest alkyne is ethyne, which is commonly called acetylene in industries. It is used with oxygen, for high-temperature cutting and welding of metals.

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 carbon atoms

alkyne
a class of organic compound that contains one or more triple bonds between carbon atoms

How are locants shown in the names of compounds?

Locants are used to identify 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

locant
a number or letter that indicates the position of a substituent or functional group in an organic compound

multiple bond
a double or triple bond in an organic compound

Worked example 9.1A

Applying IUPAC nomenclature rules to name alkanes

Apply IUPAC nomenclature rules to name the following hydrocarbon (Figure 2). (1 mark)

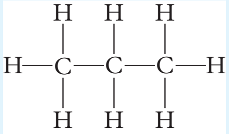


FIGURE 2 A hydrocarbon

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Apply" means use knowledge and understanding in response to a given situation or circumstance. We need to count the number of carbon atoms in the main (only) chain, recall the prefix and add the suffix. This question is worth 1 mark, so we must write the name, spelled correctly.
Step 2: Gather the required data.	The main chain has 3 carbon atoms singly bonded. So recall the prefix "prop" and the suffix "ane".
Step 3: Finalise your answer by writing the name, by recalling the prefix and adding the suffix.	Propane (1 mark)

Your turn

Apply IUPAC nomenclature rules to name the following hydrocarbon (Figure 3). (1 mark)

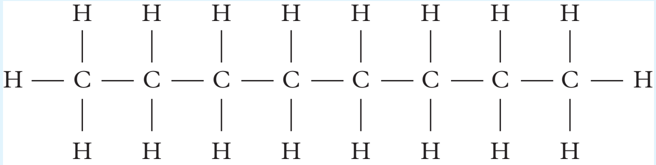


FIGURE 3 A hydrocarbon

number of the two carbon atoms in the bond. The number is included in the compound's name with hyphens on either side (e.g. hex-1-ene). 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.

Worked example 9.1B shows you how to name an alkene, and Worked example 9.1C shows you how to name an alkyne. Where there are two possibilities, the main chain is numbered in the way that will give the lowest number for the double bond position.

Study tip

When a name includes numbers and letters, a hyphen is used to separate the number from surrounding letters. Where there are two numbers in succession (e.g. for a particular type of substituent), the two numbers are separated by a comma.

What is a homologous series?

Methane, ethane, propane and butane are an example of a homologous series of compounds. A homologous series is a series of compounds with the same general formula that differ only in the length of the carbon chain. Each member of a homologous series has one more carbon atom and two more hydrogen atoms than the previous member (i.e. each member differs from the next one by $-CH_2-$). Alkenes and alkynes can form groups that are a homologous series. However, the position of the double or triple bond needs to be at the same locant for each successive member in the series. For example, all alkenes with the double bond at locant 1 are in the same series, but alkenes with the double bond at locant 2 form a different series.

Study tip

Butane gas is a common four-carbon hydrocarbon. "But" is pronounced "beaut" as in the word "beautiful".

For example, all alkynes with the triple bond at locant 1 are members of one homologous series. So hex-1-yne and oct-1-yne are members of the 1-alkyne series, but hex-3-yne from Worked example 9.1C is not.

Worked example 9.1B

Applying IUPAC nomenclature rules to name alkenes

Apply IUPAC nomenclature rules to name the following hydrocarbon (Figure 4). (1 mark)

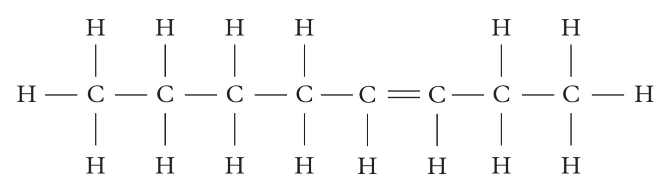


FIGURE 4 A hydrocarbon

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Apply" means use knowledge and understanding in response to a given situation or circumstance. We need to count the number of carbon atoms in the main (only) chain, recall the prefix, determine the locant and add the suffix. This question is worth 1 mark, so we must write the name, spelled correctly.
Step 2: Gather the required data.	The main chain has eight carbon atoms with one double bond. The locant carbon atom is three from the right end, and five from the left end, so use the lower number, 3. Recall the prefix "oct", how to number the double bond and the suffix "ene".
Step 3: Finalise your answer by writing the name, by recalling the prefix, writing the locant between hyphens and adding the suffix.	Oct-3-ene (1 mark)

Your turn

Apply IUPAC nomenclature rules to name the following hydrocarbon (Figure 5). (1 mark)

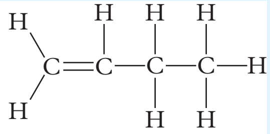


FIGURE 5 A hydrocarbon

Worked example 9.1C

Applying IUPAC nomenclature rules to name alkynes

Apply IUPAC nomenclature rules to name the following hydrocarbon (Figure 6). (1 mark)

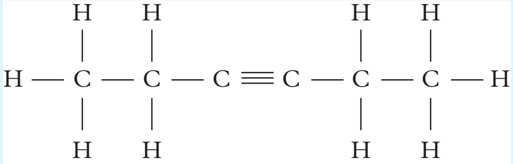


FIGURE 6 A hydrocarbon

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Apply" means use knowledge and understanding in response to a given situation or circumstance. We need to count the number of carbon atoms in the main (only) chain, recall the prefix, determine the locant and add the suffix. This question is worth 1 mark, so we must write the name, spelled correctly.
Step 2: Gather the required data.	The main chain has six carbon atoms with one triple bond. The locant carbon atom is three from the right end, and three from the left end, so use the number 3. Recall the prefix "hex", how to number the triple bond and the suffix "yne".
Step 3: Finalise your answer by writing the name, by recalling the prefix, writing the locant between hyphens and adding the suffix.	Hex-3-yne (1 mark)

Your turn

Apply IUPAC nomenclature rules to name the following hydrocarbon (Figure 7). (1 mark)

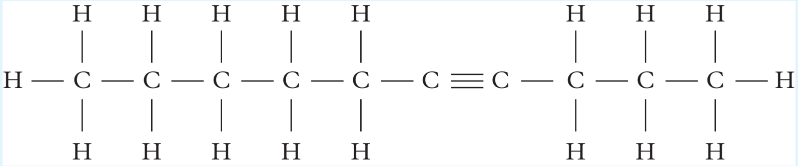


FIGURE 7 A hydrocarbon

What is a functional group?

functional group an atom or a group of atoms that has similar chemical properties whenever it appears in various compounds

Alkenes and alkynes each contain a functional group. You will learn about other types of functional groups in Lesson 9.2. **Functional group** is the term used to describe an atom or a group of atoms that has similar chemical properties whenever it appears in various compounds. Alkanes do not have any region that is relatively more reactive; however, branches of alkyl groups can affect the overall reactivity of other groups within a molecule, so alkanes and alkyl branches are functional groups. Many functional groups are reactive and can be identified by the typical reactions they undergo. The double- and triple-bonded carbon atoms in alkenes and alkynes are much more reactive than the rest of the molecule and readily undergo addition reactions.

What is the difference between saturated and unsaturated compounds?

Saturated hydrocarbons have the maximum number of hydrogen atoms possible for the number of carbon atoms present. Alkanes, both straight and branched, are saturated. All of the bonds between neighbouring carbon atoms are single bonds. Alkenes and alkynes are examples of **unsaturated hydrocarbons** because they contain less than the maximum number of hydrogen atoms possible for the number of carbon atoms present. These compounds can undergo an addition reaction to form a single bond, with each of the carbon atoms forming new bonds with the other reactant. At least one pair of neighbouring carbon atoms is in a double or triple bond. Benzene is also an unsaturated hydrocarbon, but the resonance structure means that benzene is much less reactive than alkenes and alkynes.

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). When naming such compounds, indicate the identity of the substituent as a prefix (e.g. 3-methylhexane).

Worked example 9.1D demonstrates how to name a hydrocarbon with a substituent.

Worked example 9.1D

Applying IUPAC nomenclature rules to name branched hydrocarbons

Apply IUPAC nomenclature rules to name the following hydrocarbon (Figure 8). (1 mark)

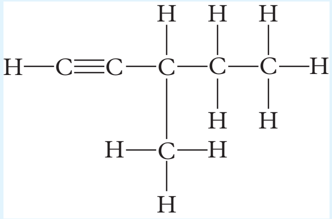


FIGURE 8 A hydrocarbon

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Apply" means use knowledge and understanding in response to a given situation or circumstance. We need to count the number of carbon atoms in the main chain, which contains the double bond, recall the prefix, determine the locant of the double bond and identity the locant of the branch and add the suffix. This question is worth 1 mark, so we must write the name, spelled correctly.
Step 2: Gather the required data.	The main chain has five carbon atoms with one triple bond, locant 1 (not 4, which is higher). The branch at locant 3 has one carbon atom, so is named "methyl". Recall the prefix "pent", how to number the triple bond and the suffix "yne".
Step 3: Finalise your answer by writing the name, recalling the prefix, writing the locant between hyphens and adding the suffix.	3-Methylpent-1-yne (1 mark)

saturated hydrocarbon
a compound of carbon and hydrogen that contains the maximum possible number of hydrogen atoms for the number of carbon atoms present

unsaturated hydrocarbon
a compound of carbon and hydrogen that contains double or triple bonds and therefore has fewer than the maximum number of hydrogen atoms for the particular number of carbon atoms

substituent
an atom or a 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. QCAA requires the use of the current naming and numbering rules.

Your turn

Apply IUPAC nomenclature rules to name the following hydrocarbon (Figure 9). (1 mark)

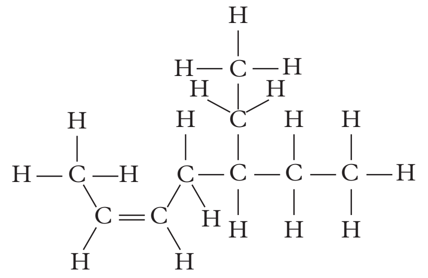


FIGURE 9 A hydrocarbon

How are hydrocarbons with multiple substituents named?

multiplier
a term used to indicate the number of substituents of the same type

When there is more than one type of substituent in a molecule, then name the substituents in alphabetical order. For example, ethyl appears before methyl.

If there is 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).

TABLE 2 Multipliers used in organic nomenclature

Number of substituents	Multiplier
2	Di
3	Tri
4	Tetra
5	Penta

Study tip

When naming organic compounds according to the IUPAC rules, avoid common errors such as not identifying the longest carbon chain, not listing the side branches in alphabetical order and not including the multipliers "di", "tri" and "tetra".

How are multiple locants assigned?

There are strict IUPAC guidelines for numbering carbon atoms in the name of a molecule.

- Assign the suffix of 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 10 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".
  - Locants for the same type of substituent group appear together and are separated by commas. 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. Notice that the numbers are separated by commas, and the last number and the following letter are separated by a hyphen.

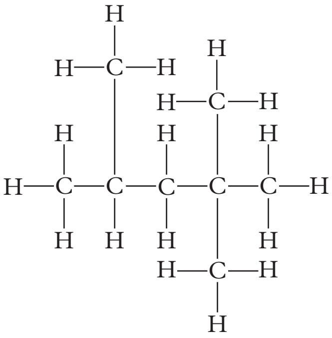


FIGURE 10 An eight-carbon hydrocarbon

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.

- 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 11 as follows.
  - The main chain has six carbons so it is hexane.
  - There are two hydrocarbon substituents – a methyl and an ethyl.
  - Since "e" appears before "m" in the alphabet, list ethyl before methyl 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.

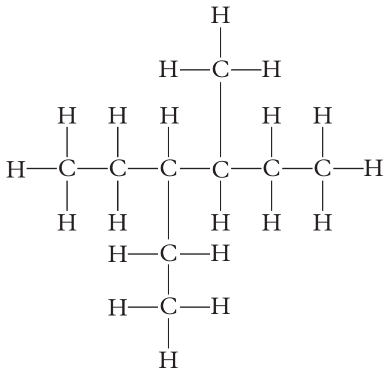


FIGURE 11 A nine-carbon hydrocarbon

Study tip

When naming organic compounds, any numbers next to each other are separated by a comma. Numbers and letters are separated by a hyphen.

Check your learning 9.1

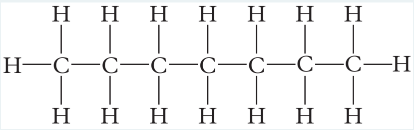
Check your learning 9.1: Complete these questions online or in your workbook.

Retrieval and comprehension

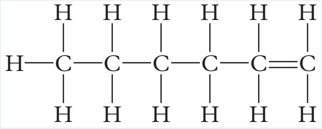
1 **Describe** the term "hydrocarbon". (1 mark)

2 **Identify** the molecule that is unsaturated from the following hydrocarbons. (1 mark)

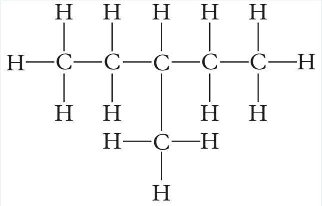
A



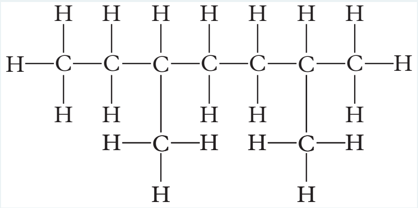
B



C



D

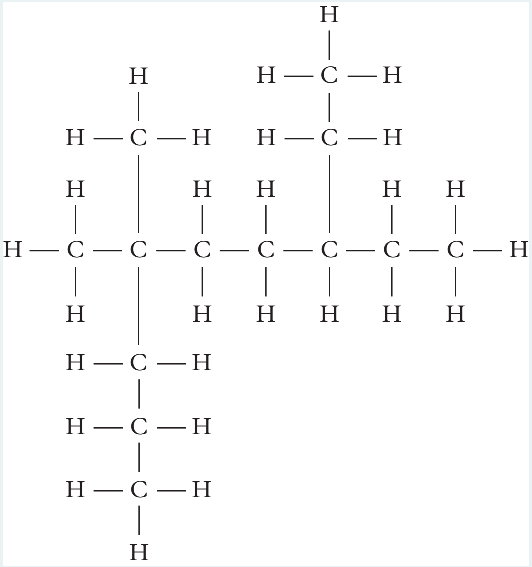


Analytical processes

3 **Apply** IUPAC rules to name the hydrocarbons in question **2**. (1 mark each = 4 marks)

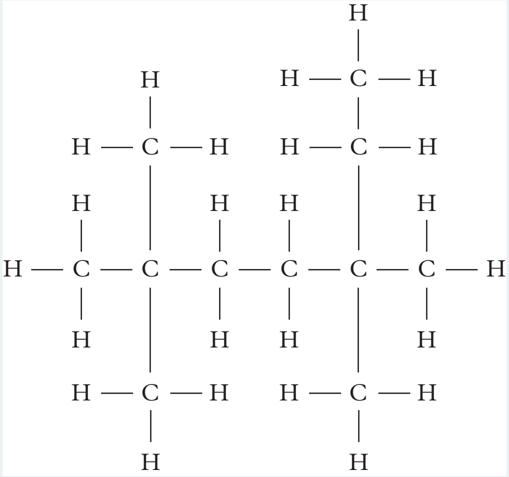
4 **Apply** IUPAC rules to name the following hydrocarbons.

a



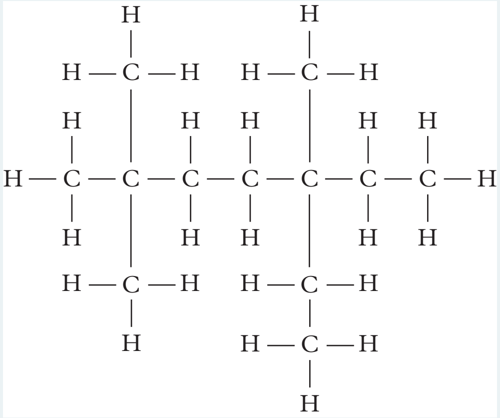
(1 mark)

b



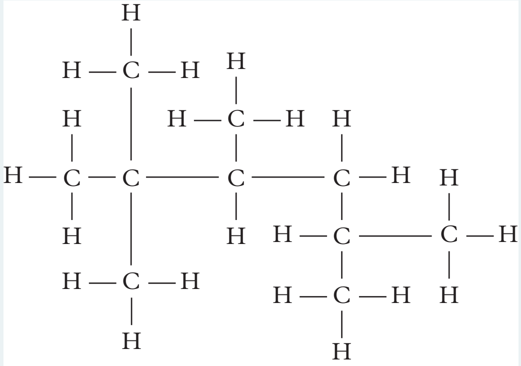
(1 mark)

c



(1 mark)

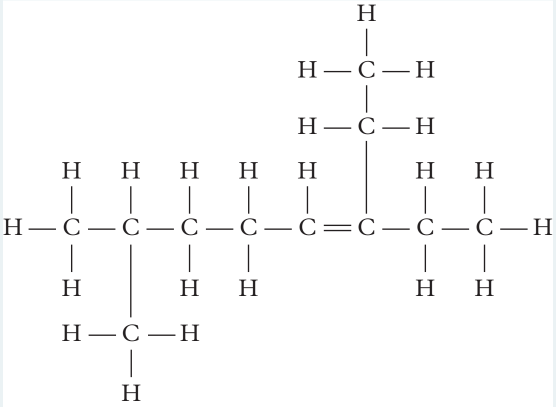
d



(1 mark)

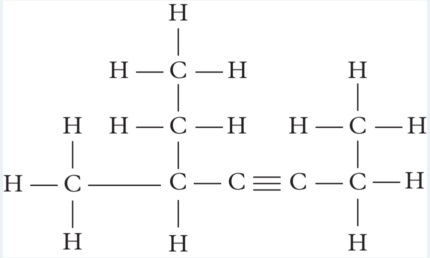
6 **Apply** IUPAC rules to name the following hydrocarbons.

a



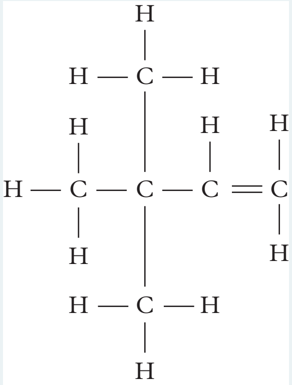
(1 mark)

b



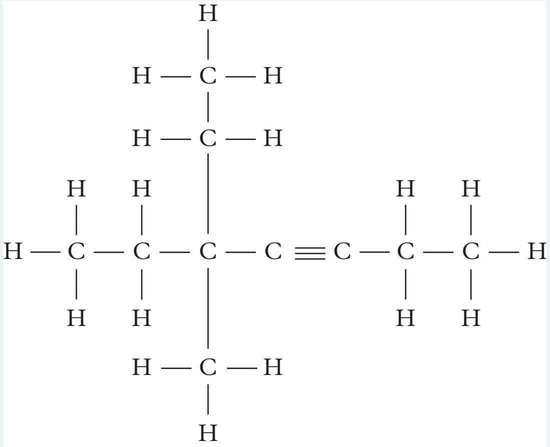
(1 mark)

c



(1 mark)

d



(1 mark)

7 **Discriminate** between saturated and unsaturated hydrocarbons and provide examples. (4 marks)

8 A student has been naming some hydrocarbons from structural diagrams. They have not applied the IUPAC rules correctly. **Apply** the IUPAC rules to name the compounds. A sketch may be used to assist.

a 2,3-Methyl-3-ethylpentane (1 mark)

b 2-Ethylhex-5-ene (1 mark)

c 4-Ethyl-4-propylpent-2-ene (1 mark)

Lesson 9.2

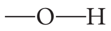
Functional groups

Key ideas

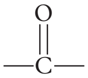
- → Organic compounds can include functional groups containing oxygen, nitrogen and various halogens.
- → The various functional groups in organic compounds determine the particular classes they belong to.
- → IUPAC nomenclature is used to name complex organic compounds that contain methyl and ethyl branches along with one other functional group.

What are some organic compounds containing oxygen?

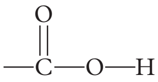
Oxygen is an element often found in organic compounds (except hydrocarbons). The most common functional groups that contain oxygen are **hydroxyl**, **carbonyl** and **carboxyl** (Figure 1).



Hydroxyl group



Carbonyl group



Carboxyl group

FIGURE 1 Common functional groups that contain oxygen

What are alcohols?

Alcohols are a class of organic compound that contain 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 (e.g. hexan-2-ol).

Learning intentions and success criteria

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 ($-C{=}O$)

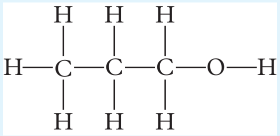
carboxyl
a functional group consisting of a hydroxyl group attached to the carbon of a carbonyl group ($-COOH$)

alcohol
a class of organic compound that contains a hydroxyl functional group ($-OH$)

Worked example 9.2A

Applying IUPAC nomenclature rules to name alcohols

Apply IUPAC nomenclature rules to name the following molecule. (1 mark)



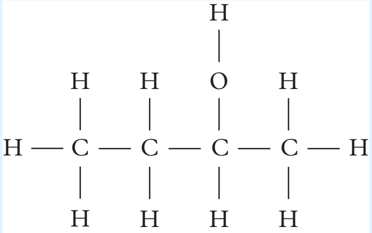
Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	“Apply” means use knowledge and understanding in response to a given situation or circumstance. We need to recognise that the functional group is a hydroxyl group, count the number of carbon atoms in the chain (which contains the hydroxyl group), recall the prefix, determine the locant of the hydroxyl group, remove “e” from the name of the alkane and add the suffix. This question is worth 1 mark, so we must write the name, spelled correctly.
Step 2: Gather the required data.	The chain has three carbon atoms. The locant of the hydroxyl group is three from the left end, and one from the left end, so use the lower number, 1. Recall the stem “propan”, how to number the functional and the suffix “ol”.

▶

Think	Do
Step 3: Finalise your answer by writing the name, recalling the stem, writing the locant between hyphens and adding the suffix.	Propan-1-ol (1 mark)

Your turn

Apply IUPAC nomenclature rules to name the following molecule. (1 mark)



What are the different types of alcohols?

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 hydroxyl 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

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 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 carbon to which the hydroxyl group is attached has two carbon atom neighbours bonded to it).

Tertiary alcohols are alcohols in which the carbon that is bonded to the hydroxyl group is bonded to three other carbons (the hydroxyl group is attached to a carbon atom that is in turn attached to three other carbon atoms).

The three types of alcohol are illustrated in Figure 2.

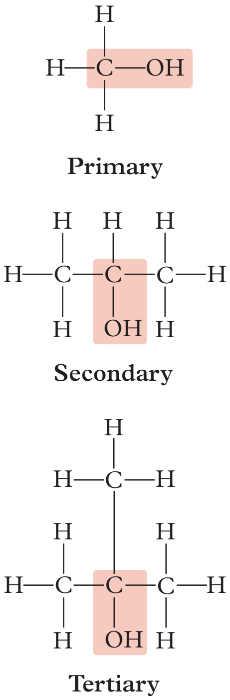


FIGURE 2 Primary, secondary and tertiary alcohols

What are aldehydes and ketones?

Aldehydes and **ketones** are two classes of organic compounds that have the carbonyl functional group, –C=O, 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 (e.g. 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.

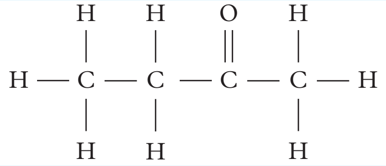
To name a ketone, identify the main chain and omit the final letter “e”. Then add “one” as a suffix, which is immediately preceded by the locant (e.g. hexan-2-one).

Worked example 9.2B

Applying IUPAC nomenclature rules to name aldehydes and ketones

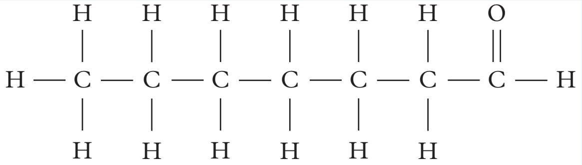
Apply IUPAC nomenclature rules to name the following molecules.

a



(1 mark)

b



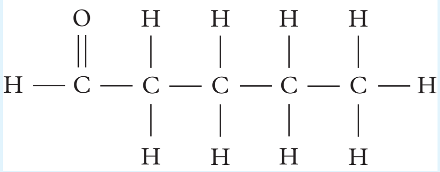
(1 mark)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	“Apply” means use knowledge and understanding in response to a given situation or circumstance. We need to count the number of carbon atoms in the main chain, which contains the double bond, recall the prefix, determine the locant of the double bond, identity the locant of the branch and add the suffix. Each part of the question is worth 1 mark, so we must write the name, spelled correctly.
Step 2: Gather the required data.	**a** The main chain has four carbon atoms with a carbonyl group. The locant carbon atom is two from the end, so it is a ketone. Recall the stem “butan”, how to number the functional group and the suffix “one”. **b** The main chain has seven carbon atoms with a carbonyl group. The locant carbon atom is at the end, so it is an aldehyde. Recall the stem “heptan” and the suffix “al”.
Step 3: Finalise your answer by writing the name, recalling the stem, writing the locant between hyphens for the ketone and adding the suffix.	**a** Butan-2-one (1 mark) **b** Heptanal (1 mark)

Your turn

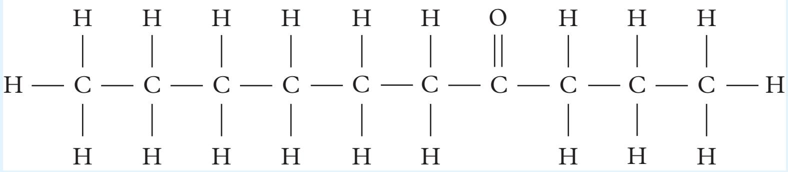
Apply IUPAC nomenclature rules to name the following molecules.

a



(1 mark)

b



(1 mark)

Study tip

The suffix for ketones is pronounced "own".

carboxylic acid
a class of organic compound that contains a carboxyl functional group

What are 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. In this functional group, the carbon atom is doubly bonded to one of the oxygen atoms, and singly bonded to the other oxygen atom, which in turn is bonded to the hydrogen atom (Figure 3). The bond between the oxygen and the hydrogen is polar, and this hydrogen atom can be donated, which makes these compounds acidic. They are weak acids.

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.

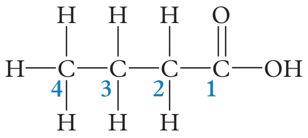


FIGURE 3 In carboxylic acids, the COOH group is assigned as carbon 1. This is butanoic acid.

What are esters?

ester
a class of organic compound that contains a carbonyl attached to an oxygen, which is bonded to another carbon

Esters are a class of organic compound that are derived from a carboxylic acid and an alcohol. An ester also contains a carboxyl group, but without a proton. The ester functional group can be considered as a carbonyl group attached to an oxygen linked to another carbon. Esters are formed from the reaction between a carboxylic acid and an alcohol. The carbonyl group and its hydrocarbon originated from the acid, while the group containing the singly bonded oxygen linked to a carbon originated from the alcohol.

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 is 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 singly bonded oxygen, name the chain and add the suffix "yl"
- neither part of the name requires locants, but any other substituent needs a locant
- write the name as two separate words.

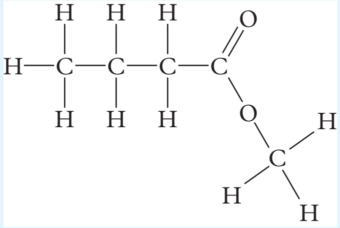
Study tip

You are not required to name amines and amides. However, you should be able to recognise and draw their structures and to use information about these compounds.

Worked example 9.2C

Applying IUPAC nomenclature rules to name esters

Apply IUPAC nomenclature rules to name the following molecule. (1 mark)



Study tip

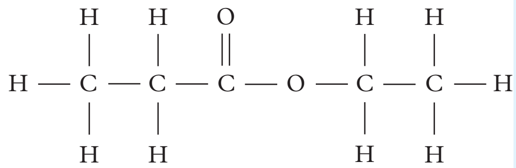
Ensure you know the difference between the terms "class of compound" and "functional group". For example, carboxylic acids are a class of compound, and they contain the carboxyl functional group in their structure.

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	“Apply” means use knowledge and understanding in response to a given situation or circumstance. We need to recognise the section of the molecule singly bonded to O, count the number of carbon atoms in that chain, use the prefix and add “yl”. We need to recognise the section of the molecule containing the carbonyl group and count the carbon atoms in it, recall the stem, by removing “e” from the name of the alkane, and add the suffix “oate”. This question is worth 1 mark, so we must write the name, spelled correctly.
Step 2: Gather the required data.	The chain bonded to the carbonyl group has four carbon atoms, so the stem is “butan”. The chain bonded to the singly bonded O has one carbon atom, so it is “methyl”.
Step 3: Finalise your answer by writing the name, recalling the stem, writing the locant between hyphens and adding the suffix.	Methyl butanoate (1 mark)

Your turn

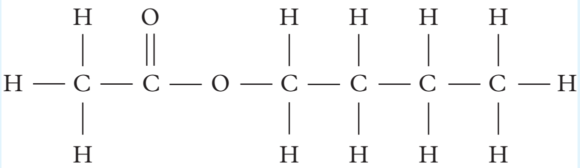
Apply IUPAC nomenclature rules to name the following molecules.

a



(1 mark)

b



(1 mark)

What are some organic compounds containing nitrogen?

Nitrogen is another element often found in organic compounds. Nitrogen-containing compounds play major roles in biological systems. **Amines** are derived from the molecule ammonia (NH_3) by replacing one or more of the hydrogen atoms with an **alkyl group** (symbolised as R). **Amides** are formed when a carboxylic acid and ammonia or an amine react; they contain both amine and carbonyl functional groups.

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).

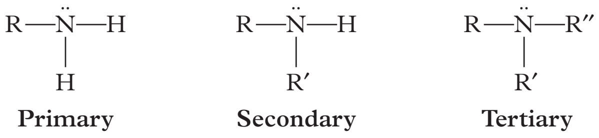


FIGURE 4 Primary, secondary and tertiary amines. R, R′ and R″ are alkyl groups.

amine
a class of organic compound that contains a nitrogen atom bonded to three other groups, either hydrogen atoms or alkyl groups

alkyl group
a group formed by removing a hydrogen from an alkane; can be present as a substituent in an organic compound

amide
a class of organic compound that contains amine and carbonyl functional groups adjacent to each other

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 nitrogen of the amide functional group (Figure 5).

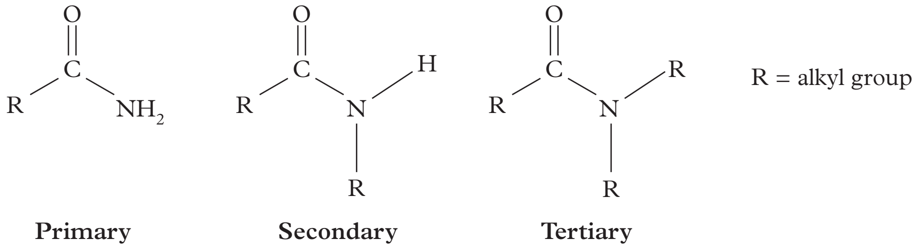


FIGURE 5 Primary, secondary and tertiary amides

What are some 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). Similarly to hydrocarbon branches, the halogen prefixes are arranged alphabetically in the name if there is more than one.

What are the different types of haloalkanes?

primary haloalkane
a haloalkane in which the carbon that is bonded to the halogen atom is bonded to one other carbon

secondary haloalkane
a haloalkane in which the carbon that is bonded to the halogen atom is bonded to two other carbons (the halogen atom is located in the middle of the chain)

tertiary haloalkane
a haloalkane in which the carbon that is bonded to the halogen atom is bonded to three other carbons

Primary haloalkanes are haloalkanes in which the carbon that is bonded to the halogen atom is only bonded to one other carbon (Figure 6A). For example, in 1-iodopropane the iodine is bonded to the carbon atom on the end of the molecule.

Secondary haloalkanes are haloalkanes in which the carbon that is bonded to the halogen atom is bonded to two other carbons (Figure 6B). For example, in 2-fluoropropane the fluorine atom is located in the middle of the main chain.

Tertiary haloalkanes are haloalkanes in which the carbon that is bonded to the halogen atom is bonded to three other carbons (Figure 6C). For example, in 2-chloro-2-methylpentane the chlorine atom is located in the middle of the main chain that also has hydrocarbon substituents.

This classification is comparable to that of primary, secondary and tertiary alcohols.

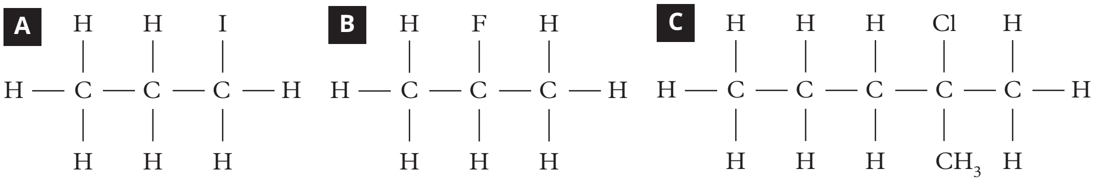
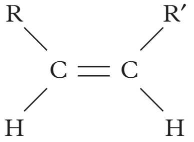
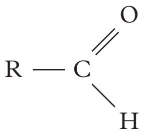
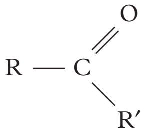
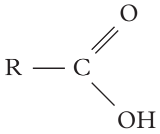
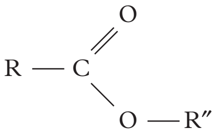
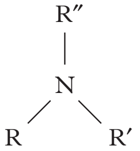
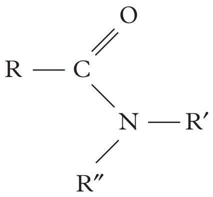


FIGURE 6 (A) Primary, (B) secondary and (C) tertiary haloalkanes

Table 1 summarises the general formula of the various classes of compounds, as well as the type of functional group present in each. R, R′ and R″ represent alkyl hydrocarbons.

TABLE 1 Classes of compounds, general formulas and functional groups present (R, R′ and R″ represent alkyl hydrocarbons)

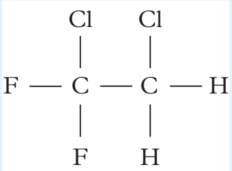
Class of compound	General formula	Functional group(s) present
Alkene		C=C double bond
Alkyne	R — C ≡ C — R′	C≡C triple bond
Alcohol	R — OH	Hydroxyl group
Aldehyde		Carbonyl group at the end of the main chain (R can be H)
Ketone		Carbonyl group not at the end of the main chain
Carboxylic acid		Carboxyl (R can be H)
Ester		Carbonyl attached to oxygen
Amine		Amino group
Amide		Carbonyl group attached to an amino group (R, R′ and R″ groups can be H)
Haloalkane	R — X	Halo group, e.g. chloro (X represents any halogen atom)

Worked example 9.2D

Applying IUPAC nomenclature to name haloalkanes

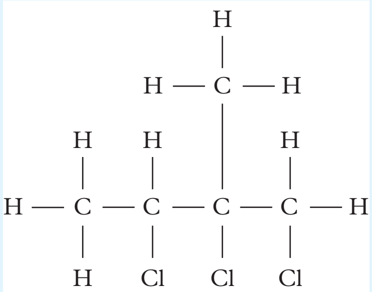
Apply IUPAC rules to name the following molecules.

a



(1 mark)

b



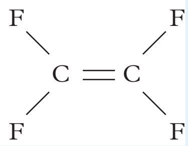
(1 mark)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	“Apply” means use knowledge and understanding in response to a given situation or circumstance. We need to count the number of carbon atoms in the main chain, identify the halogen substituents and number them to achieve the lowest numbers, and identify the branch. Use the first part of the halogen name as a prefix, and add “o”, and use a multiplier as required. Each question is worth 1 mark, so we must write the name, spelled correctly.
Step 2: Gather the required data.	**a** The molecule has a chain length of two, with two fluorine atoms on carbon atom 1, and two chlorine atoms, one on carbon 1, and one on carbon 2. Alphabetically, “chloro” is before “fluoro”. **b** The molecule has a chain length of four. Numbering from the right gives lower numbers. The three chlorine atoms are on the carbon atoms 1, 2 and 3. The methyl group is on carbon atom 2. Alphabetically, “chloro” is before “methyl”.
Step 3: Finalise your answer by writing the name, by recalling the stem, writing the locant between hyphens and adding the suffix.	**a** 1,2-Dichloro-1,1-difluoroethane (1 mark) **b** 1,2,3-Trichloro-2-methylbutane (1 mark)

Your turn

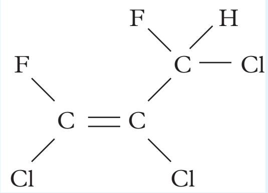
Apply IUPAC rules to name the following molecules.

a



(1 mark)

b



(1 mark)

How do we name compounds containing a functional group as well as branched chains?

Some organic compounds can have both a functional group and alkyl groups (branches) present. In these molecules, the main chain is numbered so that the functional group takes priority and has the lowest number possible. Then, the alkyl groups are numbered accordingly. If there are two possible ways to number, apply the rule of giving the lowest number to the first alkyl group alphabetically. Note that an aldehyde and a carboxylic acid would always have the functional group of carbon atom number 1. Figure 7 shows how this rule is applied.

In Figure 7A, if the chain is numbered from the right, the carbonyl group is on carbon 2 and the methyl group is on carbon 4. Numbering from the left would mean that the methyl group is on carbon 2 and the carbonyl group is on carbon 4. The first option is correct because the functional group would be 2 rather than 4 and it takes priority over a side chain. The name of the compound is 4-methylpentan-2-one.

In Figure 7B, if the chain is numbered from the right, the hydroxyl group is on carbon 3 and the methyl groups are on carbons 4 and 5. Numbering from the left would mean that the methyl groups are on carbons 2 and 3 and the hydroxyl group is on carbon 4. The first option is correct because the functional group would be 3 rather than 4. The name of the compound is 4,5-dimethylhexan-3-ol.

In Figure 7C, the hydroxyl group is number 4 no matter which end the numbering starts. However, numbering from the left would mean methyl is on carbon 2 and ethyl is on carbon 5, whereas numbering from the right would mean methyl is on carbon 3 and ethyl is on carbon 6 . Numbering from the left allows for the lowest numbers. Alphabetically, “ethyl” is before “methyl”, so it appears first in the name. The name of the compound is 5-ethyl-2-methyl-heptan-4-ol.

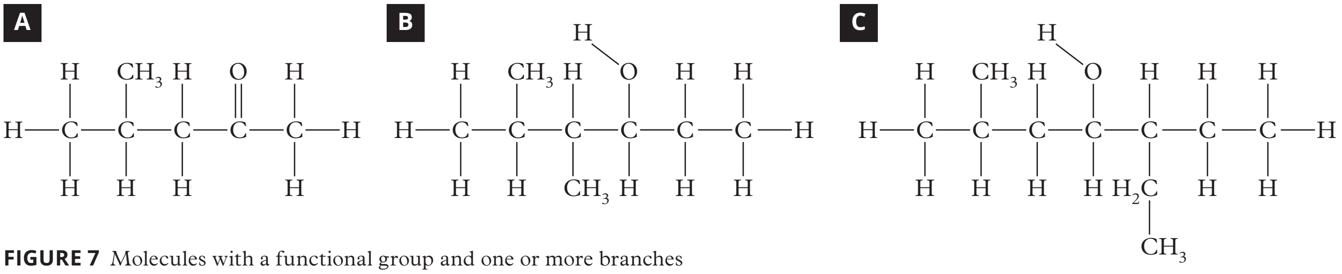


FIGURE 7 Molecules with a functional group and one or more branches

Real-world chemistry

The good oil

Lipids are organic compounds that include fatty acids and their derivatives, triglycerides. Fatty acids are carboxylic acids with alkyl carbon chains. Triglycerides are triesters of three fatty acids and the triol glycerol.

Fats and oils in foods are triglycerides. As non-polar molecules, they are nearly all insoluble in water. Lipids carry fat-soluble vitamins (A, D, E and K) into our bodies. Lipids form lipid membranes of cells and the myelin sheath of neurons.

The carboxylic acids in triglycerides are classed as either saturated or unsaturated. Unsaturated fatty acids include monounsaturated (one double bond) and polyunsaturated (more than one double bond). In unprocessed foods, the double bonds are almost always in the form of structures called *cis* isomers. Processes such as heating in deep fryers or hydrogenation to produce solid trans-fats from liquid cis-oils – that is, converting *cis* isomers to *trans* isomers. Then melting points of lipids containing fatty acids increase as the length of the carbon chain increases and decrease as the level of unsaturation (number of double bonds) increases. Saturated fats form soft solids with relatively high melting points, while unsaturated fats are liquids at room temperature. Melting points of unsaturated fatty acids are affected by geometric isomerism – *cis* conformations have lower melting points than *trans* conformations because they cannot pack as closely together.

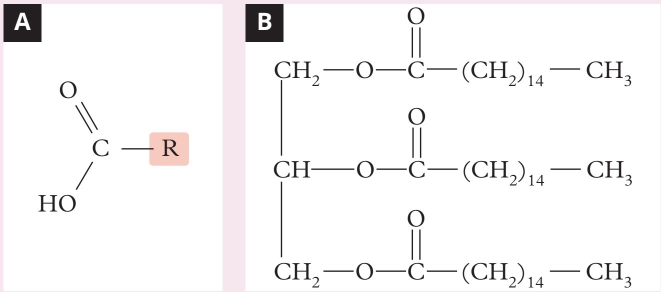


FIGURE 8 (A) The general structure of a fatty acid; and (B) the structure of a triglyceride

Apply your understanding

1 Analyse Figure 8 to:
   a **determine** the structure of glycerol (1 mark)
   b **apply** IUPAC nomenclature rules to name glycerol. (1 mark)

2 Caprylic acid is a fatty acid with the systematic name of octanoic acid. Caprylic triglyceride is found in milk and has important anti-inflammatory properties. **Determine** and **sketch** the structural formula of caprylic triglyceride. (1 mark)

3 The terminal methyl group of a fatty acid at the end of the chain furthest from the carboxyl group is called the omega carbon. Polyunsaturated fatty acids are given numbers in their names to show where the double bonds are in relation to the terminal or omega carbon. For example, an omega-3 fatty acid has the first double bond counting from the omega end at carbon atom 3.

   Research and **sketch** the structural formula for an omega-3,6,9 polyunsaturated (*cis*) fatty acid with 16 carbon atoms in the chain. (3 marks)

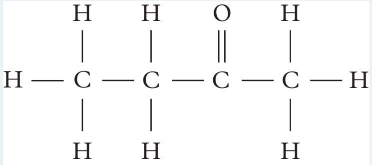
Check your learning 9.2

Check your learning 9.2: Complete these questions online or in your workbook.

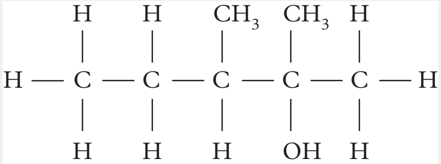
Retrieval and comprehension

1 **Describe** the structure of hydroxyl and carbonyl functional groups. (2 marks)

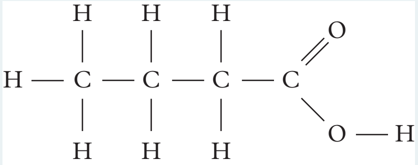
2 **Identify** the functional group present and the class of compound for each of the following molecules.

a


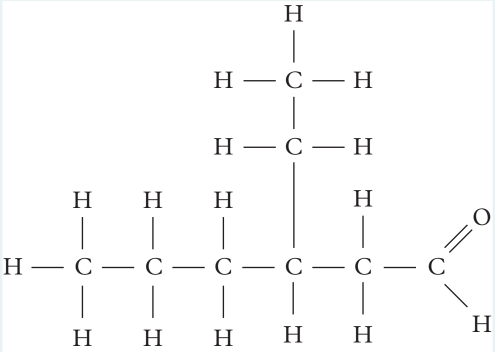
(2 marks)

b


(2 marks)

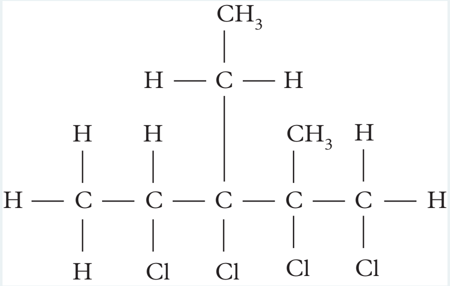
c


(2 marks)

d


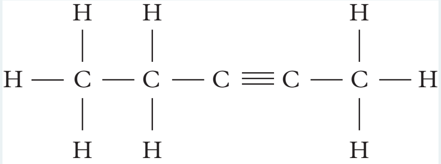
(2 marks)

e



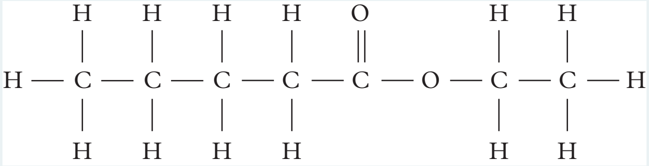
(2 marks)

f



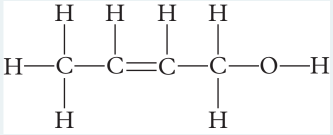
(2 marks)

g



(2 marks)

3 **Identify** the functional groups in the following organic compound.



(1 mark)

Analytical processes

4 **Apply** IUPAC rules to name the organic compounds in question **2**. (7 marks)

5 **Discriminate** between the terms “functional group” and “class of compound”, using two examples for each. (4 marks)

6 A student is confused about the numbering used for certain functional groups and has been told numbering is not always required if the main chain is short. By considering possible positions of the functional group, **determine** if numbering is required for each of the following compounds.

- **a** Propanol (1 mark)
- **b** Propene (1 mark)
- **c** Butyne (1 mark)
- **d** Butanone (1 mark)

Lesson 9.3

Representing organic compounds

Key ideas

→ Organic compounds are represented in greatest detail in extended structural formulas.

→ Condensed and line structural formulas provide less detail about the structure of organic compounds but are more compact.

→ Molecular formulas provide information about the number and identity of each element in a compound but lack information about structure and functional groups.

→ Empirical formulas provide information about the identity of each element in a compound and their simplest whole-number ratio.

→ Given one type of structural formula for a compound – extended, condensed or line – it is possible to represent the compound in one of the other types of formulas.

→ Molecular and structural formulas can be determined from the name of the organic compound.

Learning intentions and success criteria

structural formula a representation of an organic compound used to inform the arrangement and bonding of atoms

What are the different types of structural formulas?

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 or the bonding between them.

What are extended structural formulas?

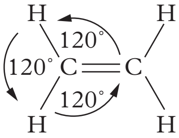


FIGURE 1 In ethene, the bonds around each carbon are drawn at angles of 120°.

Extended structural formulas provide information about both the arrangement and bonding in an organic molecule in a way that is unambiguous. The molecules represented so far throughout this module have been extended structural formulas. Single bonds are represented by a single line, and double and triple bonds are represented by two and three lines. For many compounds, with single bonds, 90° angles have been used; in fact, four single bonds around a carbon atom are arranged in three-dimensional space at angles of approximately 109°. Bonds in alkenes and alkynes can be drawn with 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 approximately 120° (Figure 1).

What are 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 triple 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 and 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

Place a dot on each "end" and "bend" of the line structural formulas, to help count the carbon atoms.

What are line structural formulas?

Line structural formulas provide information about the bonding in an organic molecule, as well as information about some of the atoms present. Line structural formulas are drawn as a zigzag line (Figure 2) for alkyl chains. Carbon atoms are not written in but are represented by the ends and corners of the diagonal lines. Hydrogen atoms bonded to C 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.

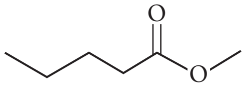


FIGURE 2 The line structural formula of methyl pentanoate

Worked example 9.3A

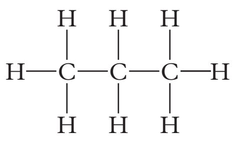
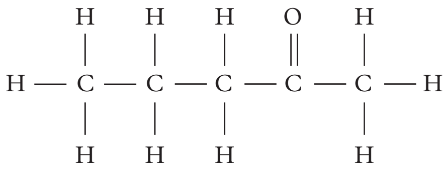
Determining extended, condensed and line structural formulas

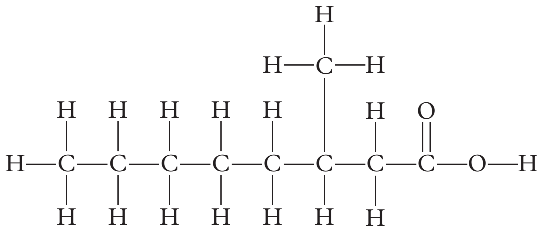
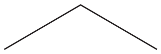
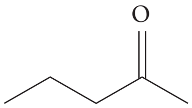
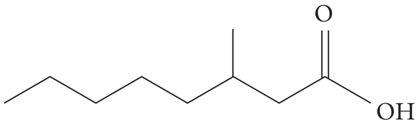
Determine extended, condensed and line structural formulas for

a propane (3 marks)

b pentan-2-one (3 marks)

c 3-methyloctanoic acid. (3 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Determine" means establish, conclude or ascertain after consideration, observation, investigation or calculation. We need to consider each part of the name and establish how that is shown in the structural formula. Each question is worth 3 marks, so we must express the three types of structural formulas.
Step 2: Analyse the information in the name.	**a** Propane has three carbon atoms singly bonded and associated hydrogen atoms. **b** Pentan-2-one has five carbon atoms in the main chain, a carbonyl group on carbon 2 and associated hydrogen atoms as required. **c** 3-Methyloct-3-enoic acid has eight carbon atoms in the main chain, a carboxyl group on carbon 1, a double bond between the carbons 3 and 4 and a methyl group on carbon 3.
Step 3: Draw the extended structural formulas for each.	**a**  (1 mark) **b**  (1 mark)

Think	Do
	c  (1 mark)
Step 4: Work through the extended structural formula, translating each part of it to a condensed formula. Remember that repeated CH_2 groups can be shown using brackets.	**a** $CH_3CH_2CH_3$ (1 mark) **b** $CH_3(CH_2)_2COCH_3$ (1 mark) **c** $CH_3(CH_2)_4CH(CH_3)CH_2COOH$ (1 mark)
Step 5: Work through the extended structural formula, representing each of the bonds between carbon atoms as a line on a zigzag structure. Show double bonds as required and functional groups containing elements other than carbon and hydrogen.	**a**  (1 mark) **b**  (1 mark) **c**  (1 mark)

Your turn

Determine extended, condensed and line structural formulas for

- **a** 2-methylbutan-2-ol (3 marks)
- **b** 2,3-dichloropropanoic acid (3 marks)
- **c** butyl ethanoate. (3 marks)

How are the structural formulas of amines and amides determined?

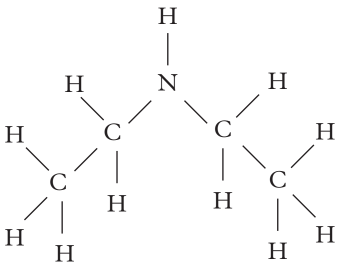
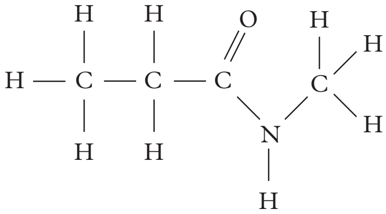
Although you are not required to name amines and amides, you should be able to determine their molecular and structural formulas. A description of the molecule can be used. Recall their general structures from Lesson 9.2.

Worked example 9.3B

Determining structural formulas for amines and amides

Determine the structural formulas for

- **a** a secondary amine with two ethyl groups (1 mark)
- **b** an amide with the carbonyl functional group on a three-member carbon chain and the amine group having a methyl group attached. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do. Step 2: Gather the required data.	"Determine" means establish, conclude or ascertain after consideration, observation, investigation or calculation. We need to consider each part of the description and establish how that is shown in the structural formula. **a** This amine is a secondary amine; it has two hydrocarbon groups and a hydrogen atom attached to the nitrogen atom. (It is somewhat analogous to the ammonia molecule, but with one or more alkyl groups attached.) **b** This amide will have a carbon chain with three carbon atoms, and a carbonyl group on the end; at the carbonyl group, it will be attached to a nitrogen atom, which also has a methyl group.
Step 3: Draw the extended structural formulas, using the information.	**a**  (1 mark) **b**  (2 marks)

Your turn

Determine the structural formulas for

a a tertiary amine with two methyl groups and a propyl group (1 mark)

b an amide with the carbonyl functional group on a two-member carbon chain and the amine group having two ethyl groups attached. (2 marks)

What are molecular and empirical formulas?

The **molecular formula** is the complete chemical formula of a covalent molecular compound that shows how many atoms of each element are in one molecule of the compound. This is not nearly as useful as the various types of structural formulas. For example, a compound with the molecular formula C_4H_8O could be an aldehyde, a ketone or an alcohol with a C=C double bond. The main chain could have four carbon atoms, or it could have three carbon atoms and a methyl branch.

The **empirical formula** shows the simplest whole-number ratio of elements in a compound. While chemists may obtain an empirical formula from experimental data, further data would always be required to determine the molar mass, the molecular structure and the functional groups present. For example, the empirical formula of ethanoic acid is CH_2O. The actual molecular formula of ethanoic acid is found by multiplying the ratios of each element by two, to obtain $C_2H_4O_2$.

molecular formula
the complete chemical formula of a compound that indicates the number of atoms of each element present

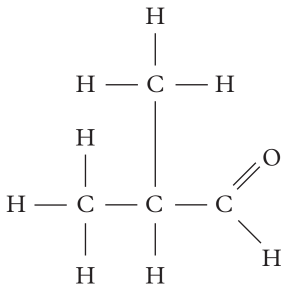
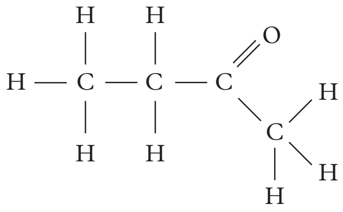
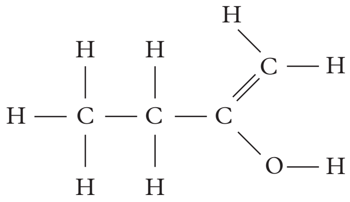
empirical formula
the simplest whole-number ratio of the elements in a compound

Worked example 9.3C

Determining molecular and structural formulas, given the name of compounds

Determine the extended structural formulas and molecular formulas for

a 2-methylpropanal (2 marks) **b** butanone (2 marks) **c** but-1-en-2-ol. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Determine" means establish, conclude or ascertain after consideration, observation, investigation or calculation. We need to consider each part of the name and establish how that is shown in the structural formula. We then need to use the structural formula to write the molecular formula. Each question is worth 2 marks, so we must show the structural formula and the molecular formula correctly.
Step 2: Gather the required data. This can be thought about and not necessarily written.	**a** 2-Methylpropanal has a three-carbon main chain, with a carbonyl group on carbon 1 and a methyl group on carbon 2. **b** Butanone has a four-member main chain with a carbonyl group on carbon 2. **c** But-1-en-2-ol has a four-carbon main chain, with a double bond between carbon 1 and carbon 2, and a hydroxyl group on carbon 2.
Step 3: Determine structural formulas for each compound using the information.	**a**  (1 mark) **b**  (1 mark) **c**  (1 mark)
Step 4: Count the carbon, hydrogen and oxygen atoms in each structural formula to determine the molecular formulas. (In this case, you will notice that three very different compounds have identical molecular formulas.)	**a** C_3H_8O (1 mark) **b** C_3H_8O (1 mark) **c** C_3H_8O (1 mark)

Your turn

Determine extended structural formulas and molecular formulas for

a ethanoic acid (2 marks) **b** ethene-1,2-diol. (2 marks)

Check your learning 9.3

Check your learning 9.3: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** the term “structural formula”. (1 mark)

2 **Explain** the steps involved in interpreting a condensed structural formula. (2 marks)

3 **Construct** the line structural formula of 2-methylhexane. (1 mark)

Analytical processes

4 **Determine** the extended, condensed and line structural formulas of

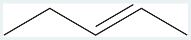
- **a** 3-methylbutanoic acid (3 marks)
- **b** 3-ethylhex-1-yne (3 marks)
- **c** propyl hexanoate (3 marks)
- **d** 4-ethyl-3,4-dimethylpentanal. (3 marks)

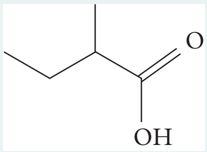
5 **Determine** the extended structural formula, the molecular formula and the empirical formula of

- **a** hexanoic acid (3 marks)
- **b** propane-1,2,3-triol (glycerol). (3 marks)

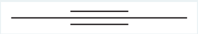
6 **Discriminate** between empirical, molecular and structural formulas, by using the compounds in question **5** as examples. Consider the type of information conveyed by each formula. (3 marks)

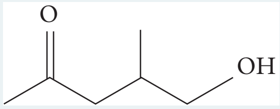
7 **Determine** the condensed structural formula for each of the following structural formulas.

a  (1 mark)

b 

(1 mark)

c  (1 mark)

d 

(1 mark)

8 **Apply** IUPAC rules to name each of the compounds in question **7a, b** and **c**. (4 marks)

9 **Determine** the extended structural formulas for the following condensed structural formulas.

- **a** $CH_3CH(CH_3)CH_2CH_3$ (1 mark)
- **b** $CH_3COCH(CH_2CH_3)CH_2CH_3$ (1 mark)
- **c** $CH_3CH(CH_3)CH(CH_3)COOH$ (1 mark)
- **d** $CH_3COOCH_2CH_2CH_2CH_3$ (1 mark)

10 **Apply** IUPAC rules to name each of the compounds in question **9**. (4 marks)

11 A student who has difficulty applying IUPAC nomenclature rules has named the following compounds as shown. For each compound, **sketch** the extended structural formula and **apply** IUPAC rules of nomenclature to provide the corrected name.

- **a** 3-hydroxy-3-methylbutane (2 marks)
- **b** 2-ethylhexan-4-ol (2 marks)

Lesson 9.4

Isomers

Key ideas

- → Isomers are molecules with the same molecular formula but different structures.
- → Isomers can be classified as structural isomers and stereoisomers. Stereoisomers are subdivided into geometrical (*cis* and *trans*) and optical isomers.
- → Isomers can be represented by structural formulas.
- → Structural formulas and IUPAC nomenclature can be used to differentiate between isomers that have the same molecular formula.

What are structural isomers?

Learning intentions and success criteria

structural isomers
two or more organic compounds that have the same atoms and molecular formula 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. Both isomers 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), reflecting the weaker intermolecular forces between its molecules.

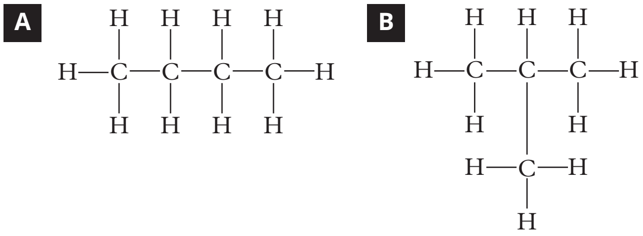


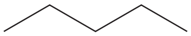
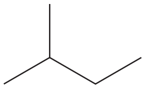
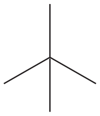
FIGURE 1 Structural isomers of C_4H_{10}: (A) butane and (B) 2-methylpropane

Worked example 9.4A

Deducing and sketching structural formulas and applying IUPAC rules of nomenclature for isomers of alkanes

Deduce and **sketch** the line structural formulas for the isomers of C_5H_{12}.

Apply IUPAC nomenclature to name them. (6 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the question is asking you to do.	"Deduce" means to draw a logical conclusion. We need to think logically about the different ways carbon atoms could be arranged in a main chain and possible branches for the information given in the formula. "Sketch" means to represent using a diagram or graph. We need to show the essential features, such as bonds and any branches. "Apply" means use knowledge and understanding in response to a given situation or circumstance. We need to count the number of carbon atoms in the main chain, identify branches and locants and number accordingly, to name each isomer. This question is worth 6 marks, so each isomer sketch and each correctly spelled name is worth 1 mark.
Step 2: Gather the required data. This can be done by thought, rather than in written notes.	This molecular formula indicates that this is an alkane, a saturated hydrocarbon with five carbon atoms. The carbon atoms can be linear or branched. There can be multiple branches.
Step 3: Sketch isomers, including pentane, by considering the locant and identity of possible branches. Take care not to produce identical molecules, viewed from a different angle.	 (1 mark)  (1 mark)  (1 mark)
Step 4: Finalise your answer by applying IUPAC rules to name each compound. Note that numbers are not required for locants for any of these names, as there is only one possible locant for butane with a single alkyl substituent, and only one possible locant for two alkyl substituents of propane. The name provided is unambiguous in this case.	The structural isomers are pentane (1 mark), 2-methylbutane (1 mark) and 2,2-dimethylpropane (1 mark).

Your turn

Deduce and **sketch** the line structural formulas for the isomers of C_4H_{10}.

Apply IUPAC nomenclature to name them. (4 marks)

What are stereoisomers?

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. Two different types of stereoisomers will be considered: geometrical isomers and optical isomers.

stereoisomers
two or more organic compounds that have the same atoms and bonding but a different spatial arrangement

What are geometrical isomers?

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.

Study tip

cis means beside. *trans* means across. *trans* is seen in words such as transport, meaning "carry across", and trans-Pacific, meaning "across the Pacific ocean".

geometrical isomers
two organic compounds that have different arrangements of atoms around a rigid double bond

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 drawn with the two methyl groups on the same side of the double bond and *trans*-but-2-ene is drawn with 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.

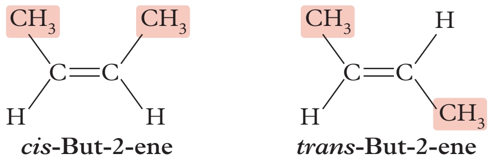


FIGURE 2 The geometrical isomers of C_4H_8: *cis*-but-2-ene and *trans*-but-2-ene

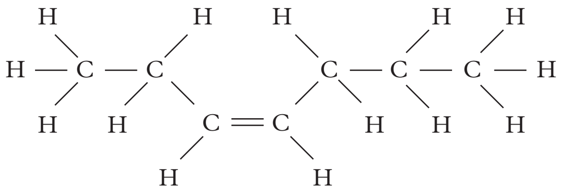
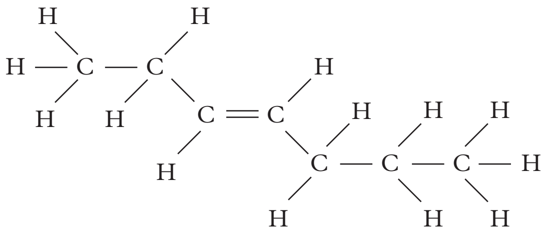
The substituents on geometrical isomers do not need to be identical, but they do need to have at least two substituents other than hydrogen attached to the double bond. This means that geometrical isomers cannot generally form on the end of the main chain, because one of the carbon atoms will only have hydrogen atoms rather than substituents. Substituted alkenes can also form geometrical isomers (e.g. 1,2-dichloroethene).

Worked example 9.4B

Deducing and sketching structural formulas and applying IUPAC rules of nomenclature for geometric isomers of alkenes

Deduce and **sketch** the extended structural formulas for the geometric isomers of hex-3-ene.
Apply IUPAC rules of nomenclature to name them. (4 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the question is asking you to do.	"Deduce" means to draw a logical conclusion. We need to think logically about the arrangement of the groups on either side of the double bond in the alkene. "Sketch" means to represent using a diagram or graph. We need to show the essential features, such as bonds and any branches. "Apply" means use knowledge and understanding in response to a given situation or circumstance. We need to use *cis* and *trans* along with the rest of the IUPAC rules. This question is worth 4 marks, so each isomer sketch and each correctly spelled name is worth 1 mark.
Step 2: Gather the required data. This can be done by thought, rather than in written notes.	The molecule is hex-3-ene, which has a double bond between carbon atoms 3 and 4. Bond angles around these two carbon atoms will be 120° and the positions of the remainder of the molecule will be *cis* (beside) or *trans* (across).

Think	Do
Step 3: Sketch the two isomers.	 (1 mark)  (1 mark)
Step 4: Finalise your answer by using *cis* and *trans* in the names.	The first structure is *cis*-hex-3-ene. (1 mark) The second structure is *trans*-hex-3-ene. (1 mark)

Your turn

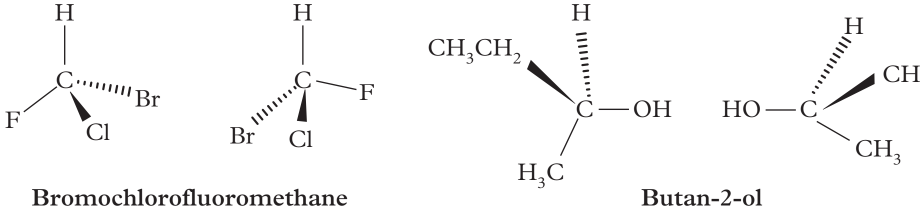
Deduce and **sketch** the extended structural formulas for the geometric isomers of pent-2-ene. **Apply** IUPAC rules of nomenclature to name them. (4 marks)

What are optical isomers?

Optical isomers are stereoisomers that have an asymmetrical (chiral) carbon atom with four different substituents covalently bonded in a tetrahedral arrangement. Optical isomers are mirror images of each other and are non-superimposable. Optical isomers are also called enantiomers.

We represent optical isomers 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 compounds that have optical isomers (Figure 3).

optical isomers
two organic compounds that have the same atoms and bonding but a different arrangement of four substituents around a chiral carbon atom



Bromochlorofluoromethane **Butan-2-ol**

FIGURE 3 The optical isomers of bromochlorofluoromethane and butan-2-ol. Notice the chiral carbon atom in each case, as well as the unsymmetrical bonding around it. IUPAC nomenclature does have names to distinguish each optical isomer, but this is not required knowledge.

Optical isomers have optical properties. When plane polarised light is passed through a solution containing a single optical isomer from a pair, the plane of the polarised light is rotated, either clockwise or anticlockwise. The mirror image of the optical isomer causes the plane of the plane polarised light to rotate in the opposite direction. A racemic mixture contains equal proportions of both isomers and does not affect polarised light. Many biological molecules have chiral centres and are optical isomers. One of these is sucrose, and the effect on plane polarised light is used in the laboratory at sugar mills. The cane juice is placed in a device called a polarimeter (pol). The amount of rotation of the plane of the polarised light is measured and is proportional to the percentage of sugar in the juice, which helps inform the basis of payments to each grower.

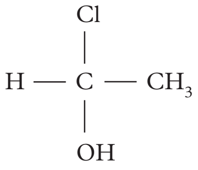
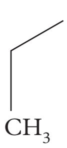
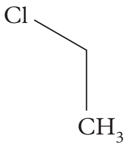
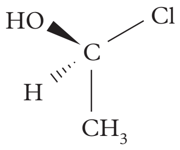
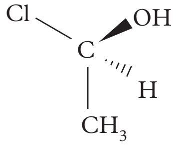
Left and right hands are examples of optical isomers because they are mirror images of each other and cannot be superimposed. Ears, feet and bird and butterfly wings (Figure 4) are also examples of optical isomers.

FIGURE 4 These butterfly wings are mirror images of each other.

Worked example 9.4C

Determining the structural formula of optical isomers for simple organic compounds

Determine the structural formulas of the two optical isomers of 1-choroethanol. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	“Determine” means establish, conclude or ascertain after consideration, observation, investigation or calculation. We need to step through the process to create mirror images in order to establish how optical isomers are shown in the structural formulas. The question is worth 2 marks, so we must show both structural formulas correctly.
Step 2: Identify the general formula and the chiral carbon atom. It may help to draw an extended, flat structural diagram in order to identify the chiral centre.	 $H-\overset{Cl}{\underset{OH}{C}}-CH_3$
Step 3: Draw the two bonds that are flat on the page, for each isomer, using a bond angle of 120° and ensuring the two are mirror images. It does not matter which substituents are chosen. In this case, CH_3 and Cl have been chosen.	 
Step 4: Finalise your answer by depicting the other two substituents with their bonds as a solid wedge and a dashed wedge, continuing to ensure the two structures are mirror images of each other.	 (1 mark)  (1 mark)

Your turn

Determine the structural formulas of the two optical isomers of 1-choro-1-fluoropropane. (2 marks)

Real-world chemistry

Computers advancing health

Cellular receptors are proteins that receive a molecular signal either inside a cell or on its surface (Figure 5). Each receptor has a specific shape and polar functional groups within that shape that the signalling molecule fits and is attracted to. The ability of a particular molecule to fit a particular receptor is described as the lock-and-key model.

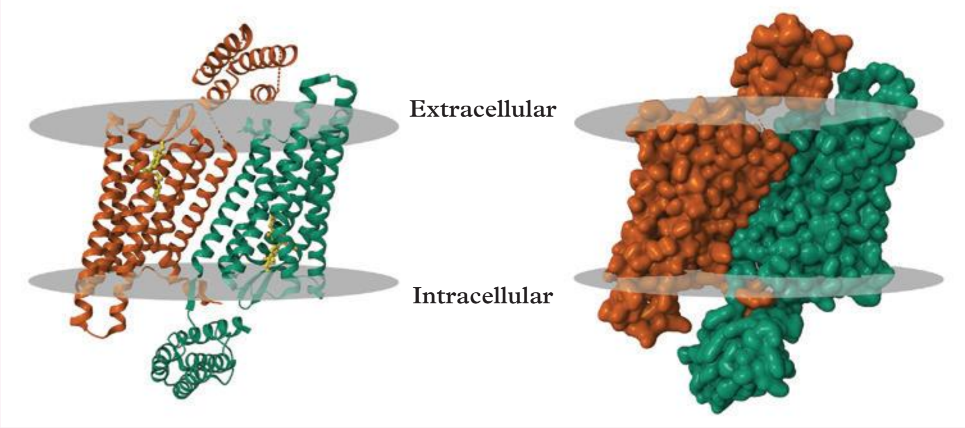


FIGURE 5 A protein receptor at the surface of a cell. The extracellular part of the receptor sticks out of the cell membrane to receive signals, while the intracellular part of the receptor protrudes into the cell. A section of the cell membrane is represented by the transparent grey discs.

Most drugs, whether pharmaceutical or illicit, can interact with specific cell receptors, acting to promote or inhibit the normal receptor/signalling molecule interaction.

Computer modelling has allowed huge advances in drug research and development. The exact shape and the functional groups within that shape of the protein receptor can be modelled. Further computer modelling then tests huge numbers of potential drug molecules to discover if the specific shape and functional groups of a potential drug interact with and can be taken up by the receptor (Figure 6). The ability to screen thousands of potentially useful drugs has greatly reduced the time it takes to develop effective medical treatments.

Computer-aided drug design (CADD) can design drug molecules that are yet to be synthesised, allowing pharmaceutical researchers to narrow their efforts to synthesising a drug molecule that they know will interact with the receptor.

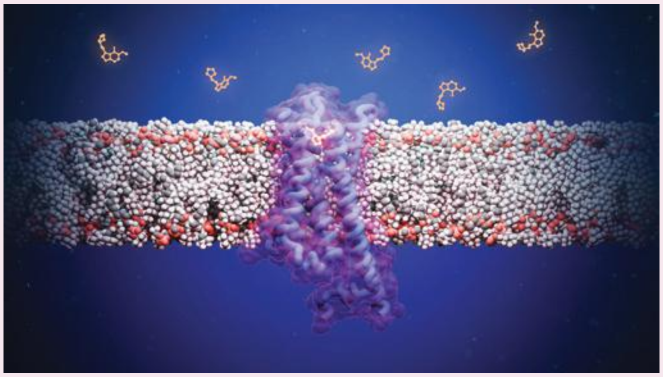


FIGURE 6 A protein receptor (purple) at the cell membrane, interacting with an antianxiety drug molecule (orange)

Apply your understanding

1 Functional groups in proteins include N–H, O–H and C=O. Use electronegativity values to **determine** which of these bonds has the greatest polarity. (3 marks)

2 Consider a drug that exists as two different optical isomers. **Infer** whether each stereoisomer would interact in the same way with a receptor. **Justify** your response. (2 marks)

3 Many drug molecules include rings such as rigid benzene rings in their structure, rather than the more flexible, straight-chain hydrocarbons. **Justify** why drug molecules tend to have these rigid shapes. (1 mark)

Challenge

Alkane structural isomers

There is no limit to the number of carbon atoms in alkane molecular formulas. This means there can be many structural isomers for alkanes with a high number of carbon atoms. **Identify** the three alkanes that do not have structural isomers. **Identify** two alkanes that have more than 1,000 different structural isomers. (5 marks)

Check your learning 9.4

Check your learning 9.4: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** the term “geometrical isomer”, using suitable examples. (4 marks)

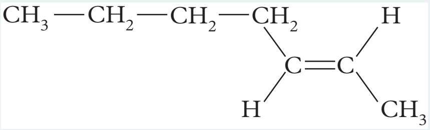
2 **Explain** the role that chirality has in stereoisomers. (2 marks)

Analytical processes

3 **Deduce** the structural isomers of C_6H_{14}. **Sketch** and name each of them. (10 marks)

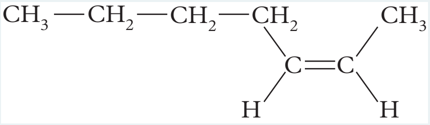
4 **Apply** IUPAC rules to name the following isomers.

a



(1 mark)

b



(1 mark)

5 For pent-2-ene

a **sketch** the two geometrical isomers (2 marks)

b **apply** IUPAC rules to name each isomer. (2 marks)

6 **Sketch** the following pairs of molecules. **Determine** whether the pairs of molecules are isomers. If they are isomers, **identify** the type of isomer. (Note: A pair of molecules may be more than one type of isomer.)

a Hex-1-ene and 2-methylpent-1-ene (3 marks)

b 2-Methylbutane and pent-2-ene (3 marks)

c 2-Methylbutan-2-ol and 3-methylbutan-2-ol (3 marks)

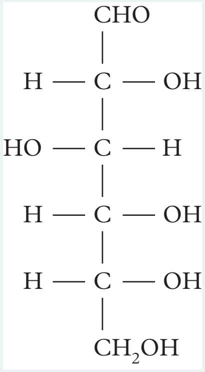
d Methyl ethanoate and propanoic acid (3 marks)

7 Use your understanding of molecular structure and chirality to answer the following.

a **Determine** the two structural formulas of the optical isomers of butan-2-ol. (2 marks)

b **Identify** the chiral carbon atom in each isomer. (1 mark)

8 The linear form of glucose is shown. **Determine** which of the six carbon atoms are chiral. (1 mark)



Lesson 9.5

Investigating organic compounds

Key ideas

→ The formulas of organic compounds can be used to determine the percentage composition of elements present.

→ Experimental data can be analysed to determine the percentage composition of organic compounds.

→ Experimental data can be analysed to determine the empirical, molecular and structural formulas of organic compounds.

How can data about organic compounds be used?

Learning intentions and success criteria

Organic chemists have many analytical methods that can be used to determine the identity and structure of a compound. Recall from Units 1 & 2 that the formula can allow the calculation of percentage composition of the elements in a compound.

Combustion data can be analysed to provide percentage composition of elements in a compound and enables the empirical formula to be determined. From the molar mass, the molecular formula and possible structural formulas can be determined.

How can we determine percentage composition from a formula?

Worked example 9.5A shows how to calculate the percentage compositions of elements in an organic compound.

Worked example 9.5A

Determining the percentage composition of elements in a compound from a formula

Determine the percentage composition of each element in propanol, which has the molecular formula C_3H_8O. (6 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	“Determine” means establish, conclude or ascertain after consideration, observation, investigation or calculation. We need to consider the formula and use relative atomic mass together with the molar masses to calculate the percentage of each element. The question is worth 6 marks, so we must show the substitution steps and express the answer for each element as a percentage.
Step 2: Select the appropriate formulas and gather the required data.	C_3H_8O contains three C atoms, eight H atoms and one O atom per molecule. $\text{RAM(C)} = 12.01\text{ g mol}^{-1}$ $\text{RAM(H)} = 1.01\text{ g mol}^{-1}$ $\text{RAM(O)} = 16.00\text{ g mol}^{-1}$ $M(C_3H_8O) = (3 \times 12.01 + 8 \times 1.01 + 1 \times 16.00)\text{ g mol}^{-1}$ $= 60.11\text{ g mol}^{-1}$

Think	Do
Step 3: Calculate to find the percentage by mass. Express the mass of each element in the compound and the molar mass of the compound as a fraction, and multiply by 100.	Percentage of C = $\frac{3 \times 12.01\ \text{g mol}^{-1}}{60.11\ \text{g mol}^{-1}} \times \frac{100}{1}\%$ (1 mark) Percentage of H = $\frac{8 \times 1.01\ \text{g mol}^{-1}}{60.11\ \text{g mol}^{-1}} \times \frac{100}{1}\%$ (1 mark) Percentage of O = $\frac{1 \times 16.00\ \text{g mol}^{-1}}{60.11\ \text{g mol}^{-1}} \times \frac{100}{1}\%$ (1 mark) (Alternatively: Percentage of O = 100% – (%C + %H) = 100% – (59.94% + 13.44%)
Step 4: Finalise your answer by rounding the numbers to an appropriate number of significant figures and include the % sign.	Percentage of C = 59.94% (1 mark) Percentage of H = 13.44% (1 mark) Percentage of O = 26.62% (1 mark)

Your turn

Determine the percentage composition of each element in ethanoic acid, which has the molecular formula $C_2H_4O_2$. (6 marks)

How can we determine percentage composition from combustion data?

When hydrocarbons or compounds containing carbon, hydrogen and oxygen undergo complete combustion, the products are carbon dioxide and water. The amounts of carbon dioxide and water can be analysed to obtain the percentage composition of the compound. Often, very small samples are used, so mmol (millimole) is used for amounts rather than mol. The percentage composition and ratios of elements are not altered. Worked example 9.5B shows this type of calculation.

Worked example 9.5B

Analysing experimental data and determining the percentage composition of an organic compound

100.0 mg of compound containing carbon, hydrogen and oxygen undergoes complete combustion to produce 237.3 mg of carbon dioxide and 121.5 mg of water vapour.

Analyse the data to **determine** the percentage composition of elements in the compound. (10 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the question is asking you to do.	"Analyse" in this context means dissect to ascertain and examine constituent parts or their relationships. "Determine" means establish, conclude or ascertain after consideration, observation, investigation or calculation. We need to recognise that the carbon in the compound will be in the carbon dioxide and the hydrogen in the compound will be in the water vapour. The oxygen in the compound will make up the remainder of the 100 mg and 100%. The question is worth 10 marks, so we must show all working and express the percentages of C, H and O.
Step 2: Select the appropriate formulas and gather the required data.	m(compound) = 100 mg $m(CO_2)$ = 237.3 mg $m(H_2O)$ = 121.5 mg

Think	Do
	$m(O_2) = ?$ $M(CO_2) = 44.01\,g\,mol^{-1} = 44.01\,mg\,mmol^{-1}$ $M(H_2O) = 18.02\,g\,mol^{-1} = 18.02\,mg\,mmol^{-1}$ $n = \frac{m}{M}$
Step 3: Calculate the amounts of carbon dioxide, carbon, water vapour and hydrogen involved in the combustion.	$n(CO_2) = \frac{237.3\ mg}{44.01\ mg\ mmol^{-1}}$ (1 mark) $= 5.392\ mmol$ $n(C) = n(CO_2) = 5.392\,mmol$ (1 mark) $n(H_2O) = \frac{121.5\ mg}{18.02\ mg\ mmol^{-1}}$ (1 mark) $= 6.74\ mmol$ $n(H) = 2 \times 6.74\,mmol$ $= 13.48\ mmol$ (1 mark)
Step 4: Calculate the masses of carbon, hydrogen in 100 mg of the compound.	$m(C) = n(CO_2) \times M(C)$ $= 5.392\,mmol \times 12.01\,mg\,mmol^{-1}$ $= 64.76\,mg$ (1 mark) $m(H) = n(H) \times M(H)$ $= 13.48\ mmol \times 1.01\,mg\,mmol^{-1}$ $= 13.62\,mg$ (1 mark)
Step 5: Use the masses of carbon and oxygen from step 4 to calculate the mass of oxygen in 100 mg of the compound. Note: If masses of C and H make up the total mass of the sample, the compound is a hydrocarbon and does not contain oxygen.	$m(O) = 100\,mg - (64.76\,mg + 13.2\,mg)$ $= 21.62\,mg$ (1 mark)
Step 6: Finalise your answer by using the masses in 100 mg of the compound and expressing them as a percentage. Since the mass of the compound was 100 mg, the masses of elements are the percentages. No further calculations are required to determine the percentage composition.	Percentage of C = 64.76% (1 mark) Percentage of H = 13.62% (1 mark) Percentage of O = 21.62% (1 mark)

Your turn

100.0 mg of compound containing carbon, hydrogen and oxygen undergoes complete combustion to produce 226.4 mg of carbon dioxide and 82.5 mg of water vapour.

Analyse the data to **determine** the percentage composition of elements in the compound. (9 marks)

How can percentage composition be used to determine empirical, molecular and structural formulas?

Experimental data can provide the percentage composition of each element in a compound. Using mole calculations, the simplest mole ratio can then be determined, leading to the empirical formula. If the molar mass is known, or can found, this enables the molecular formula to be determined. Knowledge of isomers enables possible structural formulas to be determined. Molar mass may be given, or may possibly be calculated from the pressure, volume and temperature of the compound in vapour form (see Worked example 9.5C).

Worked example 9.5C

Analysing data and determining the empirical, molecular and structural formulas of a compound

An organic compound is found to have 48.6% carbon, 8.2% hydrogen and 43.2% oxygen. The molar mass is known to be 74.09 g mol^{-1}.

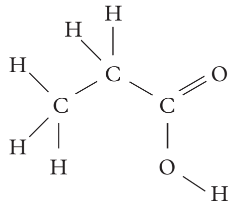
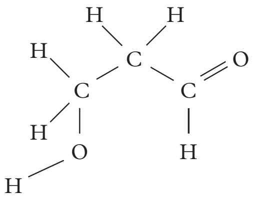
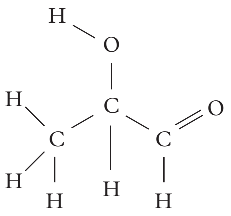
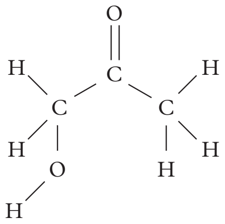
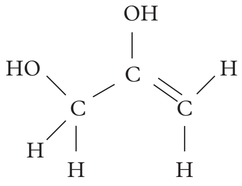
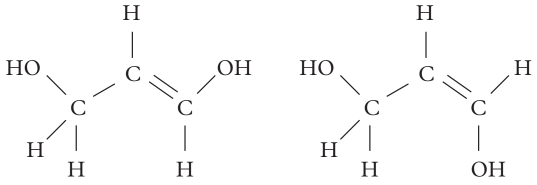
Analyse this data to **determine** the

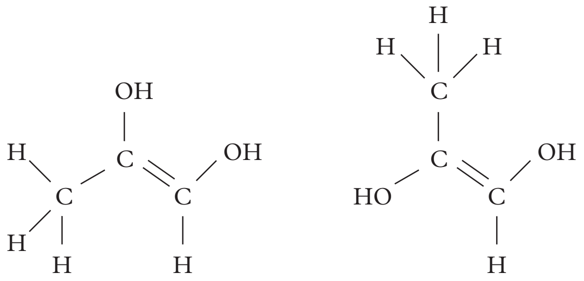
a empirical formula of the compound (5 marks)

b molecular formula of the compound (2 marks)

c possible structural formulas of the compound. (9 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the question is asking you to do.	“Analyse” in this context means dissect to ascertain and examine constituent parts or their relationships. “Determine” means establish, conclude or ascertain after consideration, observation, investigation or calculation. For part **a**, we need to use the percentages to calculate the mole ratio of the elements, and determine the empirical formula. This part is worth 5 marks, so all working out should be clearly shown. For part **b**, we need to use the molar mass and the relative molar mass of the empirical formula to determine the molecular formula. This part is worth 2 marks, so working and logical reasoning must be evident. For part **c**, we need to determine possible structures for the molecular formula. This part is worth 9 marks, so the full variety of possible structural formulas should be deduced and sketched.
Step 2: Select the appropriate formulas and gather the required data.	**a** $\% \text{ C} = 48.6\%$ $M(\text{C}) = 12.01\text{ g mol}^{-1}$ $\% \text{ H} = 8.2\%$ $M(\text{H}) = 1.01\text{ g mol}^{-1}$ $\% \text{ O} = 43.2\%$ $M(\text{O}) = 16.00\text{ g mol}^{-1}$ $n = \frac{m}{M}$
Step 3: Assume for ease of calculations, that 100.0 g of the compound has been tested. This allows the percentage of each element to represent a mass of that element.	$n(\text{C}) = \frac{48.6\text{ g}}{12.01\text{ g mol}^{-1}}$ $= 4.05\text{ mol}$ (1 mark) $n(\text{H}) = \frac{8.2\text{ g}}{1.01\text{ g mol}^{-1}}$ $= 8.12\text{ mol}$ (1 mark) $n(\text{O}) = \frac{43.2\text{ g}}{16.00\text{ g mol}^{-1}}$ $= 2.70\text{ mol}$ (1 mark)
Step 4: Write and express the mole ratio of elements to the simplest whole numbers.	Ratio C : H : O = 4.05 : 8.12 : 2.7 Dividing each number by the smallest which is 2.7 produces the ratio 1.5 : 3.00 : 1.00 Multiply by two to obtain a whole-number ratio. 3 : 6 : 2 (1 mark)
Step 5: Finalise your answer to part **a** by writing the empirical formula using the lowest whole-number ratio of elements.	The empirical formula is $C_3H_6O_2$. (1 mark)

Think	Do
Step 6: Compare the relative molar mass of the empirical formula with the actual molar mass. If necessary, multiply the subscripts in the empirical formula to obtain the molecular formula.	**b** $M(C_3H_6O_2) = 3 \times 12.01 + 8 \times 1.01 + 2 \times 16.00$ $= 74.09\ g\ mol^{-1}$ (1 mark) Note that this is the same as the molar mass, so the molecular formula is the same as the empirical formula.
Step 7: Finalise your answer to part **b** by writing the molecular formula.	The molecular formula is $C_3H_6O_2$. (1 mark)
Step 8: Finalise your answer to part **c** by deducing and sketching the structural formulas for the molecular formula.	**c**  (1 mark)  (1 mark)  (1 mark)  (1 mark)  (1 mark)  (2 marks, for showing both *cis* and *trans* isomer positions of H)

Think	Do
	 (2 marks, for showing *cis* and *trans* isomer positions of OH)

Your turn

An organic compound is found to have 40.0% carbon, 6.7% hydrogen and 53.3% oxygen. The molar mass is known to be 60.06 g mol^{-1}.

Analyse this data to **determine** the

a empirical formula of the compound (5 marks)

b molecular formula of the compound (2 marks)

c possible structural formulas of the compound. (4 marks)

How can combustion data be used to determine empirical, molecular and structural formulas?

When hydrocarbons and compounds containing only carbon, hydrogen and oxygen undergo complete combustion, the products of the reaction are carbon dioxide and water. The data from combustion reactions can be analysed to determine empirical, molecular and possible structural formulas. As in Worked example 9.5B, the number of moles of carbon in the sample burnt is the same as the number of moles of carbon dioxide. The number of moles of hydrogen in the sample burnt is twice the number of moles of water vapour.

Worked example 9.5D

Analysing data and determining the empirical, molecular and structural formulas of a compound

A 100.0 mg sample of a hydrocarbon undergoes complete combustion to produce 302 mg of carbon dioxide and 154 mg of water vapour. The molar mass of the compound is 58.14 g mol^{-1}.

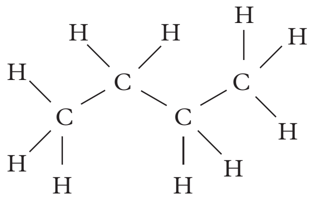
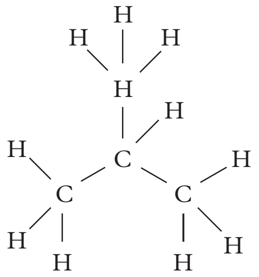
Analyse this data to **determine** the

a empirical formula of the compound (6 marks)

b molecular formula of the compound (2 marks)

c possible structural formulas of the compound. (2 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the question is asking you to do.	"Analyse" in this context means dissect to ascertain and examine constituent parts or their relationships. "Determine" means establish, conclude or ascertain after consideration, observation, investigation or calculation. For part **a**, we need to use the masses to calculate the mole ratio of the elements and determine the empirical formula. This part is worth 6 marks, so all working out should be clearly shown. For part **b**, we need to use the molar mass and the relative molar mass of the empirical formula to determine the molecular formula. This part is worth 2 marks, so the working/logical reasoning must be evident. For part **c**, we need to determine possible structures for the molecular formula. This part is worth 2 marks, so the possible structural formulas should be deduced and sketched.
Step 2: Select the appropriate formulas and gather the required data.	**a** $m(CO_2) = 302\,\text{mg}$ $M(CO_2) = 44.01\,\text{g mol}^{-1}$ $m(H_2O) = 154\,\text{mg}$ $M(H_2O) = 18.02\,\text{g mol}^{-1}$ $n = \frac{m}{M}$
Step 3: Calculate the amounts of carbon dioxide, carbon, water vapour and hydrogen involved in the combustion.	$n(CO_2) = \frac{302\text{ mg}}{44.01\text{ mg mmol}^{-1}}$ $= 6.86\text{ mmol}$ (1 mark) $n(C) = n(CO_2)$ $= 6.86\,\text{mmol}$ (1 mark) $n(H_2O) = \frac{154\text{ mg}}{18.02\text{ mg mmol}^{-1}}$ $= 8.55\text{ mmol}$ (1 mark) $n(H) = 2 \times 8.55\text{ mmol}$ $= 17.1\,\text{mmol}$ (1 mark)
Step 4: Write and express the mole ratio of elements to the simplest whole numbers. Divide both numbers by the smaller, and multiply if required to produce whole numbers.	Mole ratio C : H = 6.86 : 17.1 (dividing by 6.86) = 1 : 2.49 (then doubling) = 2 : 5 (1 mark)
Step 5: Finalise your answer to part **a** by writing the empirical formula using the lowest whole-number ratio of elements.	The empirical formula is C_2H_5. (1 mark)
Step 6: Compare the relative molar mass of the empirical formula with the actual molar mass. If necessary, multiply the subscripts in the empirical formula to obtain the molecular formula.	**b** $M(C_2H_5) = 2 \times 12.01 + 5 \times 1.01$ $= 29.07\text{ g mol}^{-1}$ (1 mark) Note that this is half the value of the molar mass, so the molecular formula is found by doubling the subscripts in the empirical formula.
Step 7: Finalise your answer to part **b** by writing the molecular formula.	The molecular formula is C_4H_{10}. (1 mark)

Think	Do
Step 8: Finalise your answer to part **c** by deducing and sketching the structural formulas for the molecular formula.	**c**  (1 mark)  (1 mark)

Your turn

A 100.0 mg sample of a hydrocarbon undergoes complete combustion to produce 313 mg of carbon dioxide and 128 mg of water vapour. The molar mass of the compound is 70.15 g mol^{-1}.

Analyse this data to **determine** the

a empirical formula of the compound (6 marks)

b molecular formula of the compound (2 marks)

c possible structural formulas of the compound. (6 marks)

How can we find molar masses and formulas using data from measurements of gases or vapours?

If an organic compound is a gas or is easily vapourised, then pressure, volume and temperature data can be gathered for a sample of the gas. This data enables the molar mass to be calculated. If the empirical formula is known, or can be found, then the molar mass enables the molecular formula to be determined. From this, possible structural formulas can be deduced and sketched. This is shown in Worked example 9.5E.

Further methods of analysis can help to confirm the identity from the possible structural formulas. Chemical reactions (Module 10) can test for the presence of particular functional groups. Other analytical methods (mass spectroscopy and infrared spectroscopy, discussed in Module 12) can determine molar mass and the presence or position of functional groups. Combining all methods is very useful when analysing compounds.

Worked example 9.5E

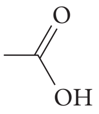
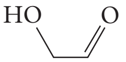
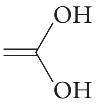
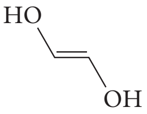
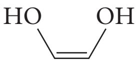
Analysing data from a gaseous organic compound to determine the molecular and structural formulas of an organic compound

An organic compound has an empirical formula of CH_2O. A 0.423 g sample was vapourised at a pressure of 101 kPa and a temperature of 100°C. The vapour sample occupied a volume of 216 mL.

Analyse the data to **determine** the

a molecular formula (4 marks)

b possible structural formulas. (5 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	“Analyse” in this context means dissect to ascertain and examine constituent parts or their relationships. “Determine” means establish, conclude or ascertain after consideration, observation, investigation or calculation. For part **a**, we need to use the gas law and the mass to calculate molar mass, then use the relative molar mass of the empirical formula to determine the molecular formula. This part is worth 4 marks, so working/logical reasoning must be evident. For part **b**, we need to determine possible structures for the molecular formula. This part is worth 5 marks, so the possible structural formulas should be deduced and sketched.
Step 2: Select the appropriate formulas and gather the required data.	$P = 101\,\text{kPa}$ $V = 216\,\text{mL} = 0.216\,\text{L}$ $n = ?$ $R = 8.31\,\text{J mol}^{-1}\,\text{K}^{-1}$ $T = 100^{\circ}\text{C} = 373\,\text{K}$ $PV = nRT$ $m = 0.423\text{ g}$ $n = \frac{m}{M}$
Step 3: Use the ideal gas law to calculate the amount of the compound present.	**a** $n = \frac{101 \times 0.216}{8.31 \times 373}$ $= 0.00704\text{ mol}$ (1 mark)
Step 4: Calculate the molar mass of the compound, using the mass of the sample and the answer from step 3.	$M = \frac{0.423\text{ g}}{0.00704\text{ mol}}$ $= 60.1\text{ g mol}^{-1}$ (1 mark)
Step 5: Calculate the relative molar mass for the empirical formula and compare with the molar mass found in step 4.	$\text{M(CH}_2\text{O)} = (12.01 + 2 \times 1.01 + 1 \times 16)\text{ g mol}^{-1}$ $= 30.03\,\text{g mol}^{-1}$ (1 mark) The actual molar mass is double this, so the subscripts in the formula need to be doubled to determine the molecular formula.
Step 6: Write the molecular formula, using the reasoning from step 5.	The molecular formula is $C_2H_4O_2$. (1 mark)
Step 7: Finalise your answer, sketching structural formulas for the possible isomers. Because there are no double bonds between carbon atoms, isomers that are alkenes do not need to be considered. (Line structural formulas have been chosen in this case, for simplicity.)	**b**  (1 mark)  (1 mark)  (1 mark)  (*trans* isomer) (1 mark)  (*cis* isomer) (1 mark)

Your turn

An organic compound has an empirical formula of CH_2. A 0.362 g sample was vapourised at a pressure of 101 kPa and a temperature of 100°C. The vapour sample occupied a volume of 198 mL.

Analyse the data to **determine** the

a molecular formula of the compound (4 marks)

b possible structural formulas of the compound. (6 marks)

Check your learning 9.5

Check your learning 9.5: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Recall** the ideal gas equation. (1 mark)

2 A 20.0 mg sample of butanol contains 4.32 mg of oxygen. **Calculate** the percentage of oxygen in butanol. (1 mark)

Analytical processes

3 An organic compound has the molecular formula of C_4H_8O. **Determine** the percentage composition of each element in the compound. (6 marks)

4 100.0 mg of a compound undergoes complete combustion to produce 255 mg of carbon dioxide and 104 mg of water vapour. **Analyse** the combustion data to determine the percentage composition of each element in the compound. (9 marks)

5 An organic compound has 48.6% carbon, 8.2% hydrogen and 43.2% oxygen. It does not contain any double bonds between carbon atoms. The molar mass is 74.09 g mol^{-1}. **Analyse** this data to **determine**

  a the empirical formula of the compound (5 marks)

  b the molecular formula of the compound (2 marks)

  c possible structural formulas of the compound that contain a carboxyl group. (3 marks)

6 A 50.0 mg sample of an unbranched hydrocarbon undergoes complete combustion to produce 156.0 mg of carbon dioxide and 63.0 mg of water vapour. The molar mass of the compound is 84.18 g mol^{-1}. **Analyse** this data to **determine**

  a the empirical formula of the compound (5 marks)

  b the molecular formula of the compound (2 marks)

  c possible structural formulas of the compound. (5 marks)

7 An organic compound has an empirical formula of C_3H_6O. It is known that the compound does not have any double bonds between carbon atoms. A 0.50 g sample was vapourised at a pressure of 100 kPa and a temperature of 100°C. The vapour sample occupied a volume of 264 mL. **Analyse** the data to **determine** the

  a molecular formula (4 marks)

  b possible structural formulas. (2 marks)

Practical

Lesson 9.6

Modelling isomers of organic molecules

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Learning intentions and success criteria

Lesson 9.7

Physical properties of organic compounds

Learning intentions and success criteria

Key ideas

→ Homologous series show trends in physical properties (boiling point, volatility, melting point, and solubility in water and organic solvents).

→ The trends in physical properties within and between the different homologous series (alkanes, alkenes, alcohols and carboxylic acids) can be explained in terms of intramolecular bonding and intermolecular forces.

What physical properties of homologous series show tends?

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**, **volatility** and **solubility** in water and organic solvents. A volatile substance is a liquid that readily evaporates at normal temperatures; it also has a measurable vapour pressure. Since organic compounds have distinctive odours, a volatile compound will be noticed by its odour when it evaporates.

Why do homologous series show trends in physical properties?

A **homologous series** is a group of organic compounds that have the same functional group but increase by one carbon atom through the series. For example, the alkanes are a homologous series and the first four members are methane, ethane, propane and butane.

melting point
the temperature at which a material changes from a solid to a liquid, which is also the temperature at which a material freezes

boiling point
the temperature at which a liquid boils, forming bubbles of vapour below the surface of the liquid

volatility
how easily a liquid substance evaporates (becomes a vapour)

solubility
the degree to which a substance dissolves in a particular solvent to make a solution (frequently expressed as grams of solute per litre of solvent)

homologous series
a group of organic compounds with the same functional group but a different number of carbon atoms in the main chain

With an increase of 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 and a larger surface area available for intermolecular attractions between neighbouring molecules, and the increased attraction causes a slight increase in the melting and boiling points because the molecules can resist phase changes in higher temperatures.

What are the trends for 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.

Table 1 lists the melting and boiling points of the first eight members of the alkane homologous series.

TABLE 1 Physical properties of the alkane homologous series

Molecular name	Formula	Melting point (°C)	Boiling point (°C)
Methane	CH_4	–182	–164
Ethane	C_2H_6	–183	–89
Propane	C_3H_8	–188	–42
Butane	C_4H_{10}	–138	–1
Pentane	C_5H_{12}	–130	36
Hexane	C_6H_{14}	–95	69
Heptane	C_7H_{16}	–91	98
Octane	C_8H_{18}	–57	125

An increase in the number of carbon atoms causes the boiling point to rise compared to other members of the same homologous series. The increase becomes smaller with each additional carbon atom, but the trend remains consistent. Due to increasing molecular size, the strength of the dispersion forces between the non-polar alkane molecules increases.

For melting points, the trend is more complex, as shown in Figure 1. For alkanes with three or more carbon atoms, their melting points increase as the size and molar mass increases. However, the increase is quite small when going from a compound with an even number of carbon atoms to a compound with an odd number of carbon atoms. For example, from butane to pentane, the increase is just 8°C, whereas from pentane to hexane, the increase is 35°C. This apparent anomaly can be explained by considering how carbon chains with an even number of carbon atoms can pack more effectively in the solid state than carbon chains with an odd number. Effective packing maximises the intermolecular attractions, making the melting point slightly higher than expected. For carbon chains with an odd number of carbon atoms, the molecules do not pack as well in the solid and so the melting point is lower than would be expected. Ethane and methane are both much smaller molecules. Ethane fits into the overall trend for molecules with an even number of carbon atoms but is anomalous when compared with propane.

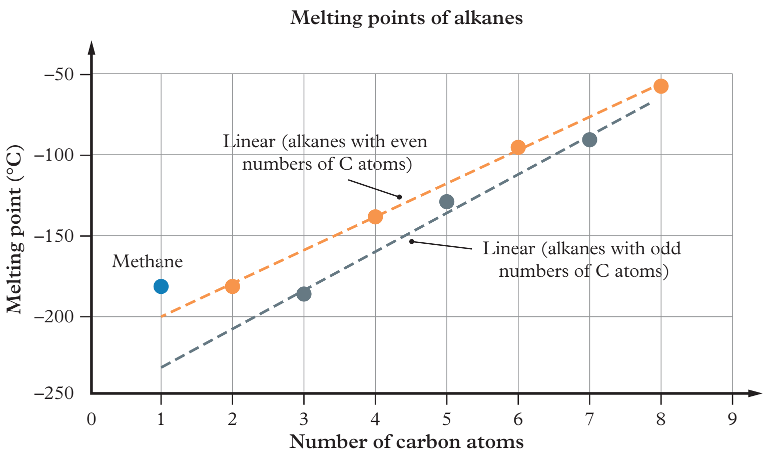


FIGURE 1 A graph showing the trends in melting points of alkanes

Methane is quite small and symmetrical, so it packs very well as the solid and thus has a somewhat higher melting point than expected.

Linear alkenes have slightly lower boiling points than the corresponding linear alkanes (Table 2). As they have two fewer hydrogen atoms, they are slightly smaller molecules and experience weaker dispersion forces.

TABLE 2 The boiling points of some hydrocarbons

Alkane	Boiling point (°C)	Alkene	Boiling point (°C)
Methane	–164		
Ethane	–89	Ethene	–104
Propane	–42	Propene	–47
Butane	–1	But-1-ene	–6
Pentane	36	Pent-1-ene	30
Hexane	69	Hex-1-ene	63
Methylpropane	–12	Methylpropene	–7
Methylbutane	28	2-Methylbut-1-ene	31
2-Methylpentane	60	2-Methylpent-1-ene	62

Branched alkanes tend to have lower boiling points than their straight-chained equivalents. This is because the branching reduces the surface area of their molecular shape. This reduces the dispersion forces. This is not always the case for melting points though as a branched structure is more compact and less flexible and may pack into the solid form more effectively.

The melting points of alkenes are broadly similar to the melting points of the corresponding alkane. For butene and higher alkenes, the melting point also depends on whether the alkene is a *cis* or *trans* isomer, as shown in Table 3.

TABLE 3 The melting points of some alkenes

Molecular name	Melting point (°C)	Molecular name	Melting point (°C)
Ethene	–169		
Propene	–185		
But-1-ene	–138	*trans*-But-2-ene	–105
		cis-But-2-ene	–139
Pent-1-ene	–130	*trans*-Pent-2-ene	–135
		cis-Pent-2-ene	–180

The melting points of *cis* isomers are generally lower than those of *trans* isomers. In *cis* isomers, the molecules have bulky side groups on the same side, and are more U shaped, so they do not pack as well in the solid. This makes them easier to melt. However, *trans* isomers can pack more closely and efficiently, which maximises intermolecular forces of attraction (Figure 2).

The first four alkanes and alkenes are all gases at standard laboratory conditions. From pentane and pentene onwards, the lower molecular mass liquids are all quite volatile due to the relatively weak intermolecular forces. They evaporate readily, and when the vapour is mixed with air, it can ignite with a spark or naked flame and react rapidly and explosively. Volatility decreases for larger hydrocarbons because the intermolecular forces are larger.

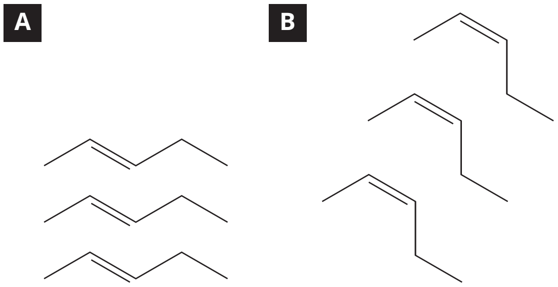


FIGURE 2 (A) *trans*-Pent-2-ene molecules can pack more closely in the solid state. (B) *cis*-Pent-2-ene molecules are unable to pack as closely together.

Additionally, the smaller liquid hydrocarbons and their vapours are toxic, and great care must be taken when using them.

All 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 tetrachloromethane.

Challenge

Boiling points of hydrocarbons

Construct a graph of the boiling points of the first six alkanes, the first five alkenes and the first three branched alkanes and alkenes. **Identify** the different trends in the data and discuss why the boiling points change between the different hydrocarbons. (7 marks)

What are the trends for 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 oxygen and hydrogen (Figure 3). In addition, the bond between carbon and oxygen is polar and gives rise to dipole–dipole interactions. These two additional stronger types of intermolecular forces mean that the melting and boiling points of alcohols are significantly higher than the hydrocarbons.

Table 4 lists the melting and boiling points of some alcohols. The boiling points increase in a regular fashion, because the size of the molecule increases, which leads to stronger intermolecular forces. Melting points for propanol and above show a similar increase. Ethanol and methanol are anomalous, and both have higher than expected melting points. This is due to these smaller molecules being able to pack very effectively into the solid form. 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.

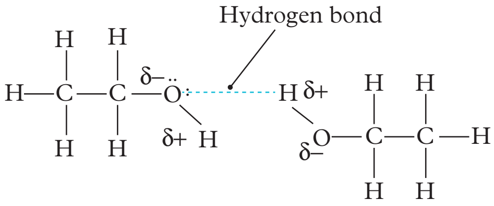


FIGURE 3 Hydrogen bonding between alcohol molecules

TABLE 4 The melting and boiling points of some alcohols

Alcohol	Melting point (°C)	Boiling point (°C)
Methanol	–98	65
Ethan-1-ol	–114	78
Propan-1-ol	–126	97
Butan-1-ol	–89	117
Pentan-1-ol	–60	138
Hexan-1-ol	–54	157
Ethane-1,2-diol	–13	198
Propane-1,2,3-triol	18	290

Some alcohols, such as methanol and ethanol, are relatively volatile, but volatility decreases as the alcohols increase in size through the homologous series.

miscible
completely soluble

Alcohols are soluble in organic solvents. Methanol, ethanol and propanol are **miscible** in all proportions in water. The molecules can form hydrogen bonds with water molecules, and the non-polar part of these molecules is relatively small and does not prevent dissolving in water. As the number of carbon atoms in the alcohol increases, the non-polar part of the molecule becomes larger and more significant compared to the small polar OH group. For this reason, the solubility in water decreases rapidly once alcohols have four or more carbons.

What are the trends for carboxylic acids?

The carbonyl and hydroxyl of the carboxyl functional group are both quite polar. In the pure solid or liquid form, molecules of carboxylic acids arrange themselves to form a structure that is double the size of the acid molecule (Figure 4). This structure is called a **dimer**. It behaves as though it is a molecule with double the molecular mass. For this reason, carboxylic acids have significantly higher boiling points and melting points (Table 5) than the corresponding alcohols (and most other organic compounds). Larger molecules have larger boiling points. The trend for melting points is more complicated, due to some molecular sizes packing more effectively into the solid form and being more difficult to melt. The smaller carboxylic acids are volatile.

dimer
a structure consisting of two identical molecules linked together; they may be linked by chemical bonds into a larger molecule, or simply held in place by intermolecular forces

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 propanone.

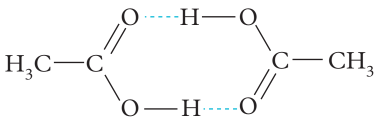


FIGURE 4 Dimer formation between carboxylic acid molecules

TABLE 5 The melting and boiling points of some carboxylic acids

Carboxylic acid	Melting point (°C)	Boiling point (°C)
Methanoic acid	8	101
Ethanoic acid	17	118
Propanoic acid	–21	141
Butanoic acid	–5	164
Pentanoic acid	–24	186
Hexanoic acid	–4	205

Skill drill

Communicating information to a specific audience for a specific purpose

Science inquiry skill: Communicating scientifically (Lesson 1.9)

Oral presentations

Biotechnology applications which rely on chemistry are used for disease detection, development of new and personalised pharmaceutical treatments, biofuels, textiles, genetically modified and sustainable food crops, bioremediation or environmental applications, forensic investigation, and in paper, plastic, personal care and detergent manufacturing.

Select one of the applications mentioned and create a three-minute speech to present to the class. This can be done in a group.

Practise your skills

Brainstorm ideas and select one of the biotechnology applications to base your speech on.

a Research, **summarise** and **organise** relevant information on your chosen application. (5 marks)

b **Express** the information in a logical sequence. (5 marks)

Check your learning 9.7

Check your learning 9.7: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** the term "homologous series" and provide examples. (2 marks)

2 **Explain** the role of intermolecular forces in determining the physical properties of organic compounds. (4 marks)

3 **Describe** the term "volatile". (2 marks)

4 For a non-polar solvent

  a **describe** the term (1 mark)

  b **explain** why some organic compounds dissolve in non-polar solvents but are insoluble in water. (2 marks)

5 **Describe** the term "miscible". (1 mark)

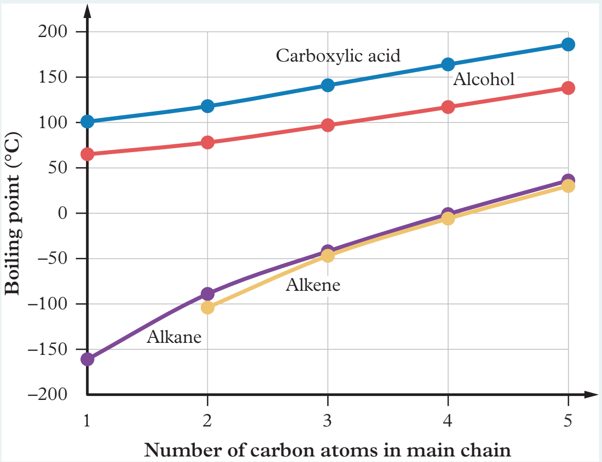
Knowledge utilisation

6 **Analyse** the data in the following table to **predict** the

  a boiling point of nonane. **Justify** your prediction. (2 marks)

  b melting points of nonane and decane. **Justify** your predictions. (2 marks)

7 **Analyse** the data in the following graph and **discuss** the significance of the trendlines with respect to the functional groups in each of the organic compounds. (6 marks)



8 **Investigate** the properties of ethylene glycol and its effects on the properties of water. (4 marks)

9 **Evaluate** the significance of hydrophobicity in members of a homologous series. (3 marks)

Molecular name	Formula	Melting point (°C)	Boiling point (°C)
Methane	CH_4	–182	–164
Ethane	C_2H_6	–183	–89
Propane	C_3H_8	–188	–42
Butane	C_4H_{10}	–138	–1
Pentane	C_5H_{12}	–130	36
Hexane	C_6H_{14}	–95	69
Heptane	C_7H_{16}	–91	98
Octane	C_8H_{18}	–57	125

Practical

Lesson 9.8

Investigating properties of homologous series

Learning intentions and success criteria

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

MODULE 9

Lesson 9.9

Review: Structure of organic compounds

Summary

9.1

- Simple hydrocarbons contain carbon and hydrogen only and are named according to IUPAC rules of nomenclature.
- Hydrocarbons can contain single, double or triple bonds, which are named according to IUPAC rules and described as saturated or unsaturated.
- Groups of compounds with similar structures and differing only in the length of their carbon chain are described as a homologous series.
- Branched hydrocarbons are named according to IUPAC rules, including the locant and the prefix for the branch.

9.2

- Organic compounds can include functional groups containing oxygen, nitrogen and various halogens.
- The various functional groups in organic compounds determine the particular classes they belong to.
- IUPAC nomenclature is used to name complex organic compounds that contain methyl and ethyl branches along with one other functional group.
- IUPAC nomenclature is used to name classes of compounds, including alcohols, aldehydes, ketones, carboxylic acids, haloalkanes and esters for both linear molecules and molecules with alkyl branches.

9.3

- Organic compounds are represented in greatest detail in extended structural formulas.
- Condensed and line structural formulas provide less detail about the structure of organic compounds but are more compact.
- Molecular formulas provide information about the number and identity of each element in a compound but lack information about structure and functional groups.
- Empirical formulas provide information about the identity of each element in a compound and their simplest whole-number ratio.
- Given one type of structural formula for a compound – extended, condensed or line – it is possible to represent the compound in one of the other types of formulas.
- Molecular and structural formulas can be determined from the name of the organic compound.

9.4

- Isomers are molecules with the same molecular formula but different structures.
- Isomers can be classified as structural isomers and stereoisomers. Stereoisomers are subdivided into geometrical (*cis* and *trans*) and optical isomers.
- Isomers can be represented by structural formulas.
- Structural formulas and IUPAC nomenclature can be used to differentiate between isomers that have the same molecular formula.

9.5

- The formulas of organic compounds can be used to determine the percentage composition of elements present.
- Experimental data can be analysed to determine the percentage composition of organic compounds.
- Experimental data can be analysed to determine the empirical, molecular and structural formulas of organic compounds.

9.6

- Practical: Modelling isomers of organic molecules

9.7

- Homologous series show trends in physical properties (boiling point, volatility, melting point, and solubility in water and organic solvents).

9.7
- The trends in physical properties within and between the different homologous series (alkanes, alkenes, alcohols and carboxylic acids) can be explained in terms of intramolecular bonding and intermolecular forces.

9.8
- Practical: Investigating properties of homologous series

Review questions 9.9A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

1 An alkene is best described as a hydrocarbon containing

A only single carbon bonds.
B only double carbon bonds.
C one or more triple carbon bonds.
D one or more double carbon bonds.

2 A functional group is

A an atom or a group of atoms that has similar chemical properties whenever it appears in various compounds.
B interchangeable with the term "class of compound" and has a name such as ester, amide and aldehyde.
C the location of polar sections and chemical reactivity in an organic compound.
D a part of an organic molecule that contains one or more atoms other than carbon and hydrogen, for example a halogen, nitrogen or oxygen.

3 A condensed structural formula provides information about

A only the number of atoms.
B only the atom arrangement.
C the bonding and atom arrangement.
D only the bonding between the atoms.

4 The physical properties of organic compounds include

A melting points, boiling points and solubility.
B the stability and reactivity of the organic compound.
C which atoms and bonds are present in the molecule.
D how toxic an organic compound is to the environment.

5 The molecular formula of an organic compound

A enables the structure to be sketched.
B is usually the same as the empirical formula.
C can be determined using combustion data alone.
D enables the percentage composition of elements in the molecule to be determined.

6 A primary amine is best described as an organic compound containing a nitrogen atom

A triple bonded to a carbon.
B double bonded to an oxygen.
C attached to an alkyl group and two hydrogens.
D attached to carbonyl groups and hydrogens.

7 Which of the following hydrocarbons has six carbon atoms?

A Butane
B Ethane
C Hexane
D Octane

8 "Stereoisomers" is a general term used to describe

A structural and geometric isomers.
B optical isomers and structural isomers.
C optical isomers and geometric isomers.
D optical isomers and chiral centre isomers.

9 A compound containing a carbon with a double bond to an oxygen could be

A a ketone or an ester.
B an amine or an ester.
C an alcohol or a ketone.
D an alcohol or an amine.

10 The type of structural formula that shows the bonds between carbons (and their surrounding hydrogens) in a hydrocarbon is known as

A line.
B basic.
C extended.
D condensed.

Review questions 9.9B Short response

Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

11 **Describe** the structure of the carboxyl functional group. (1 mark)

12 **Define** the three types of alcohols. (3 marks)

13 **Describe** the term "structural isomer". (1 mark)

14 **Explain** how geometrical isomers and optical isomers are both classified as stereoisomers. (3 marks)

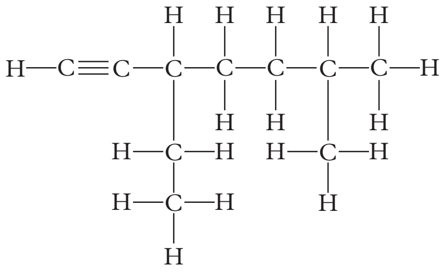
15 **Describe** the features of a homologous series. Use an example. (2 marks)

16 **Explain** the boiling point trend within members of a homologous series. (2 marks)

17 **Explain** the trend in volatility within members of a homologous series. (2 marks)

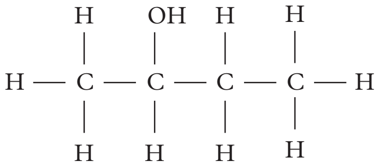
18 **Identify** the functional groups in the following organic compounds.

a



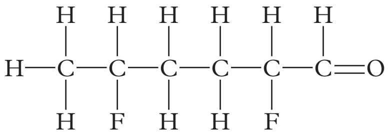
(1 mark)

b



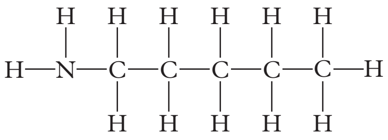
(1 mark)

c



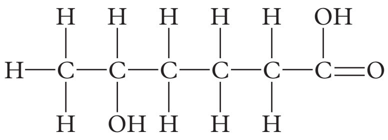
(1 mark)

d



(1 mark)

e



(1 mark)

19 **Sketch** the fifth alkane in the homologous series of all alkanes. (1 mark)

20 **Sketch** the two geometrical isomers of 2,3-dichlorobut-2-ene. (2 marks)

21 **Sketch** the following molecules as extended structural formulas:
2,3,3-trichlorobutanoic acid and propyl ethanoate. (3 marks)

22 **Calculate** the gradient and y-intercept for the mathematical relationship represented by the boiling point data in Table 1, Lesson 9.7. (4 marks)

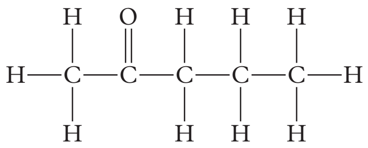
23 **Identify** the functional group(s) and draw diagrams of

- **a** 3-ethyl-4,4-dimethylpent-1-ene (1 mark)
- **b** 2,3,4-trimethyloctanal. (2 marks)

24 **Sketch** a diagram of the molecule hexyl methanoate. (1 mark)

Analytical processes

25 **Apply** IUPAC rules to name the organic compound. (1 mark)

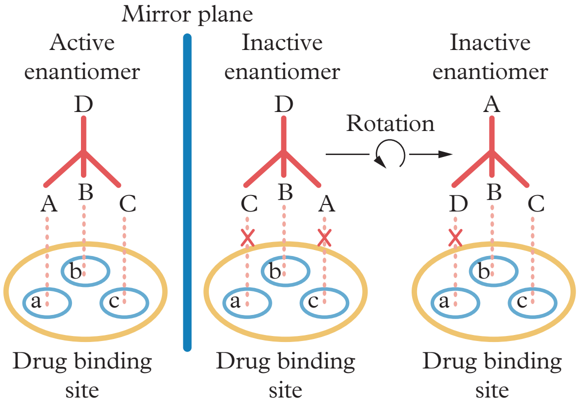


26 **Deduce** the extended and condensed structural formulas of 3-methylbut-1-yne. (2 marks)

27 **Apply** IUPAC rules to name the organic molecules in question **18a**, **b** and **c**. (3 marks)

28 **Deduce** the structural isomers of C_6H_{14}. **Sketch** and name each of them. (10 marks)

29 **Analyse** the following diagram of two optical isomers (enantiomers) of a drug 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. (4 marks)



30 **Compare** the structures of 1-chlorobutane and 2-chlorobutane to determine whether either of these compounds exists as a pair of optical isomers. (4 marks)

31 A 100.0 mg sample of an organic compound containing oxygen undergoes complete combustion to produce 198 mg of carbon dioxide and 80 mg of water vapour. The molar mass of the compound is 88.12 g mol^{-1}. An aqueous solution of the compound reacts with sodium hydrogen carbonate to produce small bubbles of carbon dioxide gas. **Analyse** this data to **determine** the

- **a** empirical formula of the compound (5 marks)
- **b** molecular formula of the compound (2 marks)
- **c** structural formula and name of the compound. (2 marks)

32 Propan-2-ol has the common name of isopropyl alcohol. It is available commercially and is also a component of cleaning fluids for the lenses of spectacles. **Apply** your knowledge of the structure and physical properties of propan-2-ol to **determine** why it is more useful than other possible cleaning agents for this purpose. (4 marks)

Knowledge utilisation

33 *trans*-Hept-2-ene has a melting point of –109°C. **Predict** the melting point of *cis*-hept-2-ene and **justify** your prediction. (2 marks)

34 An algebraic expression of the alkane class of organic compounds is represented as C_nH_{2n+2}, where n is any number.

Investigate the algebraic expressions used to represent the 1-alkene, 1-alkyne, primary alcohol and carboxylic acid classes of organic compounds. (4 marks)

35 **Evaluate** the names of the following organic compounds by considering the structural formulas. **Discuss** the errors made, and provide the correct names.

- **a** 3-methylbut-2-yne (2 marks)
- **b** 2,3-dimethyl-4-ethylnonane (2 marks)
- **c** Butan-1-one (2 marks)
- **d** 2-ethyl-2-methylhexane (2 marks)
- **e** 2-propyl-3-bromo-4-ethyl-5-fluoro-6-methylhexan-1-ol (2 marks)

36 **Investigate** the history of the drug thalidomide, which exists as two optical isomers, and draw a conclusion about the influence of different shaped isomers on the pharmacological action of a drug. (4 marks)

Data drill

Analysing melting point trends

The melting point of a substance is the temperature at which it transitions from a solid to a liquid (at a particular pressure). For covalent molecular substances, the melting point depends on the types and relative strength of the intermolecular forces as well as the packing efficiency within the solid. The molecular mass in amu is related to the size of the molecule. The electronegativity differences in bonds and the symmetry of a molecule determine the types of intermolecular forces. Molecules that can pack closer together with less wasted space experience increased intermolecular forces.

The melting points of four linear (unbranched) homologous series, the alkanes, the 1-alkenes (where the double bond is on locant 1), primary alcohols and carboxylic acids, are graphed in Figure 1 and Figure 2.

These compounds all contain bonds between C and H. Additionally, alcohols and carboxylic acids contain bonds between C and O and between O and H (C–H, C–O and O–H).

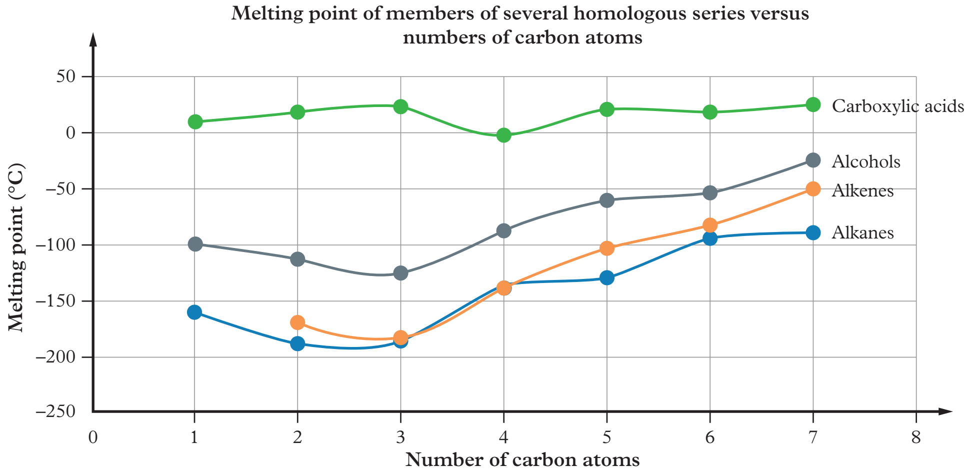


FIGURE 1 Melting points as a function of number of carbon atoms

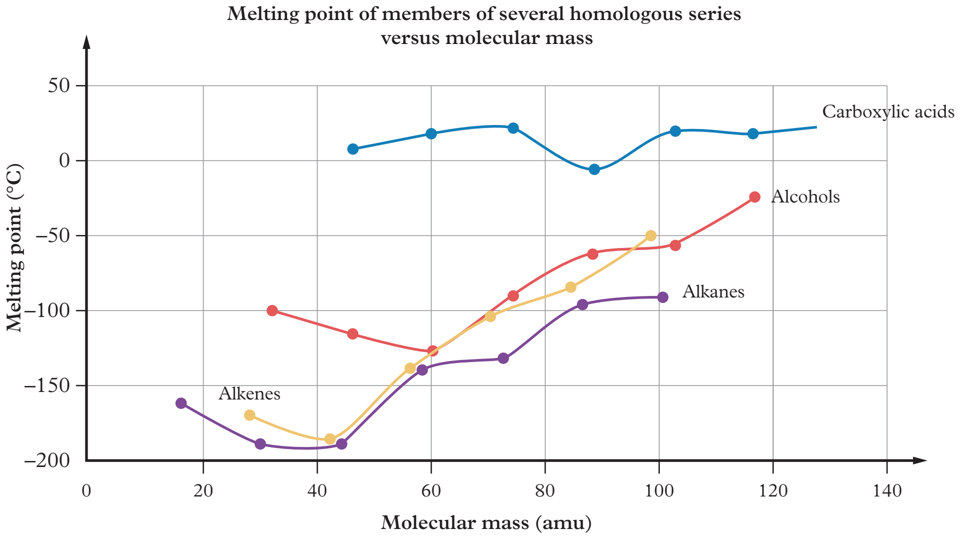


FIGURE 2 Melting points as a function of molecular mass

The QCAA *Formula and data book* may be used for the following questions.

Apply understanding

1 **Identify** the melting point of the alkane with seven carbon atoms. (1 mark)

2 **Calculate** the electronegativity differences of the three bonds mentioned in the text (C–H, C–O and O–H). **Determine** the most polar of the three bonds based on your calculations. (4 marks)

Analyse data

3 **Identify** the trend in melting points for the alcohols. (2 marks)

4 **Compare** the trends in melting points for the alkanes and the alkenes. (3 marks)

Interpret evidence

5 **Predict** the melting points of the alcohol and the carboxylic acid with eight carbon atoms. (2 marks)

6 For the predictions made in question **5**, interpret the evidence to **determine** the confidence in the predicted values. (4 marks)

Module 9 checklist: Structure of organic compounds

MODULE 10

Organic reactions and reaction pathways

Introduction

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 produce cellulose in plants and DNA in cells and take part in the biochemical pathways within our bodies.

Organic compounds react at the site of functional groups, and each functional group takes part in specific chemical reactions. These reactions can be used to identify the functional group present. More importantly, they can be used in the design of chemical pathways to synthesise specific products. In Module 9, you learnt that the physical properties of organic compounds can be predicted from the functional group present. It is often said that organic chemistry is the chemistry of functional groups, because these groups are the key to understanding both physical and chemical properties.

Prior knowledge

Prior knowledge quiz

Check your understanding of concepts related to organic reactions and reaction pathways before you start.

Subject matter

Science understanding

→ Identify that an organic compound displays characteristic chemical properties and undergoes specific reactions based on the functional group present.

→ Determine, using equations, the reaction of
- alkanes with halogens (X_2)
- haloalkanes with halogens (X_2), sodium hydroxide and ammonia
- alkenes with water, halogens (X_2), hydrogen (H_2) and hydrogen halides (HX)
- alcohols with hydrogen halides (HX)
- carboxylic acid with alcohol to form esters, and with amines to form amides.

- → Determine, using equations, reactions including the
  - – oxidation of alcohols
  - – combustion of alkanes and alcohols
  - – addition of alkenes to form poly(alkenes)
  - – reduction of alkynes and alkenes to form alkanes
  - – elimination of haloalkanes to form alkenes.
- → Identify reactions as addition, elimination, substitution or redox (oxidation-reduction). (Reaction mechanism for substitution and elimination reactions are not required.)
- → Determine the primary, secondary and tertiary carbon atoms in haloalkanes and alcohols.
- → Describe the acid-base properties of carboxylic acids and amines.
- → Explain that esterification is a reversible reaction.
- → Discriminate between
  - – alkanes and alkenes using bromine water
  - – primary, secondary and tertiary alcohols using acidified potassium dichromate(VI) and potassium manganate(VII).
- → Apply Markovnikov's rule to determine the products for addition reactions of alkenes with hydrogen halides (HX) and water.
- → Determine reaction pathways, including reagents, condition and chemical equations, given the starting materials and the product/s formed.
- → Interpret chemical tests to distinguish between alkanes and alkenes; and primary, secondary and tertiary alcohols.

Science as a human endeavour

- → Appreciate that organochlorine compounds, such as DDT, chlordane and lindane, were identified as powerful insecticides in the 1950s because their structure makes them chemically unreactive.
- → Explore the relationship between the chemical structure of insecticides, their effectiveness as an insecticide, and their persistence and bioaccumulation in the environment.

Source: *Chemistry 2025 v 1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

Practicals

oxforddigital **These lessons are available on Oxford Digital.**

Lesson 10.2 Testing for saturation
Lesson 10.4 Testing alcohols

Lesson 10.1
Addition and elimination reactions

Key ideas

→ Addition reactions break a double or triple bond and replace it with two substituents. Addition reactions include hydrogenation, halogenation, hydrohalogenation or hydration reaction.

→ Markovnikov's rule explains the general trend that, in the addition of an asymmetrical reagent, the hydrogen atom will bond to the carbon that already has the most hydrogen atoms.

→ 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 them with a double bond.

Learning intentions and success criteria

addition the addition of substituents across a carbon–carbon multiple bond

hydrogenation the addition of hydrogen across a carbon–carbon multiple bond

halogenation the addition of a halogen across a carbon–carbon multiple bond

Study tip

To refresh your understanding of saturated hydrocarbons, which have only single carbon–carbon bonds, see Lesson 9.1. Unsaturated hydrocarbons contain double or triple bonds between carbon atoms.

What are addition reactions?

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 is the addition of hydrogen (H_2) across a double or triple bond. Temperatures of 150–300°C are required, as well as a metal catalyst. 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 and the word "heat" below the arrow (Figure 1). Lesson 10.3 will discuss how the addition of hydrogen is also classed as a reduction reaction.

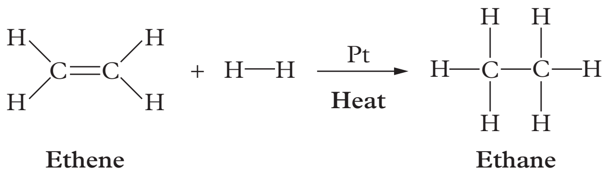


FIGURE 1 Hydrogenation of ethene with heat and a platinum catalyst forms ethane.

Halogenation

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).

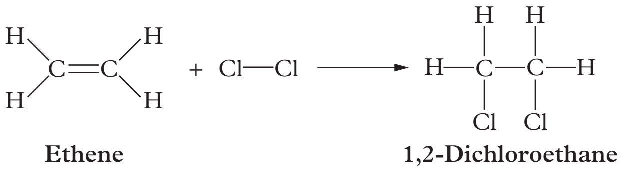


FIGURE 2 Halogenation (chlorination) of ethene to produce 1,2-dichloroethane does not require a catalyst.

Which chemical tests are used to distinguish between 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 rapidly 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 may be saturated (an alkane) and cannot undergo an addition reaction, or it may be an unsaturated, aromatic compound which undergoes addition reactions less easily and requires a catalyst and heat.

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. Like the halogenation reaction, hydrohalogenation does not require heat or catalysts.

hydrohalogenation the addition of a hydrogen atom and a halogen atom across a double bond

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 4). 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 5). This has become known as Markovnikov's rule.

FIGURE 4 Vladimir Markovnikov, the Russian chemist who devised Markovnikov's rule

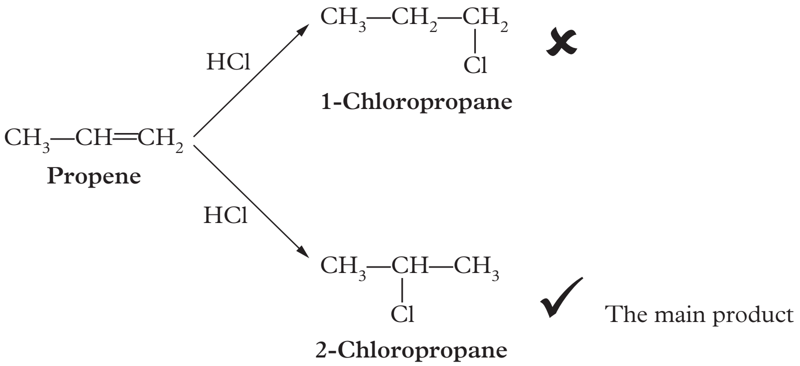


FIGURE 5 The hydrohalogenation of propene. According to Markovnikov's rule, when HCl adds across the double bond, hydrogen adds to the carbon with the most hydrogens and chlorine adds to the carbon with the least hydrogens.

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, although the exact percentages depend on the reactants and conditions. The products then need to be separated and 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 different conditions, depending on whether a primary, secondary or tertiary alcohol is being produced (Table 1). For the production of primary alcohols such as ethanol, high temperatures (300°C), high pressures and a catalyst in the form of trace amounts of sulfuric or phosphoric acid are required. The hydration of ethene to produce ethanol, using phosphoric acid as a catalyst at 300°C and 6,000 kPa (Figure 6).

TABLE 1 The conditions for the hydration of alkenes to form different types of alcohols

Alcohol type	Example	Temperature (°C)	Pressure (kPa)	Catalyst
Primary	ethene → ethanol	about 300	6,000–7,000	H_3PO_4
Secondary	propene → propan-2-ol	100–250	500	H_2SO_4/H_3PO_4
Tertiary	2-methylpropene → 2-methylpropan-2-ol	25–100	100	H_2SO_4

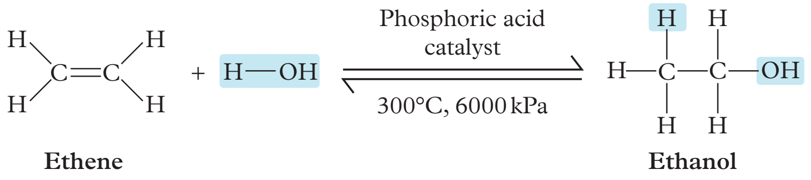


FIGURE 6 The hydration of ethene to produce the primary alcohol ethanol requires high temperatures and pressures and a catalyst.

Hydration of non-symmetric alkenes also follows Markovnikov's rule, with the OH from water mostly bonding to the carbon atom with the smaller number of hydrogen atoms bonded to it.

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.

Study tip

To remember which addition reactions require high temperatures and catalysts and which do not, recall that halogens are electronegative and typically react to accept electrons, so halogens and hydrohalogens react easily with the electrons present in double and triple bonds. Other reactants require heat and catalysts.

What is polymerisation of alkenes by addition?

Addition 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 alkene 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 also occur 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).

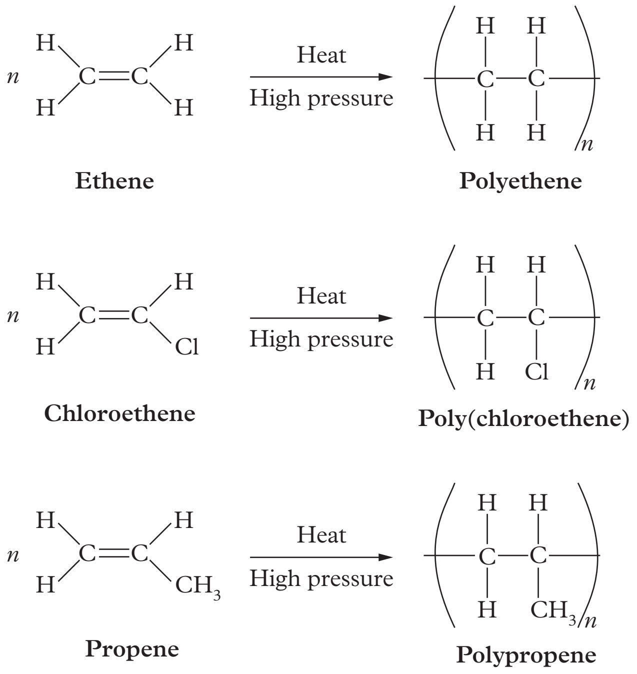


FIGURE 7 Polymerisation of several alkenes to form polyalkenes

Polymerisation of alkenes 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.

addition 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

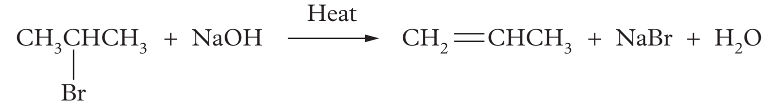
Study tip

It is important to write the reaction conditions on the chemical equation arrow and to show *n* moles of the alkene making a chain of *n* repeating units.

What are 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. You will learn about substitution reactions in Lesson 10.6. When using ethanol as a solvent, higher temperatures and higher concentrations of sodium hydroxide all favour the haloalkane undergoing an elimination reaction (Figure 8).



$$\underset{\displaystyle \mathrm{Br}}{\mathrm{CH_3CHCH_3}} + \mathrm{NaOH} \xrightarrow{\text{Heat}} \mathrm{CH_2{=}CHCH_3} + \mathrm{NaBr} + \mathrm{H_2O}$$

2-Bromopropane **Propene**

FIGURE 8 The elimination of secondary haloalkane: 2-bromopropane reacts with sodium hydroxide in ethanol to produce propene, sodium bromide and water.

elimination reaction
the removal of substituents to form a multiple bond

reflux
a technique in chemistry where a reaction mixture is kept boiling, with the vapours being condensed and collected in the reaction mixture

Study tip

To help remember the reactant and product characteristics, consider elimination reactions as being the opposite of addition reactions.

Skill drill

Constructing questions for investigation

Science inquiry skill: Planning investigations (Lesson 1.4) and Preparing for your research investigation (Lesson 1.12)

Your research investigation requires you to respond to a given claim. To do so, you need to provide a clear rationale showing the development of the question from the claim, and the question itself should be specific and relevant. Since the claim will be broad and general, your rationale will show how you have narrowed your focus to make the question specific. This skill drill is an opportunity to practise how to write questions from a claim.

The following claim was suggested about green polymers: "Green polymers are produced from renewable resources and have a smaller ecological footprint than that of other synthetic polymers."

FIGURE 9 Recycled plastic in the form of granules

Practise your skills

1 **Identify** the key terms in the claim. (3 marks)
2 **Define** the key terms. (3 marks)
3 **Create** two research questions for this claim. (2 marks)

Check your learning 10.1

Check your learning 10.1: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain** how the level of saturation of a hydrocarbon can be determined by chemical reactions. (2 marks)

2 **Describe** Markovnikov's rule and when it is applicable. (2 marks)

3 **Identify** the reagents and conditions required for

- **a** hydrogenation (1 mark)
- **b** halogenation (for a bromo substituent) (1 mark)
- **c** hydrohalogenation (for a chloro substituent) (1 mark)
- **d** hydration. (1 mark)

Analytical processes

4 **Determine** the balanced chemical equations to make one or more products for the addition reaction of oct-3-ene with

- **a** water (2 marks)
- **b** fluorine gas (1 mark)
- **c** hydrogen bromide. (2 marks)

5 **Determine** the balanced chemical equation to form the more likely of the two products for the reaction between

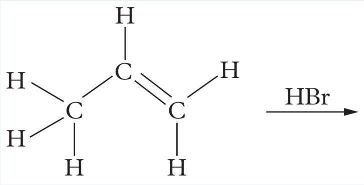
- **a** propene and hydrogen bromide (3 marks)
- **b** but-1-ene and water (3 marks)
- **c** 2-methylbut-2-ene and hydrogen chloride. (3 marks)

6 **Determine** the balanced chemical equation for the

- **a** polymerisation of five monomers of ethene (1 mark)
- **b** elimination reaction of 3-bromopentane, in which the major product is the *trans* isomer (1 mark)
- **c** the polymerisation of 1,1,2,2-tetrafluoroethene to make the polymer known as Teflon. Write the equation in the format shown in Figure 7. (1 mark)

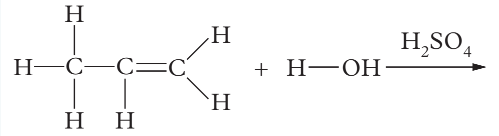
7 **Interpret** the diagrams to **identify** all the products formed.

a



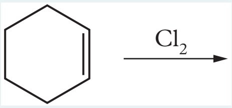
(2 marks)

b



(2 marks)

c



(1 mark)

8 An alkene has the formula C_5H_{10}. It is known to have a methyl branch. It reacts with HBr.

- **a** **Determine** the three possible structural formulas of the alkene. (3 marks)
- **b** For each of the isomers identified in part **a**, **deduce** all possible products from the reaction with HBr. (6 marks)
- **c** For each pair of products of each isomer, **compare** the relative amounts produced (i.e. is one a major product and the other minor, or will they be produced in similar amounts?). (3 marks)

Practical

Lesson 10.2

Testing for saturation

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Learning intentions and success criteria

Lesson 10.3

Oxidation and reduction reactions

Key ideas

- Oxidation reactions for organic compounds can be identified easily due to 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 that have 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
- Primary, secondary and tertiary alcohols can be distinguished from each other by using oxidation reactions as chemical tests.

What are oxidation reactions?

Oxidation reactions are defined as the loss of electrons. For organic chemicals, this can be recognised by either 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.

Learning intentions and success criteria

oxidation reaction
an organic reaction involving the gain of oxygen atoms or the loss of hydrogen atoms

reduction reaction
an organic reaction involving the loss of oxygen atoms or the gain of hydrogen atoms

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 often results in the initial aldehyde product being further oxidised to 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(VI) ($K_2Cr_2O_7$) that has been acidified with concentrated sulfuric acid (H_2SO_4) (Figure 1). Potassium manganate(VII) acidified with concentrated sulfuric acid is also a common oxidising agent.

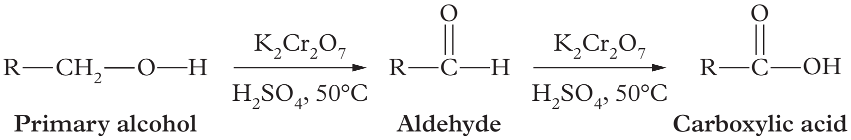


FIGURE 1 The oxidation of a primary alcohol to an aldehyde and then a carboxylic acid

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).

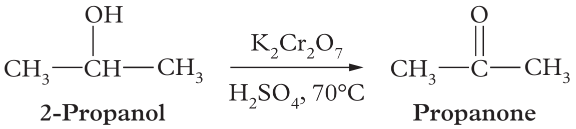


FIGURE 2 The oxidation of a secondary alcohol to a ketone: 2-propanol is oxidised to propanone.

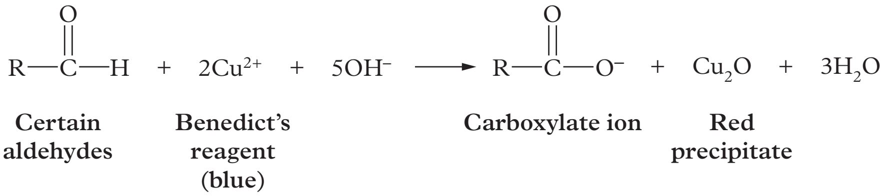
Which chemical tests are used to distinguish primary, secondary and tertiary alcohols?

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 when 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). Tertiary alcohols do not undergo oxidation at all. To distinguish between primary and secondary alcohols, you need to oxidise the alcohol to an aldehyde or ketone first. To decide whether 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.

Oxidising reagents that can be used to distinguish an aldehyde from a ketone include:

- potassium manganate(VII) ($KMnO_4$) (a purple aqueous solution), which is reduced to manganese dioxide (MnO_2), a brown precipitate
- potassium dichromate(VI) ($K_2Cr_2O_7$) (an orange aqueous solution), which is reduced to Cr^{3+}, a green aqueous solution
- Benedict's solution – copper(II) sulfate ($CuSO_4$) (blue), which is reduced to copper(II) oxide (CuO), a bright red precipitate (Figure 3).



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + 2Cu^{2+} + 5OH^- \longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^- + Cu_2O + 3H_2O$$

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.

What are complete combustion reactions?

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 many decades ago to prevent the methane spreading.

$$\underset{\text{Propane}}{C_3H_8} + \underset{\text{Oxygen gas}}{5O_2} \longrightarrow \underset{\text{Carbon dioxide}}{3CO_2} + \underset{\text{Water}}{4H_2O} + \text{Heat and light}$$

FIGURE 5 The combustion of propane to produce carbon dioxide and water

Common fuels are alcohols and alkanes, such as ethanol, butane, propane (Figure 5) and methane.

What are reduction reactions?

Reduction reactions are defined as the gain of electrons. For organic chemicals, this reduction occurs with 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 Module 6.

Reduction of alkenes

Alkenes are reduced when hydrogen is added across a double bond, increasing the level of saturation of the hydrocarbon. These reactions require high temperatures (150–300°C), hydrogen gas and a finely divided metal catalyst (Pt, Pd or Ni). They are also known as catalytic hydrogenation.

Reduction of alkynes

Alkynes are reduced when hydrogen is added across a triple bond, increasing the level of saturation of the hydrocarbon. This occurs in two stages: hydrogen is added to the alkyne, to form an alkene; and then the alkene reacts further with hydrogen to form an alkane. A finely divided metal catalyst and high temperature are required for both steps.

Check your learning 10.3

Check your learning 10.3: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain** how the type of alcohol can be identified by tests that use chemical reactions. (3 marks)

2 **Describe** combustion reactions. (1 mark)

3 **Identify** the reagents and conditions required for oxidation and reduction reactions. (4 marks)

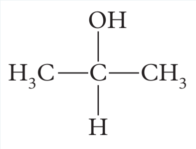
Analytical processes

4 **Apply** IUPAC rules to name the product of the oxidation of 2-methylhexan-3-ol. (1 mark)

5 **Determine** the balanced chemical equation for the oxidation of propan-2-ol. (1 mark)

6 **Classify** the following alcohols as primary, secondary or tertiary, and name them according to IUPAC rules.

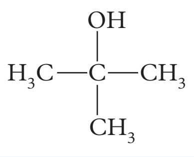
a



$H_3C-\overset{\text{OH}}{\underset{\text{H}}{C}}-CH_3$

(2 marks)

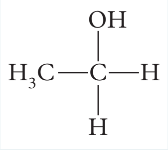
b



$H_3C-\overset{\text{OH}}{\underset{CH_3}{C}}-CH_3$

(2 marks)

c



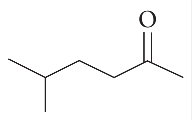
$H_3C-\overset{\text{OH}}{\underset{\text{H}}{C}}-H$

(2 marks)

7 **Determine** the balanced chemical equations for both stages of the reduction of propyne, using hydrogen gas and a nickel catalyst. (2 marks)

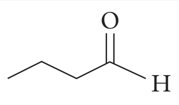
8 **Identify** the alcohol used to produce the following.

a



(1 mark)

b



(1 mark)

Practical

Lesson 10.4

Testing alcohols

Learning intentions and success criteria

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Lesson 10.5

Condensation reactions and organic acids and bases

Key ideas

- → Condensation reactions combine two reactants to form a large organic product (an ester or amide) with water as a by-product.
- → Carboxylic acids are weak acids, and can undergo a reversible reaction by donating a proton to water, which forms a solution that turns blue litmus red.
- → Amines are weak bases, and can undergo a reversible reaction with water, accepting protons to form a conjugate base and forming a solution that turns red litmus blue.

Learning intentions and success criteria

What are carboxylic acids?

Carboxylic acids are organic acids that have the carboxyl functional group (–COOH). They are classified as acids because the hydrogen in the carboxyl group can be donated to another substance that can accept protons, including water.

Ethanoic acid is a carboxylic acid. Vinegar is a dilute solution of ethanoic acid, and the following reaction shows ethanoic acid acting as a proton donor in this solution:

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

The double arrow shows that this is a reversible reaction, which reaches equilibrium. The K_a of carboxylic acids is typically very small, meaning that only a very small percentage of the reactants form products at any time. However, the pH of aqueous solutions of carboxylic acids is still below 7, and they will turn blue litmus red.

Worked example 10.5A

Describing the acid–base properties of carboxylic acids

Describe the acid–base properties of pentanoic acid. Include an equation. (3 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Describe" means to give an account of the characteristics or features of something. We need to use knowledge of acids and bases to show how pentanoic acid is classified as an acid and matches the features of an acid. This question is worth 3 marks, so we must express a balanced chemical equation together with two other features.
Step 2: Select the appropriate formulas and gather the required data.	Recall that pentanoic acid has the formula $CH_3(CH_2)_3COOH$ and that acids donate protons.
Step 3: Write the balanced equation, with double arrows and state symbols.	$CH_3(CH_2)_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3(CH_2)_3COO^-(aq) + H_3O^+(aq)$ (1 mark)

Think	Do
Step 4: Finalise your answer by describing the proton donation occurring in the chemical reaction and the significance this has for the pH of the solution.	In aqueous solution, the pentanoic acid molecule can donate a proton to a water molecule, which increases [H_3O^+] in a reversible reaction, in which the equilibrium strongly favours reactants. (1 mark) The resulting solution has a higher [H_3O^+] than a neutral solution, and thus a pH < 7, meaning pentanoic acid is an acid. (1 mark)

Your turn

Describe the acid–base properties of propanoic acid. Include an equation. (3 marks)

What are amines?

Amines are organic compounds that have a nitrogen bonded to one or more alkyl (or aryl) groups. They are classified as bases because the lone pair of electrons on the nitrogen in the amine can accept a proton from another substance that can donate protons, including water.

Methanamine is an amine. The following reaction shows methanamine acting as a proton acceptor in aqueous solution:

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

The double arrow shows that this is a reversible reaction, which reaches equilibrium. The K_b of amines is typically small, and approximately 7% of an amine will be ionised at any time. The pH of aqueous solutions of amines is greater than 7, and they will turn red litmus blue.

Worked example 10.5B

Describing the acid–base properties of amines

Describe the acid–base properties of triethylamine ($N(CH_2CH_3)_3$), whose structural formula is shown in Figure 1. Include an equation. (3 marks)

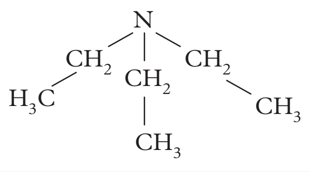


FIGURE 1 Triethylamine

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Describe" means to give an account of the characteristics or features of something. We need to use knowledge of acids and bases to show how triethylamine is classified as a base and matches the features of a base. This question is worth 3 marks, so we must express a balanced chemical equation together with two other features.
Step 2: Select the appropriate formulas and gather the required data.	The given formula is $N(CH_2CH_3)_3$. Recall that bases accept protons.
Step 3: Write the balanced equation with double arrows and state symbols.	$N(CH_2CH_3)_3(aq) + H_2O(l) \rightleftharpoons NH(CH_2CH_3)_3^+(aq) + OH^-(aq)$ (1 mark)
Step 4: Finalise your answer by describing the proton donation occurring in the chemical reaction and the significance this has for the pH of the solution.	In aqueous solution, the triethylamine molecule can accept a proton from a water molecule, which increases [OH^-] in a reversible reaction, in which the equilibrium favours reactants. (1 mark) The resulting solution has a higher concentration of [OH^-] than a neutral solution, and thus a pH > 7, meaning triethylamine is a base. (1 mark)

Your turn

Describe the acid–base properties of trimethylamine ($N(CH_3)_3$) whose structural formula is shown in Figure 2. Include an equation. (3 marks)

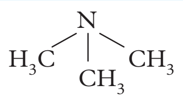


FIGURE 2 Trimethylamine

What are condensation reactions and how are esters formed?

A **condensation reaction** occurs when two molecules combine to form a larger molecule and a small **by-product** such as water. Amides and esters can be synthesised by condensation 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 hydroxyl group of an alcohol. The reaction requires heat and trace amounts of a mineral acid catalyst such as concentrated sulfuric acid. It is a reversible reaction and reaches equilibrium. As a result, the percentage yield of esterification is always considerably less than 100% and any product needs to undergo purification to separate it from leftover reactants.

The main chain and the carbonyl group of the ester is derived from the main chain of the carboxylic acid (R in Figure 3). The alcohol main chain together with the oxygen from the alcohol forms the ester substituent (OR′ in Figure 3). 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 noted for having strong smells, often sweet and fruity.

condensation reaction
a reaction in which two organic compounds combine to produce a main product and another small molecule, frequently water

by-product
a product of a chemical reaction that was not the main or intended product

esterification
a condensation reaction between a carboxylic acid and alcohol to produce an ester

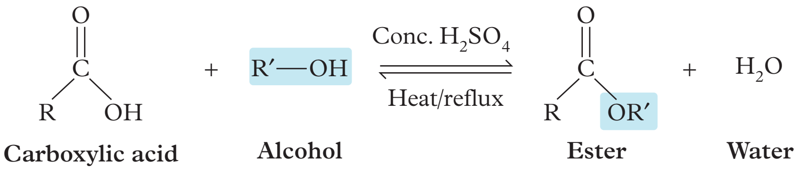


FIGURE 3 An esterification reaction

Because the reaction in Figure 3 is reversible, it is not carried out in aqueous solution. Water is a product, and the presence of large amounts of water in aqueous solution would drive the reaction towards the reactants. Even when a pure sample of an ester is exposed to water or moisture at room temperature, the water reacts slowly with some of the ester, forming the original acid and alcohol. Because water takes part in this reverse reaction, it is called hydrolysis. The equilibrium constant for both the forward and reverse reactions must include water, unlike previously studied equilibrium constants such as K_a.

Worked example 10.5C

Determining the equation for the reaction between a carboxylic acid and an alcohol and applying IUPAC rules to name the product

For the reaction between propanoic acid and hexan-1-ol

a **determine** the balanced chemical equation, showing catalysts and conditions (1 mark)

b **apply** IUPAC rules to name the main product. (1 mark)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the question is asking you to do.	"Determine" means establish, conclude or ascertain after consideration. We need to consider the final ester that would be produced from this particular carboxylic acid and alcohol. "Apply" means use knowledge and understanding in response to a given situation or circumstance. We need to use knowledge of naming conventions of esters, together with the number of carbon atoms in the main and substituent chains of the ester. Each question is worth 1 mark, so we must express both the chemical equation and name using all conventions.
Step 2: Select the appropriate formulas and gather the required data.	Propanoic acid: CH_3CH_2COOH Hexan-1-ol: $CH_3(CH_2)_4CH_2OH$
Step 3: Write the balanced equation, showing the catalyst and conditions. If desired, a structural formula could be shown for the ester.	**a** $CH_3CH_2COOH + CH_3(CH_2)_4CH_2OH \xrightleftharpoons[\text{heat}]{\text{conc. } H_2SO_4}$ $CH_3CH_2COOCH_2(CH_2)_4CH_3$ (1 mark)
Step 4: Finalise your answer by applying rules to name the ester.	**b** The substituent chain has six carbon atoms, the "yl" is used, the main chain has three carbon atoms and the suffix "oate" is used. Hexyl propanoate (1 mark)

Your turn

For the reaction between butanoic acid and propan-1-ol

a **determine** the balanced chemical equation, showing catalysts and conditions (1 mark)

b **apply** IUPAC rules to name the main product. (1 mark)

Real-world chemistry

DDT: a friend that became a foe

Dichlorodiphenyltrichloroethane, commonly known as DDT, is a synthetic insecticide formed in a condensation reaction (Figure 4). It was commonly used in the 1940s as a highly effective way to control insect-borne diseases such as malaria and typhus. By the 1950s, it was hailed as a miracle and greatly reduced human and animal deaths. In 1962, biologist Rachel Carson published a book, *Silent Spring*, noting the persistence of DDT molecules in the environment, the bioaccumulation in animal fats in food chains and the harmful effects of residual DDT on many forms of wildlife. This included effects on top predators such as eagles, which laid thin-shelled eggs that failed to hatch. Effects on humans include an increase in obesity and diseases of some organs.

The DDT molecule is not readily biodegradable because bacteria in soil and water are often unable to readily break it down and animals cannot digest or metabolise it: its structure does not resemble molecules in the natural environment. DDT can be broken down by sunlight, but it readily adsorbs onto soils and water sediments and the breakdown products are themselves toxic. The half-life of DDT in water is about 150 years – the time taken for 50% of the original amount to decompose. DDT is now banned for almost all purposes, except for indoor use in a few African countries to manage malaria.

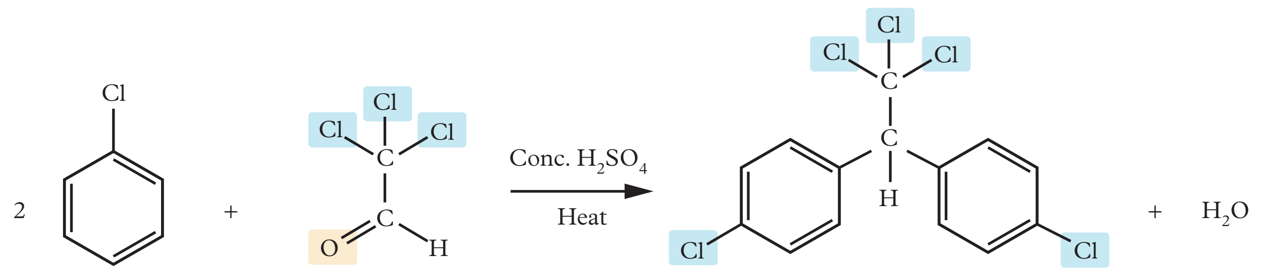


FIGURE 4 A summary of the multi-step condensation reaction for the formation of DDT

Apply your understanding

1 **Define** "biodegradable" and "bioaccumulation". (2 marks)

2 Research the chemical structures of the molecules listed in Table 1. By considering the polarity of molecules, **describe** why these molecules would be likely to dissolve in fats, and bioaccumulate, if they are not biodegradable. (3 marks)

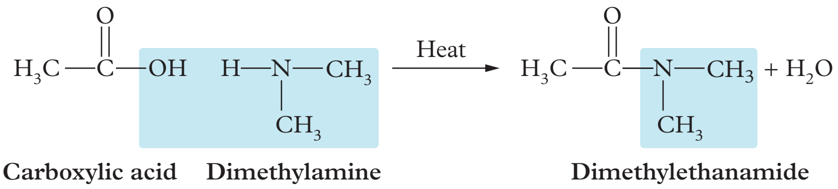
3 Pyrethrins are natural compounds produced to ward off insect attack. Some synthetic insecticides are designed with a similar structure. **Predict** whether pyrethrins and similar synthetic insecticides would be likely to be more or less biodegradable than DDT and **justify** your reasoning. (2 marks)

TABLE 1 Several insecticides, their source and uses/effects

Insecticide	Source	Uses/effects
DDT	Synthetic	For control of insects that carry diseases Wide range of effects on humans and land and marine organisms
Carbaryl	Synthetic	To prevent insect damage to a wide range of crops Acute and chronic toxicity to humans
Pyrethrins	Natural, chemicals extracted from chrysanthemum flowers	For control of fleas, mosquitoes, flies, moths, ants and others In low doses is not considered toxic to humans and other mammals

How are amides synthesised?

Amides can be 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 esterification). The by-product, water, comes from the hydroxyl group and a hydrogen from the amine functional group (Figure 5).



$$H_3C-\overset{\overset{O}{\|}}{C}-OH \quad H-\underset{\underset{CH_3}{|}}{N}-CH_3 \xrightarrow{\text{Heat}} H_3C-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{N}-CH_3 + H_2O$$

FIGURE 5 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 the amine reactant is still present (Figure 6).

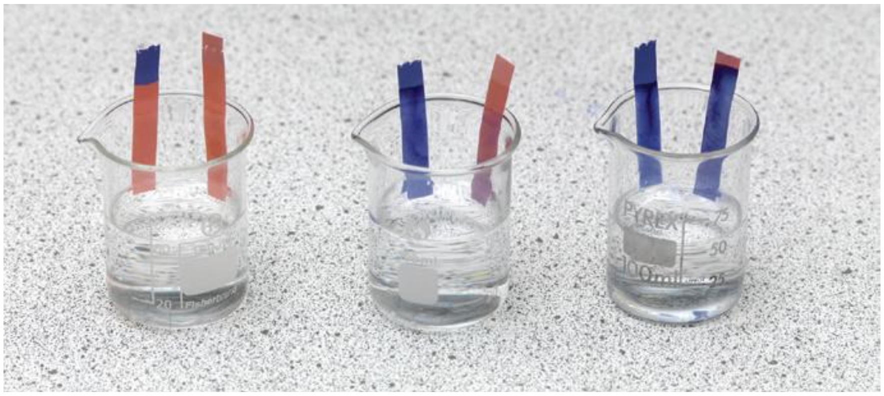


FIGURE 6 Red and blue litmus paper can be used to determine the progress of esterification and amide syntheses.

Challenge

Calculating K_c for an organic reaction

5 mL of ethanol (0.0857 mol) and 5 mL of ethanoic acid (0.0875 mol) were combined to make a total volume of 10 mL. Sufficient time for the reaction to reach equilibrium was allowed. At this time, the amount of ethanoic acid was found to be 0.0295 mol.

Assuming no overall change in the volume of the mixture occurred, **calculate** K_c for this reaction. (6 marks)

Check your learning 10.5

Check your learning 10.5: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** the term “condensation reaction”. (1 mark)

2 **Explain** the process of esterification. (2 marks)

3 **Identify** the reagents and conditions required for the two types of condensation reactions. (2 marks)

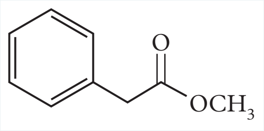
Analytical processes

4 **Determine** the balanced chemical equation for the condensation of pentanoic acid with

- a octan-2-ol (1 mark)
- b ethanamine ($NH_2CH_2CH_3$). (1 mark)

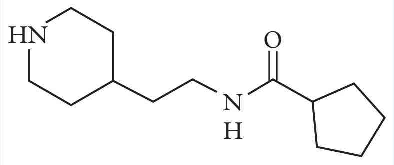
5 **Analyse** the diagrams of condensation products to **determine** and draw the reactants that were involved in the condensation reactions.

a



(2 marks)

b



(2 marks)

Lesson 10.6

Substitution reactions and reaction pathways

Key ideas

- → Substitution reactions are reactions in which a substituent on a saturated hydrocarbon is replaced by another.
- → Halogens substitute onto hydrocarbons in the presence of UV light or at high temperatures, replacing a hydrogen atom.
- → To replace a halogen in a substitution reaction, additional experimental conditions are required (such as heating under reflux and use of an organic solvent). Halogens can be substituted for hydroxyls, other halogens and amines. Hydroxyl groups in alcohols can be substituted by the halogen in a halogen hydride.

Learning intentions and success criteria

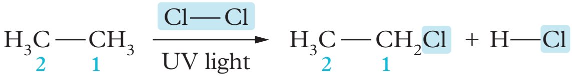
What are substitution reactions?

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
a reaction in which one substituent in a saturated organic compound is replaced by another

Substitution of alkanes

Haloalkanes can be 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).



$$\underset{2}{H_3C}-\underset{1}{CH_3} \xrightarrow[\text{UV light}]{Cl-Cl} \underset{2}{H_3C}-\underset{1}{CH_2}Cl + H-Cl$$

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 monohaloalkane under the same conditions to cause a second substitution of a hydrogen atom with a halogen (Figure 2).

$$CH_3Cl + Cl_2 \xrightarrow[\text{or heat}]{\text{UV light}} CH_2Cl_2 + HCl$$

FIGURE 2 A second substitution reaction

Study tip

Haloalkanes can also be called halogenoalkanes or alkyl halides.

What are primary, secondary and tertiary haloalkanes?

Haloalkanes can be classified as primary, secondary or tertiary (Figure 3) depending on the number of hydrogens on the 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.

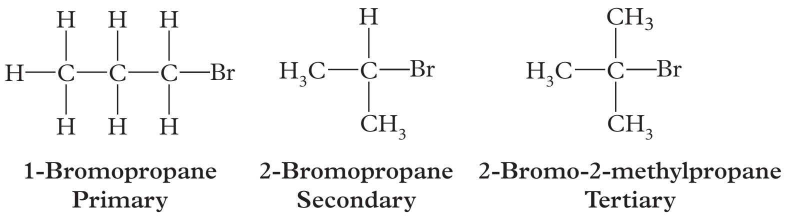


FIGURE 3 Primary, secondary and tertiary bromopropanes

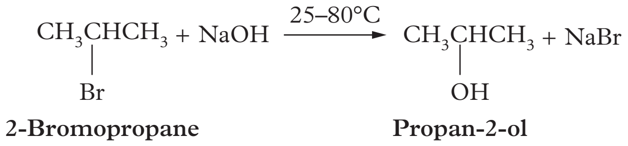
The carbon–halogen bond in haloalkanes is polar. This polarity makes the carbon atom electron poor and susceptible to substitution reactions by reagents that have a non-bonding pair of electrons. Reagents that can substitute the halogen atom include iodide (I^-), hydroxide (OH^-), chloride (Cl^-), ammonia (NH_3), ethanoate (CH_3CO^-) and methanol (CH_3OH).

How do haloalkanes react with sodium hydroxide?

If you heat a haloalkane with a solution of sodium hydroxide or potassium hydroxide in 50:50 ethanol and water under reflux, the halogen substituent is replaced by a hydroxyl functional group to produce 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).



$$CH_3\underset{\displaystyle Br}{C}HCH_3 + NaOH \xrightarrow{25\text{–}80°C} CH_3\underset{\displaystyle OH}{C}HCH_3 + NaBr$$

FIGURE 4 Substitution of a haloalkane to form an alcohol: 2-bromopropane reacts with sodium hydroxide to produce propan-2-ol.

How do haloalkanes react with 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). The iodide ion is the most reactive halide ion for this type of substitution, followed by bromide and then chloride.

$$R\text{–}X(aq) + NaI(aq) \xrightarrow[\text{Stir}]{\text{Ethanol}} R\text{–}I(aq) + NaX(s)$$

FIGURE 5 The substitution of a haloalkane to form another haloalkane

How do haloalkanes react with 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, where the product is a primary amine.

$$CH_3CH_2Br + 2NH_3 \xrightarrow[\text{Stir}]{\text{Ethanol, sealed tube}} CH_3CH_2NH_2 + NH_4Br$$

Bromoethane **Ammonia** **Ethanamine** **Ammonium bromide**

FIGURE 6 The substitution of a haloalkane to form an amine

How do alcohols react with hydrogen halides?

The hydroxyl group of an alcohol can undergo a substitution reaction with the halogen of a hydrogen halide. Hydrogen iodide (HI) is the most reactive, followed by HCl, and then HBr. HF is unreactive. Tertiary alcohols react more rapidly than secondary alcohols, and primary alcohols react the most slowly. The reaction occurs in the presence of a catalyst, usually H_2SO_4. The product is a haloalkane where the hydroxyl group has been replaced by the halogen in the hydrogen halide.

Anhydrous zinc chloride also acts as a catalyst when concentrated HCl is used at the hydrogen halide. This reactant and catalyst can be used to test for whether an alcohol is primary, secondary or tertiary.

How can we use reaction pathways?

A **reaction pathway** is a series of chemical reactions that enables one or more starting reactants to produce a desired product. All the reactions studied in this lesson can be conducted as single reactions but can also form part of a multi-step reaction pathway. Figure 7 shows a chart linking all the classes of compounds studied with the arrows showing some of the reactions needed to produce each one. Some reactions studied in this module are not shown by an arrow.

reaction pathway
a series of chemical reactions in which one or more reactants produces a desired product

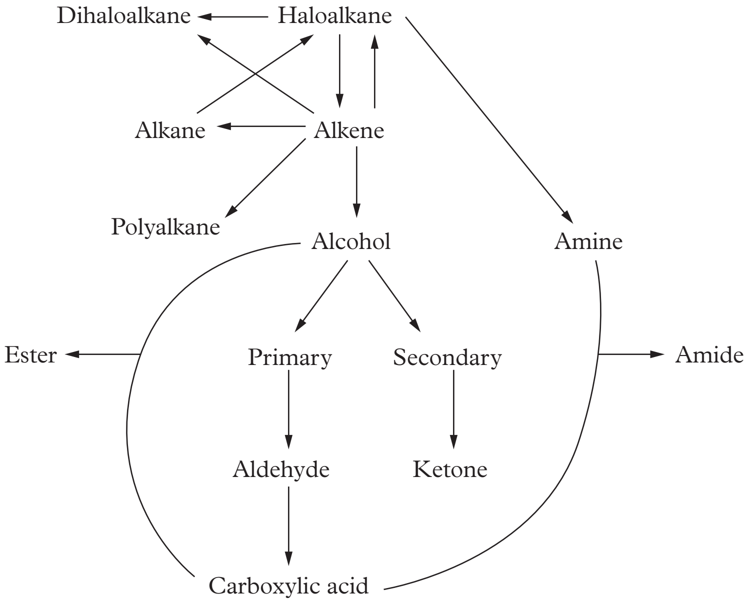


FIGURE 7 A chart showing classes of compounds. This chart can be used to determine reaction pathways to synthesise a desired compound in a multi-step process.

Source: *Chemistry 2025 Formula and data book* © State of Queensland (QCAA) 2025

Check your learning 10.6

Check your learning 10.6: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** the term “substitution reaction”. (1 mark)

2 **Identify** the type of haloalkane that predominantly undergoes
  - **a** a substitution reaction (1 mark)
  - **b** an elimination reaction. (1 mark)

3 **Identify** the reagents and conditions required for substitution reactions that form
  - **a** haloalkanes (1 mark)
  - **b** dihaloalkanes (1 mark)
  - **c** alcohols. (1 mark)

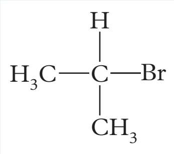
4 Sketch two copies of Figure 7.
  - **a** On the first copy, for each arrow, **identify** whether the reaction shown is addition, elimination, reduction, oxidation. condensation or substitution. (6 marks)
  - **b** On the second copy, for each arrow, **identify** the reagents and conditions required for each reaction. (6 marks)

Analytical processes

5 **Determine** the balanced chemical equation for the substitution of
  - **a** ethane with chlorine gas (1 mark)
  - **b** fluoromethane with chlorine gas. (1 mark)

6 **Classify** the following haloalkanes as primary, secondary or tertiary, and name them according to IUPAC rules.

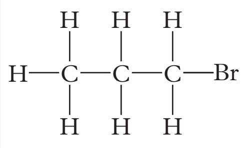
a



$H_3C{-}\overset{H}{\underset{CH_3}{C}}{-}Br$

(2 marks)

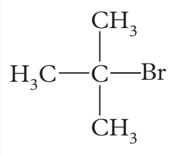
b



$H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}Br$

(2 marks)

c



$H_3C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Br$

(2 marks)

7 **Determine** the balanced chemical equation for the substitution of 4-bromononane with
  - **a** sodium hydroxide (1 mark)
  - **b** ammonia, to produce a primary amine. (1 mark)

8 **Determine** the balanced chemical equation for the substitution of 2-methylbutan-2-ol with HI. (1 mark)

9 **Determine** the series of balanced chemical equations, including conditions, to synthesise
  - **a** ethanol from ethane (2 marks)
  - **b** ethyl propanoate from ethanol and propanol. (3 marks)

MODULE 10

Lesson 10.7

Review: Organic reactions and reaction pathways

Summary

10.1
- Addition reactions break a double or triple bond and replace it with two substituents. Addition reactions include hydrogenation, halogenation, hydrohalogenation or hydration reaction.
- Markovnikov's rule explains the general trend that, in the addition of an asymmetrical reagent, the hydrogen atom will bond to the carbon that already has the most hydrogen atoms.
- 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 them with a double bond.

10.2
- Practical: Testing for saturation

10.3
- Oxidation reactions for organic compounds can be identified easily due to 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 that have 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
- Primary, secondary and tertiary alcohols can be distinguished from each other by using oxidation reactions as chemical tests.

10.4
- Practical: Testing alcohols

10.5
- Condensation reactions combine two reactants to form a large organic product (an ester or amide) with water as a by-product.
- Carboxylic acids are weak acids, and can undergo a reversible reaction by donating a proton to water, which forms a solution that turns blue litmus red.
- Amines are weak bases, and can undergo a reversible reaction with water, accepting protons to form a conjugate base and forming a solution that turns red litmus blue.

10.6
- Substitution reactions are reactions in which a substituent on a saturated hydrocarbon is replaced by another.
- Halogens substitute onto hydrocarbons in the presence of UV light or at high temperatures, 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 hydroxyls, other halogens and amines. Hydroxyl groups in alcohols can be substituted by the halogen in a halogen hydride.

Review questions 10.7A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

1 You can identify an organic compound's class by studying its
- **A** elements.
- **B** molar mass.
- **C** formula.
- **D** chemical properties.

2 A combustion reaction is a type of
- **A** addition.
- **B** oxidation.
- **C** reduction.
- **D** elimination.

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 hydrogen atom in the
- **A** hydrohalide reagent will bond to the carbon from the double bond that has the most hydrogen atoms attached.
- **B** hydrohalide reagent will bond to the carbon from the double bond that has the least hydrogen atoms attached.
- **C** pure halogen reagent will bond to the carbon from the double bond that has the least hydrogen atoms attached.
- **D** hydrogen atom in the pure halogen 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 one substituent.
- **B** one substituent to replace with a double bond.
- **C** two substituents to replace with a double bond.
- **D** a double bond to replace with two substituents.

6 Alcohols can be formed by
- **A** addition, oxidation or substitution.
- **B** substitution, condensation or reduction.
- **C** addition, reduction or condensation.
- **D** reduction, oxidation or condensation.

7 Which of the following is true for substitution reactions?
- **A** Esterification is always carried out by using a substitution reaction.
- **B** Substitution reactions form one possible product only.
- **C** Substitution reactions can produce haloalkanes from alkanes.
- **D** Substitution reactions occur with saturated and unsaturated linear hydrocarbons.

8 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.

9 When using sodium hydroxide, what are the experimental conditions required to favour an elimination reaction over a substitution reaction?
- **A** Water as a solvent and low temperatures
- **B** Water as a solvent and high temperatures
- **C** Ethanol as a solvent and low temperatures
- **D** Ethanol as a solvent and high temperatures

10 What type of reaction can be used to distinguish tertiary alcohols from primary and secondary alcohols?
- **A** Addition
- **B** Oxidation
- **C** Reduction
- **D** Hydrogenation

Review questions 10.7B Short response

Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

11 **Describe** the terms “oxidation” and “reduction” in relation to organic chemistry. (2 marks)

12 **Describe** the acidic and basic properties of functional groups in carboxylic acids and amines, using examples. (4 marks)

13 **Describe** with chemical equations how ethanol can be synthesised from ethane. Include catalysts and conditions (2 marks)

14 **Explain** what the term “reversible” represents in reference to esterification reactions. (2 marks)

15 **Identify** the reagents and conditions required for an

- **a** elimination reaction of a haloalkane (1 mark)
- **b** addition of water (1 mark)
- **c** addition polymerisation. (1 mark)

16 **Explain**, using equations, the reaction that forms alkanes from alkenes. (2 marks)

17 **Describe**, using equations as examples

- **a** hydrogenation (2 marks)
- **b** halogenation (2 marks)
- **c** hydrohalogenation (2 marks)
- **d** hydration (2 marks)
- **e** polymerisation (2 marks)
- **f** elimination (2 marks)
- **g** oxidation (2 marks)
- **h** reduction (2 marks)
- **I** esterification (2 marks)
- **j** amide synthesis (2 marks)
- **k** substitution. (2 marks)

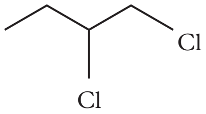
Analytical processes

18 **Determine** the balanced chemical equation for the combustion of butane gas. (1 mark)

19 **Apply** IUPAC rules to name the products formed when pentan-1-ol oxidises. (2 marks)

20 **Contrast** the terms “class” and “functional group”. (2 marks)

21 **Analyse** the following structure. It was synthesised from an unsaturated hydrocarbon and one other reactant. Identify both reactants used to form this compound. (2 marks)



22 **Determine** the balanced chemical equation for the polymerisation of *n* monomers of propene. (1 mark)

23 **Apply** IUPAC rules to name the reactant that oxidises to form propanal. (1 mark)

24 **Compare** saturated alkanes and unsaturated alkenes in terms of their bonding and reactivity with bromine water. (2 marks)

25 **Determine** the products for the reaction of

- **a** ethane and bromine (1 mark)
- **b** but-1-ene and iodine (1 mark)
- **c** propene and water (1 mark)
- **d** 3-bromoheptane and sodium hydroxide (1 mark)
- **e** pent-2-yne and two equivalents of fluorine (1 mark)
- **f** heptan-4-ol and butanoic acid. (1 mark)

26 **Interpret** the following condensed structural formulas to **identify** the alcohols that were oxidised to produce them.

- **a** CH_3CH_2CHO (1 mark)
- **b** $CH_3(CH_2)_4CO_2H$ (1 mark)
- **c** $CH_3CH_2COCH_2CH_3$ (1 mark)

27 Pent-1-ene and pent-2-ene both undergo acid-catalysed hydration.

a **Deduce** and **sketch** the possible products of the reaction with pent-1-ene and **determine** their IUPAC names. (4 marks)

b **Deduce** and **sketch** the possible products of the reaction with pent-2-ene and **determine** their IUPAC names. (4 marks)

c **Contrast** these hydration reactions by deducing the relative proportions of each of the two products formed in each reaction. (3 marks)

28 Consider the following reactions.

Reaction 1: $X + KOH(aq) \rightarrow CH_3CH_2OH(l) + KCl(aq)$

Reaction 2: $CH_3CH_2OH(l) + Y \rightarrow CH_3COOH(l)$

Reaction 3: $CH_3COOH(l) + CH_3OH(l) \rightarrow Z + H_2O(l)$

a **Deduce** the possible identities of the reactants or products signified by X, Y and Z. (3 marks)

b **Deduce** the type of reaction for each of the three reactions. (3 marks)

29 **Determine** the reaction pathways, including reagents, conditions and balanced chemical equations to form:

a a primary amine with a propyl group from propene. (2 marks)

b butanoic acid from 1-chlorobutane (3 marks)

c pentyl propanoate from 1-bromopentane and 1-bromopropane. (4 marks)

Knowledge utilisation

30 Pentyl propanoate could also be synthesised from pent-1-ene and propene, using additional steps in the reaction pathways. **Evaluate** the effectiveness of preparing pentyl propanoate from pent-1-ene and propene, by discussing any additional considerations of the process. (4 marks)

31 Aromatic compounds participate in substitution reactions rather than addition reactions. **Discuss** how this takes place, despite the fact that they are usually depicted in structural formulas as having numerous double bonds. (2 marks)

32 The following figure shows two unlabelled beakers containing 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. (4 marks) (Hint: There are multiple possible answers for both liquids A and B. The correct answers for both have the longest possible main chain.)

Data drill

Reactions and reaction pathways

An unbranched compound, A, has the molecular formula C_4H_8, reacts readily with HBr, and forms two products, B and C. B and C are separated, and each reacted with NaOH solution, without heating, to form E and F respectively. E is then heated strongly with acidified potassium manganate(VII) to produce G. An aqueous solution of compound G turns blue litmus red. Compound G and compound F are heated under reflux with a small amount of concentrated sulfuric acid, to produce compound H. H has a distinctive odour.

Apply understanding

1 **Determine** the structural formulas of the two possible isomers with the molecular formula C_4H_8. (2 marks)

2 Only one of the isomers in question **1** reacts with HBr to form two different compounds as described. **Identify** and **determine** the IUPAC name of the isomer. (2 marks)

Analyse data

3 **Organise** compounds A to H into a reaction pathway diagram, using arrows to show the direction of each reaction described. (4 marks)

Interpret evidence

4 **Deduce** the structural formula of compound H. **Justify** your reasoning. (3 marks)

5 Compound F is heated with an acidified potassium dichromate solution. **Predict** whether a reaction will occur and the product if a reaction occurs. **Justify** your prediction. (3 marks)

Module 10 checklist: Organic reactions and reaction pathways

MODULE 11

Organic materials: Structure and function

Introduction

Living organisms depend on organic compounds, including amino acids, tripeptides and saccharides. Other common organic materials used in the world today contain large molecules called polymers, formed by reaction of smaller units called monomers. The monomers polymerise to make polymers. Some polymers can then hydrolyse to break down into their monomer components in an infinite cycle. The functional groups in biological compounds as well as those in polymers have a significant effect on the physical properties and reactivity of each molecule, ultimately determining its function.

Prior knowledge

Prior knowledge quiz

Check your understanding of concepts related to organic materials: structure and function before you start.

Subject matter

Science understanding

→ Describe the structural features of
  - amino acids, tripeptides, monosaccharides and disaccharides
  - polyethene (LDPE and HDPE), polypropene (syntactic, isotactic and atactic) and polytetrafluorethene (Teflon)
  - polylactic acid (PLA), polyamide (nylon) and polyester.

→ Explain how properties, including strength, density and biodegradability of polymers can be related to the structures of the materials.

→ Explain the acid-base properties of 2-amino acids, including the formation of zwitterions.

Source: *Chemistry 2025 v1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

Lesson 11.1
Carbohydrates

Key ideas

- → Monosaccharides are sugar monomers with three to seven carbon atoms and consist of a carbon chain with several hydroxyl groups, and either an aldehyde or a ketone.
- → In aqueous solution, all but the smaller monosaccharides exist as two or three forms in dynamic equilibrium – a straight chain and two different ring forms, called alpha and beta, with 5- or 6-membered rings.
- → Disaccharides are dimers of monosaccharides that are joined by glycosidic linkages.
- → Sucrose is an example of a disaccharide.

Learning intentions and success criteria

monosaccharide
a single sugar monomer

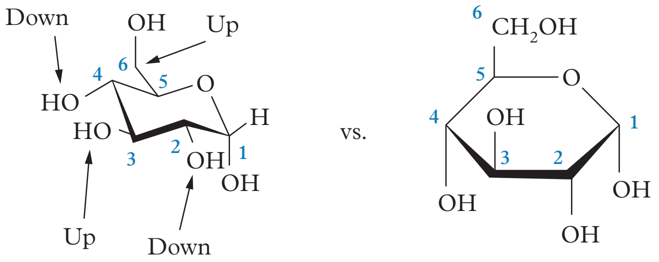
carbohydrate
a molecule consisting of carbon (C), hydrogen (H) and oxygen (O) having the general formula C*x*(H_2O)*y* (although they do not have water molecules within their structure); carbohydrates include saccharides (sugars), starches and cellulose

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.

What are monosaccharides?

Monosaccharides are sugar monomers that have the empirical formula CH_2O; many commonly encountered monosaccharides have six carbon atoms and the molecular formula $C_6H_{12}O_6$. They are the simplest of the compounds known as **carbohydrates**. They consist of a carbon chain with several hydroxyl groups attached, and either an aldehyde or a ketone functional group. The smaller monosaccharides exist in a chain form, and never in ring form. In aqueous solution, the larger monosaccharides exist as three forms in dynamic equilibrium – a straight chain and either of two cyclic structures called alpha and beta, with either a 5-membered or 6-membered ring, because these ring sizes are more stable than others. The ring structures are formed by the aldehyde or ketone group reacting with one of the hydroxyl groups of the same molecule to form a ring. The three-dimensional structure of the ring can be drawn in different styles; Haworth projections and chair conformations are commonly used (Figure 1). The straight chain can be represented two-dimensionally in a diagram called a Fischer projection (Figure 2).



Chair conformation **Haworth projection**

FIGURE 1 The chair conformation and Haworth projection of α-glucose. In both the chair conformation and the Haworth projection, one of the OH groups, labelled down, projects below the neighbouring atoms in the ring, while the other, labelled up, projects above the neighbouring atoms in the ring.

Glucose and fructose are common monosaccharides. They are in fruits and vegetables. Glucose contains an aldehyde and thus is classified as an aldose; fructose contains a ketone functional group and thus is classified as a ketose. These functional groups are more easily seen in the Fischer projections (Figure 2).

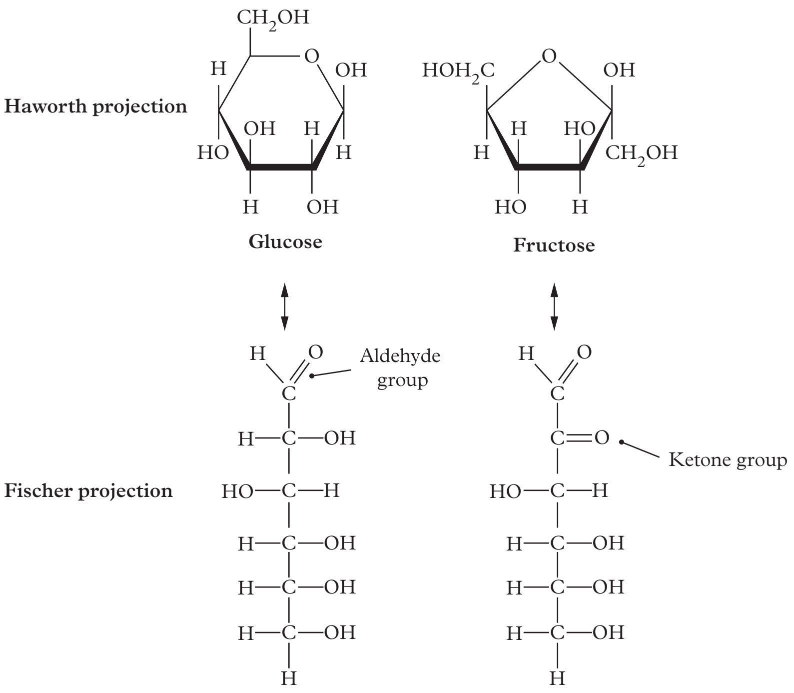


FIGURE 2 The Haworth and Fischer projections of glucose and fructose

Glucose

Glucose also exists in two ring configurations – alpha (α) and beta (β). The configurations differ in the position of the hydroxyl functional group on 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 upwards 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. It also has a melting point approximately 5°C higher than that of α-glucose, because the molecules can pack more closely and can form hydrogen bonds with neighbouring molecules more easily.

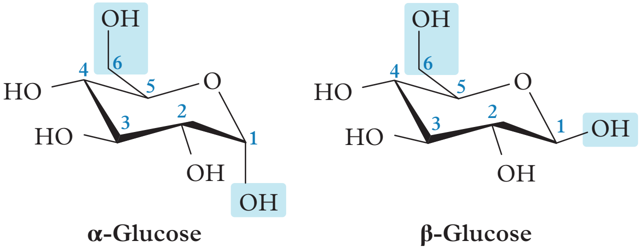


FIGURE 3 The structures of α-glucose and β-glucose in the chair conformation

What are disaccharides?

disaccharide two sugar monomers bonded together

Disaccharides are simple sugars made from two monosaccharides in a condensation polymerisation reaction that also produces a water molecule. Some common disaccharides such as sucrose have the molecular formula $C_{12}H_{22}O_{11}$, and the Haworth projection shows the two rings from the original monosaccharides. Haworth projections are a simpler two-dimensional diagram, but still retain useful information about the three-dimensional

glycosidic linkage a bond that connects sugar monomers together

structure of the ring forms of the molecule, such as the relative orientation of substituents. Sucrose (table sugar) is a common disaccharide consisting of a glucose molecule bonded to a fructose molecule through an α-1,β-2-**glycosidic linkage** (Figure 4). The numbering of this linkage refers to the carbon atoms in the two rings that make up the structure of the disaccharide that are bonded to the oxygen atom between the two rings. The ring on the left in Figure 4 is bonded through carbon 1, and the ring on the right is bonded through carbon 2.

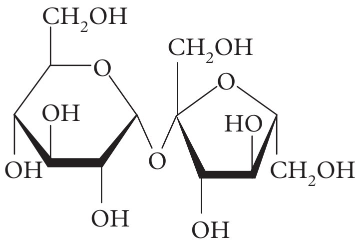


FIGURE 4 The structure of sucrose in the Haworth projection

Check your learning 11.1

Check your learning 11.1: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** the term "glycosidic linkage". (2 marks)

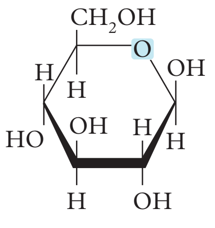
Analytical processes

2 Monosaccharides can be classified as aldoses or ketoses. **Contrast** the structures. (1 mark)

3 **Contrast** the straight chain and α-ring structures of glucose and fructose. (2 marks)

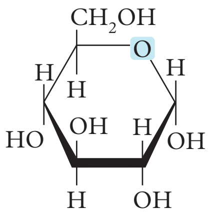
4 **Interpret** the following diagrams to classify each as α-glucose or β-glucose. **Determine** whether the structures are represented as chair confirmations or Haworth projections.

a



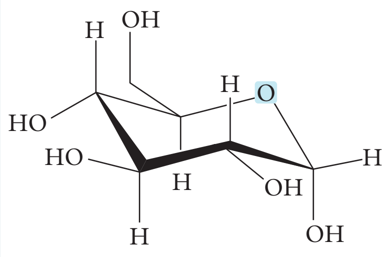
(1 mark)

b



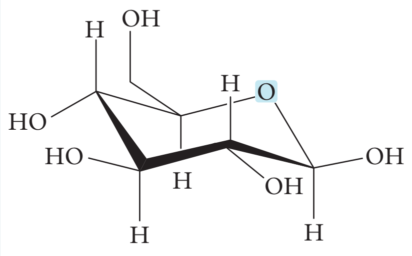
(1 mark)

c



(1 mark)

d



(1 mark)

Lesson 11.2
Amino acids and peptides

Key ideas

→ Amino acids have both amino and carboxyl functional groups. They have acid–base properties and can act as proton donors and proton acceptors.

→ At a pH known as their isoelectric point, amino acids undergo internal transfer of a proton from the carboxyl group to the amino group to form a zwitterion.

→ At pH values above the isoelectric point, amino acids donate a proton and become a negative ion, whereas at pH values below the isoelectric point, they accept a proton and become a positive ion.

→ Peptides form when amino acid monomers bond through a peptide bond.

→ Tripeptides consist of three amino acids bonded together.

What are amino acids?

Amino acids and the molecules made from them are important biological molecules. Their structural features relate to their physical and chemical properties. Amino acids are organic compounds with both amino ($-NH_2$) and carboxyl ($-COOH$) functional groups. There are 20 common amino acids that make up the proteins in the human body. They differ in their side chain (**R group**). The side chain 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).

Learning intentions and success criteria

R group
the side chain of an amino acid

Zwitterions

Amino acids contain an acidic carboxyl group and a basic amino group, so they can undergo internal transfer of a hydrogen ion. The hydrogen ion from the acidic carboxyl group is released 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). Due to this complete transfer of charge, solid amino acid molecules each contain a positive ionic section and a negative ionic section and have stronger than usual intermolecular forces. As a result, they have higher melting points than would be expected for covalent molecules. Ionic bonds occur in this section of the molecule in addition to the much weaker intermolecular forces. Additionally, due to the presence of a positive end and a negative end, amino acids are quite soluble in water. Polar water molecules experience a strong attraction to the ionic regions of amino acid molecules.

zwitterion
a molecule that has separate positively and negatively charged parts

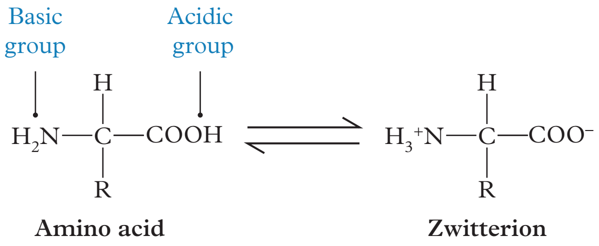
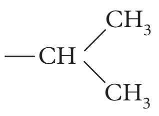
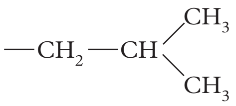
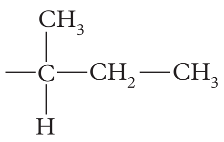
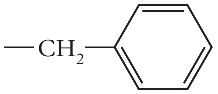
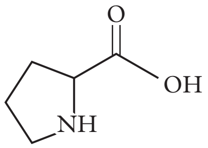
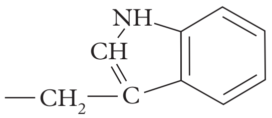
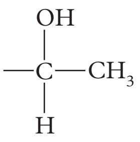
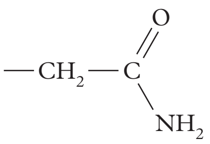
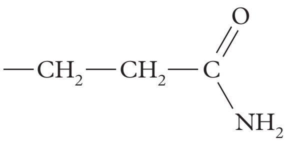
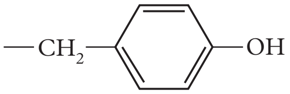
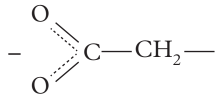
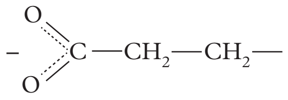
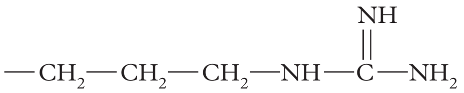
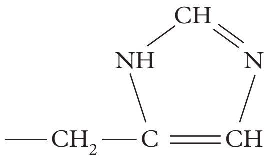


FIGURE 1 The general structure of an amino acid

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 *Formula and data book* for the external assessment.

TABLE 1 The 20 amino acids in the human body. Notice that glycine has a single hydrogen atom rather than a side chain incorporating one of more carbon atoms. The complete structure of proline is shown, as the "side chain" actually forms a ring with the nitrogen atom in the amino group.

Polarity and acid–base properties	Common name	Symbol		Side chain
Non-polar neutral	Glycine	Gly	G	$-H$
	Alanine	Ala	A	$-CH_3$
	Valine	Val	V	
	Leucine	Leu	L	
	Isoleucine	Ile	I	 $-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-CH_2-CH_3$
	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	 $-\overset{\displaystyle OH}{\underset{\displaystyle H}{C}}-CH_3$
	Asparagine	Asn	N	
	Glutamine	Gln	Q	
	Tyrosine	Try	Y	

Polarity and acid–base properties	Common name	Symbol		Side chain
Polar acidic	Aspartic acid	Asp	D	
	Glutamic acid	Glu	E	
Polar basic	Lysine	Lys	K	$-CH_2-CH_2-CH_2-CH_2-NH_2$
	Arginine	Arg	R	 $-CH_2-CH_2-CH_2-NH-\overset{\overset{NH}{\Vert}}{C}-NH_2$
	Histidine	His	H	

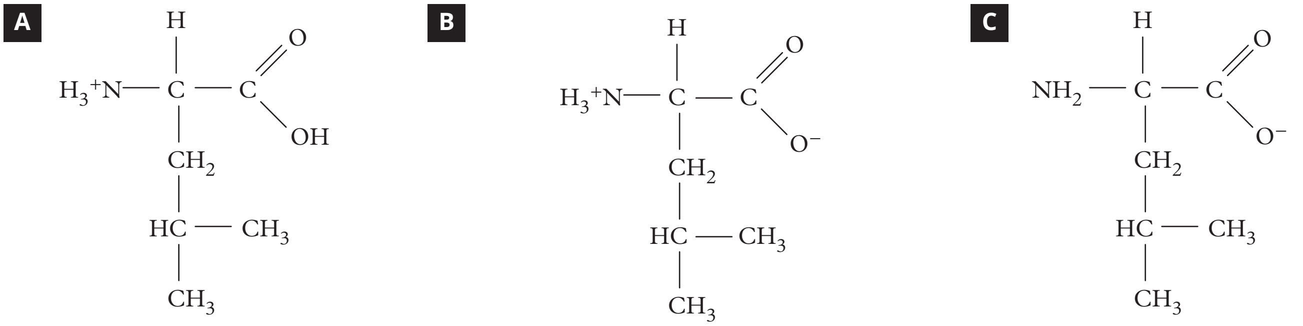
The 20 amino acids in the human body are also known as 2-amino acids because the amine group is on the second carbon atom in the main chain, the carbon with the carboxyl group being numbered 1. The R group or side chain of each of the amino acids varies considerably in both size and composition. It may be polar or non-polar and can be acidic (proton donating) or basic (proton accepting), affecting the physical and chemical properties of the amino acid and molecules made of amino acids.

Study tip

Carboxyl groups (–COOH) on the side chain mean the amino acid are acidic. Where nitrogen is present on the side chain, the side chain can accept a proton and the amino acid will be basic. Hydroxyl (–OH) and carbonyl (–CO) groups on the side chain will be polar. Review intermolecular forces in Unit 2 and acids and bases in Unit 3.

How do amino acids act in solution?

All amino acids have a pH called their isoelectric point, which differs for each amino acid. At this pH, when in solution, the amino acid is electrically neutral overall, and in the form of its zwitterion. For example, leucine (Leu) has a pH of 6.0 at the isoelectric point. If the pH is lower than the isoelectric point, there is an excess of protons in the solution, and the $-COO^-$ section of the amino acid accepts an extra proton, making the amino acid positively charged overall. If the pH of the solution is higher than the pH at isoelectric point, there are fewer protons in the solution, and a proton is removed from the $-NH_3^+$ section of the amino acid. The amino acid then becomes negatively charged overall. Figure 2 illustrates this for leucine.



pH below isoelectric point, amino acid accepts a proton to form a positive ion

Zwitterion form of leucine in a solution at pH = 6.0

pH above isoelectric point, amino acid donates a proton to form a negative ion

FIGURE 2 Leucine at pH values (A) below, (B) at and (C) above pH 6.0, which is its pH at the isoelectric point

Acid–base reactions of amino acids

It can be seen that amino acids readily react to both donate and accept protons, depending on the pH of the solution. This means that they can react with both acids and bases.

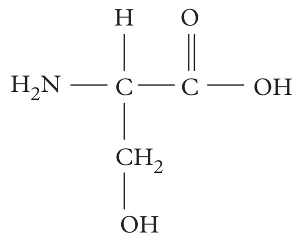
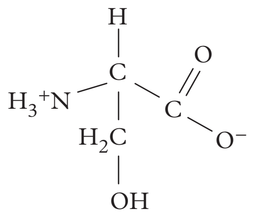
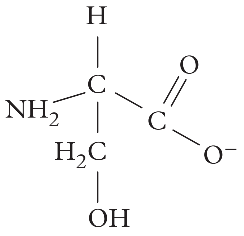
Worked example 11.2A

Explaining zwitterions and the acid–base properties of 2-amino acids

For the amino acid serine (Ser), **explain**

a how serine forms a zwitterion (2 marks)

b the structure of serine in a neutral solution, with pH 7.0. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	“Explain” means to make an idea or situation plain or clear by describing it in more detail or revealing relevant facts; give an account; provide additional information. We need to describe zwitterion formation for this amino acid and provide a diagram. We need to identify the pH at the isoelectric point for serine and describe its form at pH 7.0. Each question is worth 2 marks, so we must have enough detail including diagrams.
Step 2: Select the appropriate formulas and gather the required data.	The structure and pH at isoelectric point for serine can be found in the QCAA *Formula and data book*. Serine (Ser)  5.7
Step 3: Describe how a zwitterion is formed.	**a** Serine can undergo internal proton transfer, in which H^+ from $-COOH$ is transferred to the $-NH_2$ group, making a negatively charged $-COO^-$ group and a positively charged $-NH_3^+$, causing the molecule to form a zwitterion. (1 mark)
Step 4: Draw the structure of the zwitterion.	 (1 mark)
Step 5: Use the pH at isoelectric point and the given pH to explain the form of the amino acid.	**b** Serine has a pH at isoelectric point of 5.7. At pH 7.0, there will be fewer protons available, and so serine will donate a proton to the water in the solution. This means serine will be present in the form of a negative ion. (1 mark)
Step 6: Finalise your answer by drawing a diagram of serine at pH 7.0.	 (1 mark)

Your turn

For the amino acid threonine (Thr), **explain**

a how threonine forms a zwitterion (2 marks)

b the structure of threonine in a solution with a pH of 3.0. (2 marks)

Worked example 11.2B

Explaining the acid–base properties of amino acids

Using the 2-amino acid valine as an example, **explain** how amino acids in the zwitterion form can react with

a hydrochloric acid (2 marks)

b sodium hydroxide. (2 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	"Explain" means make an idea or situation plain or clear by describing it in more detail or revealing relevant facts. We need to write the chemical reactions of the zwitterion form of valine with both an acid and a base and make clear the acid–base properties of the amino acid. Each question is worth 2 marks, so we must express a balanced chemical equation and its significance for both parts.
Step 2: Select the appropriate formulas and gather the required data. Find the formula of valine from the *Formula and data book*. It can be written, rather than drawn. Recall the formulas of propanoic acid and sodium hydroxide.	Valine: $H_2NCH(CH(CH_3)CH_3)COOH$ Hydrochloric acid: HCl, which will be in the form of H_3O^+ and Cl^- Sodium hydroxide: NaOH
Step 3: Write a balanced equation for the reaction between the valine zwitterion and propanoic acid.	**a** $H_3{}^+NCH(CH(CH_3)CH_3)COO^-(aq) + HCl(aq) \rightarrow H_3{}^+NCH(CH(CH_3)CH_3)COOH(aq) + Cl^-(aq)$ (1 mark)
Step 4: Write a balanced equation for the reaction between the valine zwitterion and sodium hydroxide.	**b** $H_3{}^+NCH(CH(CH_3)CH_3)COO^-(aq) + NaOH(aq) \rightarrow H_2NCH(CH(CH_3)CH_3)COO^-(aq) + H_2O(l) + Na^+(aq)$ (1 mark)
Step 5: Finalise your answer by providing detail about how the zwitterion can accept a proton and donate a proton, depending on the reactant.	**a** The negatively charged region ($–COO^-$) of the valine zwitterion acts as a base and accepts a proton from the hydrochloric acid. (1 mark) **b** The positively charged region (H_3N^+) of the valine zwitterion acts as an acid and donates a proton to the hydroxide ion of NaOH, forming water. Na^+ is a spectator ion. (1 mark)

Your turn

Using the 2-amino acid phenylalanine as an example, **explain** how amino acids in the zwitterion form can react with

a hydrochloric acid (2 marks)

b potassium hydroxide solution. (2 marks)

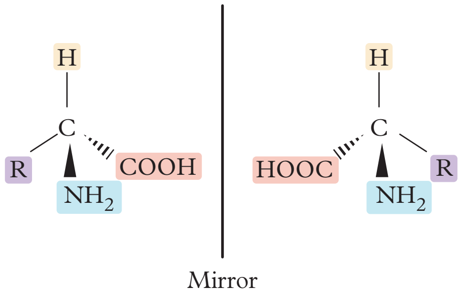


FIGURE 3 Stereoisomers of amino acids. The isomer on the right predominantly occurs in nature.

peptide
a molecule made of amino acid monomers

peptide bond
the bond formed in a condensation reaction between the carboxyl group of one amino acid and the amine group of another amino acid; water has been eliminated

tripeptide
a molecule consisting of three amino acids joined by two peptide bonds

Study tip

You may focus on peptides, including enzymes and proteins, in your research investigation. For the external examination, the subject matter extends to amino acids and tripeptides, but not the larger peptide molecules.

Study tip

Diagrams for tripeptides are not always drawn in the orientation shown in Figure 4. Even if the orientation is different, look for an amino terminus, a carboxy terminus and two peptide bonds that join the C of a carbonyl group to the N of an amino group. The R groups can then be deduced.

What optical isomers exist for amino acids?

The 2-carbon of all amino acids except for glycine is chiral because it has four different substituents, and thus there are two possible mirror-image isomers (Figure 3). Living organisms predominantly produce and use the same stereoisomers of amino acids.

What are peptides?

Peptides are molecules consisting of two or more amino acids bonded together. The bond forms in a condensation reaction between the carboxyl group (–COOH) of one amino acid and the amino group (–NH_2) of the next amino acid; peptides are all amides, and polyamides. The bond is known as a **peptide bond**.

Peptides include dipeptides, tripeptides, tetrapeptides as well as enzymes and proteins, which contain many amino acids.

What are tripeptides?

Tripeptides are molecules made up of three amino acids bonded through two peptide bonds. Occasionally, the two ends form a third peptide bond, creating a ring-shaped tripeptide. Many tripeptides exist in our cells and carry out a huge range of functions, including signalling the release of hormones, and as antioxidants, to remove molecules called free radicals that would otherwise cause damage and premature ageing of our cells.

What are the structural features of tripeptides?

Because tripeptides have an amine group at one end and a carboxyl group at the other end, they can both accept and donate protons in the same way that amino acids can, so they too have acid–base properties.

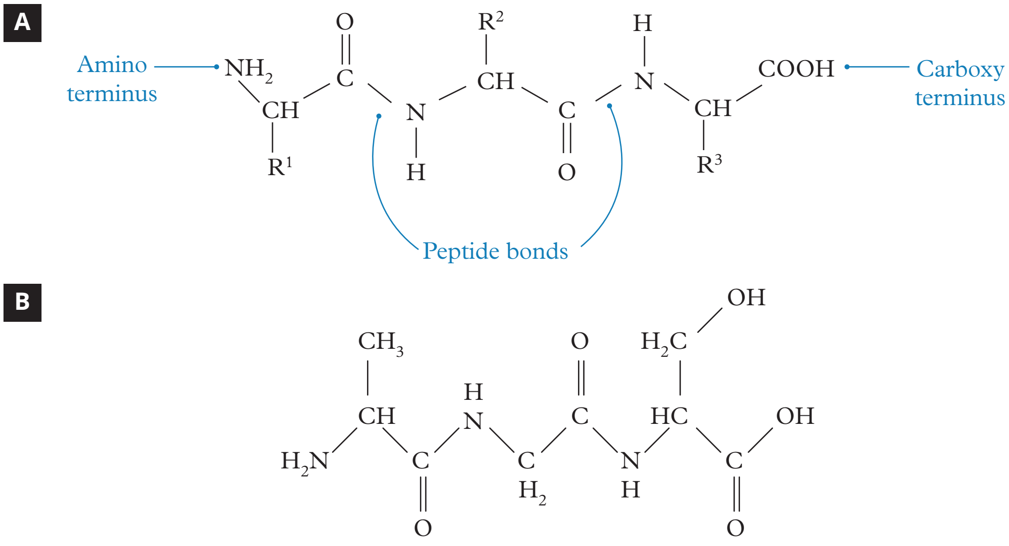


FIGURE 4 (A) The general structure of a tripeptide showing the two peptide bonds connecting three amino acids with different R groups. (B) This tripeptide consists of alanine at the amino end, glycine in the middle and serine at the acid end.

Check your learning 11.2

Check your learning 11.2: Complete these questions online or in your workbook.

Retrieval and comprehension

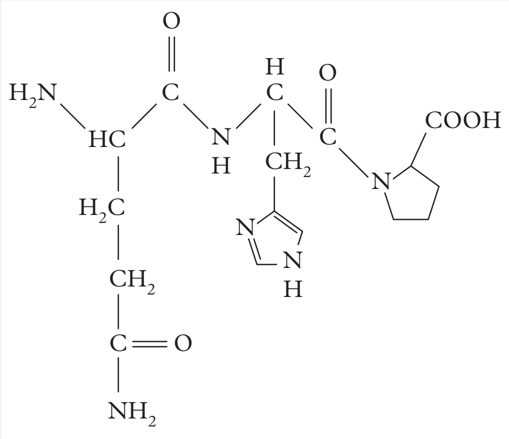
1 **Describe** the structure of an amino acid. (3 marks)

2 **Explain** how an amino acid can act as both an acid and a base. (2 marks)

3 **Explain**
  - a how isoleucine forms a zwitterion (2 marks)
  - b the structure of isoleucine in a solution, with pH 9.0. (2 marks)

4 **Describe** the general structure of a tripeptide, including the bonding to form a tripeptide from amino acids. (3 marks)

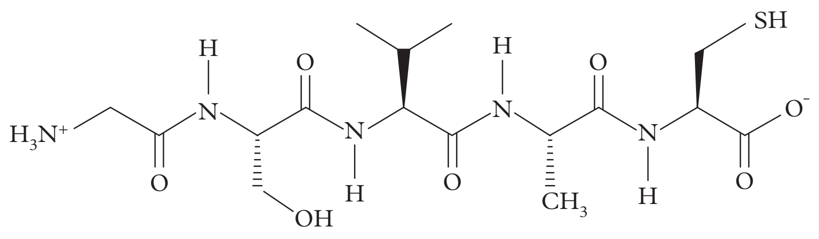
5 Thyrotropin-releasing hormone is made from the tripeptide structure shown. **Describe** the structure of this hormone in terms of the amino acids present and the bonding. (3 marks)



Analytical processes

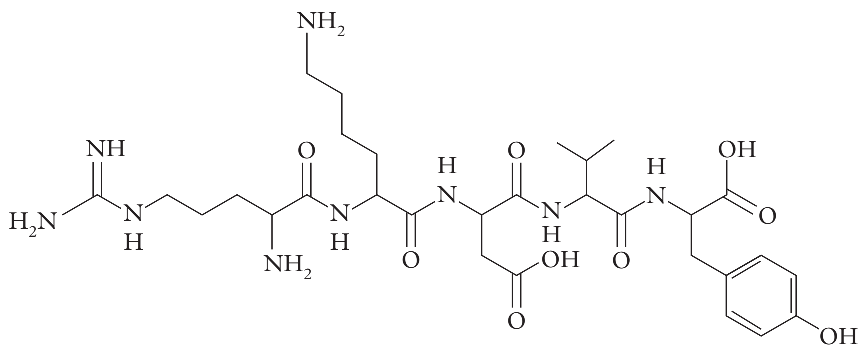
6 **Analyse** these polypeptides to **identify** the location of the peptide bonds, and each of the amino acids in the sequence.

a



(2 marks)

b



(2 marks)

7 The zwitterion of glycine can be written as $H_3{}^+NCH_2COO^-$. **Determine** the balanced chemical equation for the reaction between a solution of nitric acid and the glycine zwitterion. (1 mark)

Lesson 11.3
Polymers

Key ideas

→ Synthetic polymers can be formed by either condensation or addition reactions.

→ Synthetic polymers formed by addition include polyethene, polypropene and polytetrafluoroethene (Teflon).

→ Synthetic polymers formed by condensation include polylactic acid (PLA), polyamides such as nylon, and polyester.

→ Synthetic polymers can be designed with properties to suit different purposes, such as strength, density, lack of reactivity, plasticity and biodegradability.

→ The properties of synthetic polymers are related to the structure of the materials, including variables such as the chain length, the nature, size and arrangement of substituents, the degree of branching and the mix of stereoisomers, if applicable.

What are polymers?

Learning intentions and success criteria

macromolecule
a very large molecule

In 1920, German chemist Hermann Staudinger demonstrated that synthetic polymers were molecules of high molecular mass (**macromolecules**) that were made of many small molecules (monomers). 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.

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.

What are some useful properties of polymers?

The composition of a polymer chain determines its properties, including how strong, dense, reactive and plastic it is.

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.

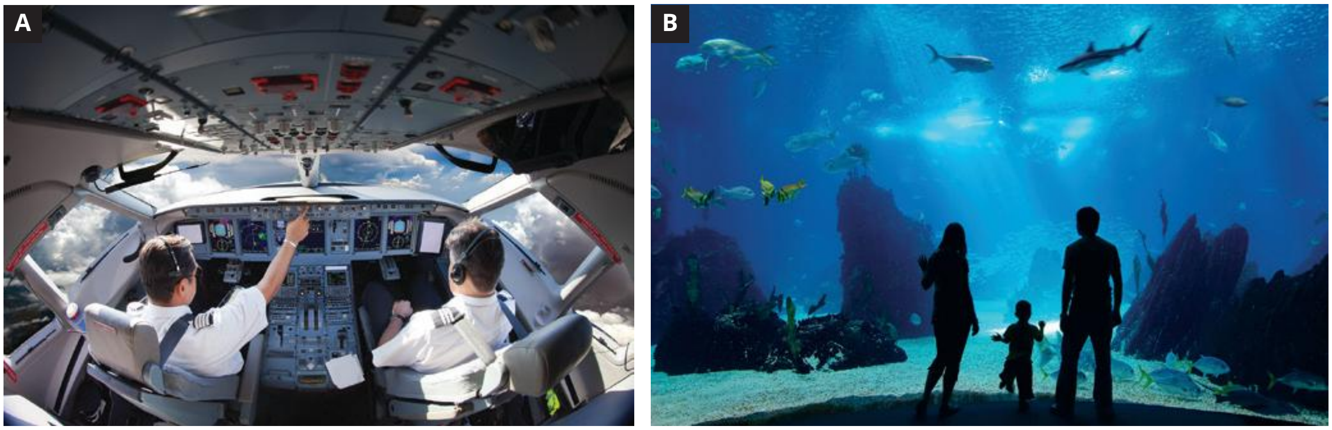


FIGURE 2 (A) Aircraft windscreens and (B) aquarium windows are commonly made of polymethyl methacrylate instead of glass.

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.

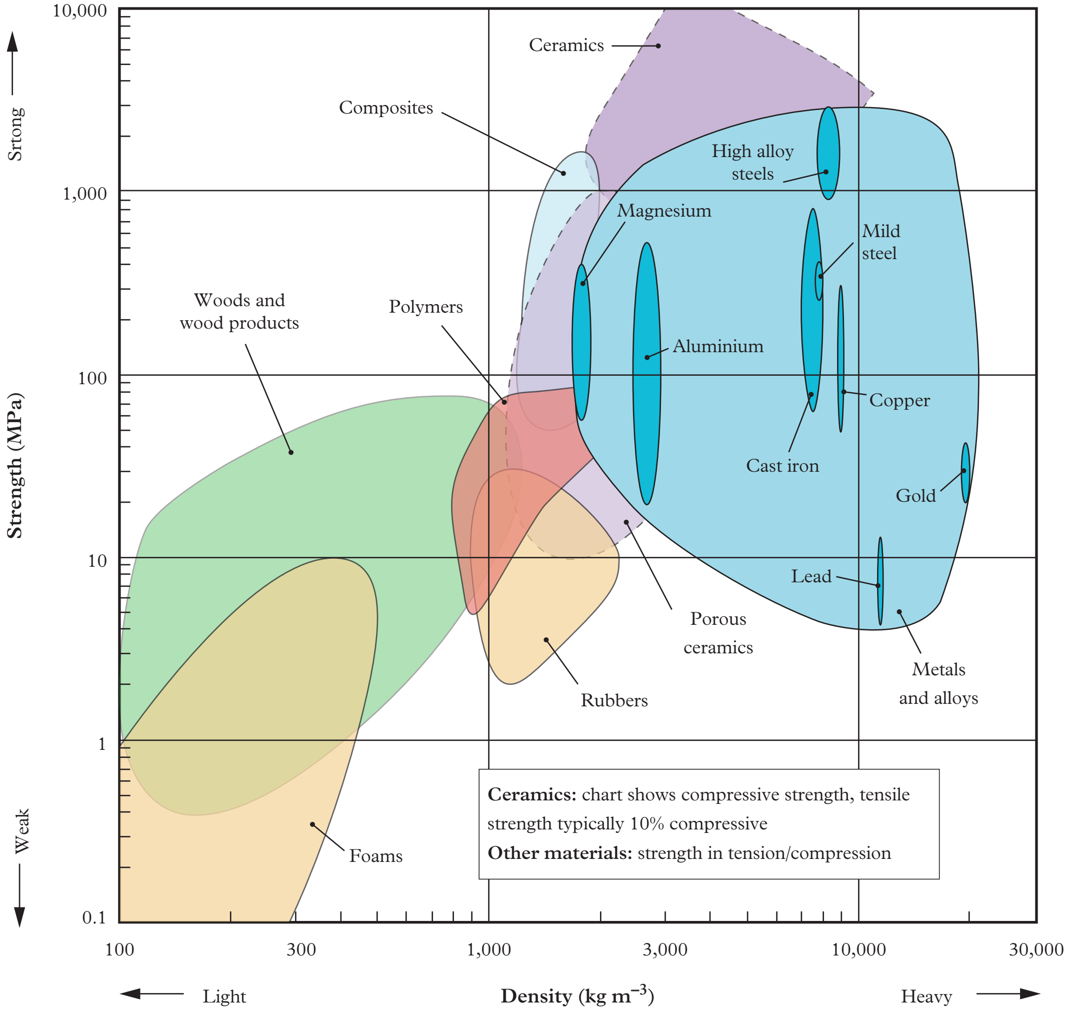


FIGURE 4 The density and strength of polymers compared with other materials

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, and therefore 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.

Plasticity

thermoplastic
a type of polymer that can be moulded into new shapes

Some polymer molecules are **thermoplastic** and can be heated or worked under pressure and reshaped, allowing them to be easily moulded into new objects. This is because thermoplastic polymers have weak intermolecular forces between polymer chains rather than strong chemical bonds (Figure 5). These weak intermolecular forces require less energy to break than covalent bonds, allowing the polymer to soften when forces are applied or become fluid when heated. For example, a plastic milk bottle melts when heated, and on cooling to room temperature the bottle sets with the new moulded shape.

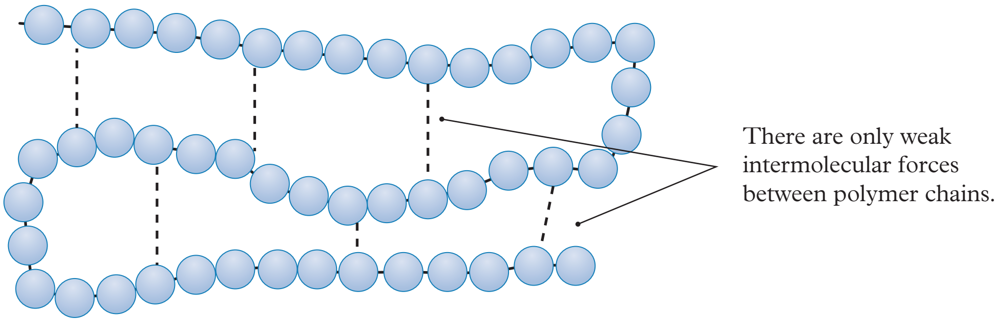


FIGURE 5 Thermoplastic polymers only have weak molecular forces between chains, allowing them to be easily reshaped.

Thermosetting polymers can only be shaped once when they are first formed. When heated again, they cannot form into a new shape. For example, a two-part epoxy glue forms bonds between the two parts when setting and takes on a permanent shape. This is because thermosetting polymers are crosslinked with covalent bonds between polymer chains. The energy required to break these covalent bonds is much higher than that required to break the weak intermolecular forces in thermoplastic polymers.

thermosetting
a type of a polymer that, once set in its shape, cannot take on a new shape when subjected to heat and/or pressure; this is because it forms multiple cross-linking covalent bonds between parts of the polymer chain as it cures

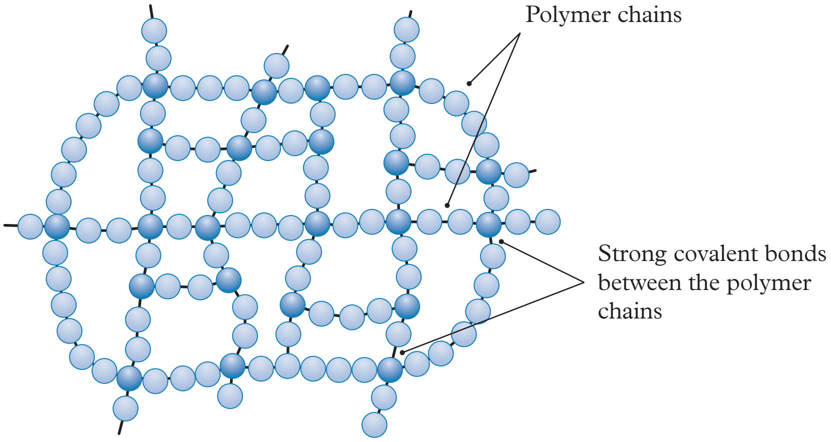


FIGURE 6 Thermosetting polymers have strong covalent bond cross links between chains.

Are polymers biodegradable?

Most polymers are made from fossil fuels and are **non-renewable** and most are not **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 (e.g. 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. An example of a 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 7). 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. A fungus that breaks down and digests polyurethane has been discovered in fallen foliage of common ivy in Buenos Aires, Argentina. Other microorganisms can break down polyethene. Some scientists even suggest that microorganisms are now evolving to have genes capable of breaking down plastics.

non-renewable
a source material or its product that exists in finite amounts that are not replenished

biodegradable
can be broken down by living organisms

biodegradation
the breakdown of a substance, such as plastic, by microorganisms

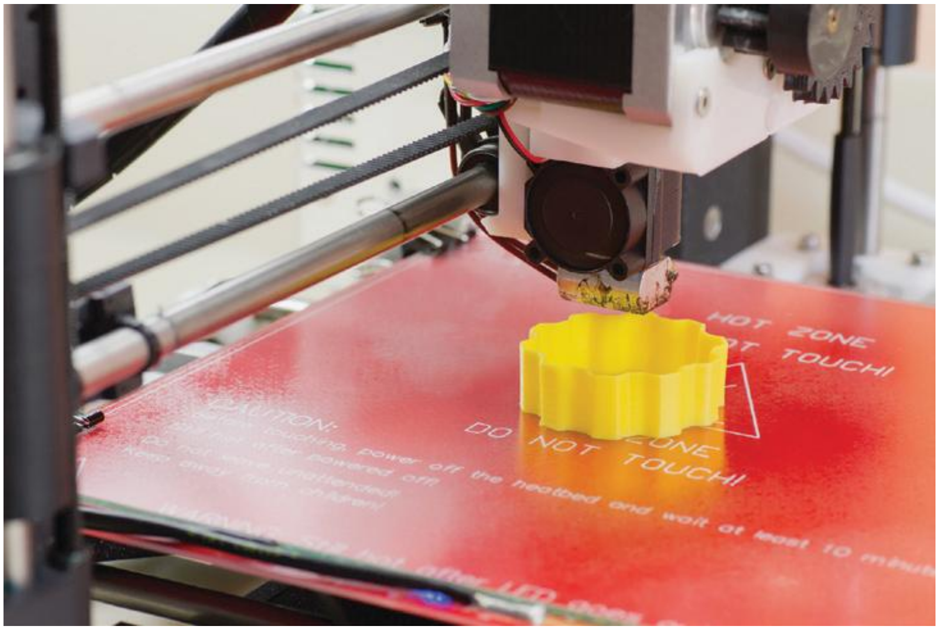


FIGURE 7 Biodegradable polylactic acid is used in 3D printers.

What are addition polymers?

addition polymer a polymer made from alkene monomer units that bond together in an addition reaction

Addition polymers are formed from alkene monomers. Polymerisation occurs when the double bond opens up to become a single bond, as many monomers join end to end.

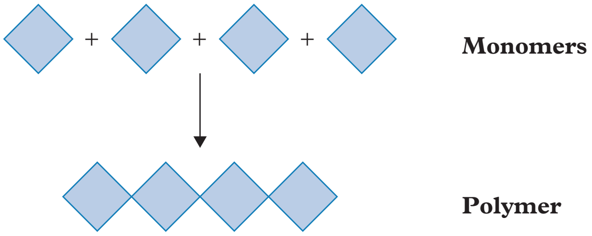


FIGURE 8 Addition polymerisation involves an addition reaction of monomers to form a polymer.

Polyethene

Polyethene (also called polyethylene and polythene) is the polymer of ethene and the most common plastic to date (Figure 9). When the polyethene chain is approximately 200 carbons long, it has the consistency of wax, but the larger the polymer the harder its consistency.

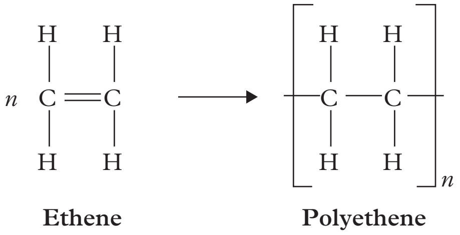


FIGURE 9 Polyethene – a polymer of ethene. The *n* in the equation shows that *n* molecules of ethene bond to form the polymer product, which has *n* monomer units bonded together.

Because of the number of electrons present in such a large molecule, polymers experience significant dispersion forces. However, dispersion forces are only effective when the molecules are near each other. Therefore, the amount of branching on a polymer will affect the dispersion forces experienced. Polyethene exists in two forms:

- high-density polyethene (HDPE), which has minimal branching off the main chain
- low-density polyethene (LDPE), which has frequent branching off the main chain and the branches are longer.

FIGURE 10 Types of branching in polyethene – high-density (HDPE) and low-density (LDPE) polyethene

HDPE has minimal branching and forms regions where molecules are organised in a mostly regular arrangement described as **crystalline**. This arrangement positions molecules in close contact with each other, maximising dispersion forces between neighbouring molecules. Because of this this arrangement, HDPE is stronger, harder and more **rigid** than LDPE and has a melting point of 120°C to 135°C. Because of its strength, hardness and high melting point, HDPE is used for chemical tanks, water pipes, cutting boards and other applications where a relatively light but high-strength product is required. The non-branching of the molecules means that HDPE is easily recycled while retaining its useful properties.

crystalline
describes regions in polymers where the polymer molecules are arranged in a regular way

rigid
unable to change shape

amorphous
describes how polymer molecules are arranged randomly

LDPE has a higher degree of branching, and therefore has fewer dispersion forces and is weaker. The molecular arrangement is **amorphous** and much more random and tangled, with the molecules being further apart. Because of the amorphous arrangement of polymer molecules, LDPE is strong, but not hard or rigid, has a lower density than HDPE and has a melting point of 105°C to 115°C. As a hydrocarbon polymer, LDPE is chemically resistant (insoluble at room temperature) and easy to clean. These properties make it suitable for use as plastic milk bottles, laboratory wash bottles and plastic bags. It is also used in medical devices such as orthotics and prosthetics.

Both types of polyethene are resistant to chemicals such as strong acids, strong bases and mild oxidising agents. This feature makes polyethene less biodegradable because organisms such as soil bacteria cannot attack it.

What are substituted polymers?

Substituted polymers of ethene are very common and include polyvinyl chloride (PVC) and polytetrafluoroethene (PTFE) as shown in Figure 11. PTFE is the polymer of 1,1,2,2-tetrafluoroethene. It 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 opposite side of the polymer. As a result, PTFE is hydrophobic and feels smooth and slightly slippery because it forms a surface with very low frictional forces. It is a relatively dense polymer, has a high melting point, and is strong. Due to the strength of the C–F bonds, it is chemically unreactive. It is the major component of Teflon – the non-stick surface of frying pans and is also used in thread tape by plumbers, containers for highly corrosive chemicals and industrial and medical uses that require a low-friction, chemically inert surface.

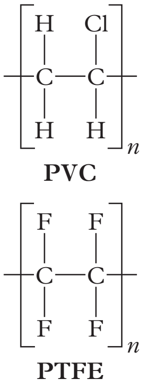


FIGURE 11 Substituted polymers – polyvinyl chloride (PVC) and polytetrafluoroethene (PTFE)

Polypropene (also known as polypropylene) is the polymer of propene. It is an asymmetrically substituted polymer that contains many **chiral centres**, resulting in three stereoisomers: isotactic, syntactic and atactic (Figure 12). 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 and has a melting point of 165°C. It is strong and is 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.

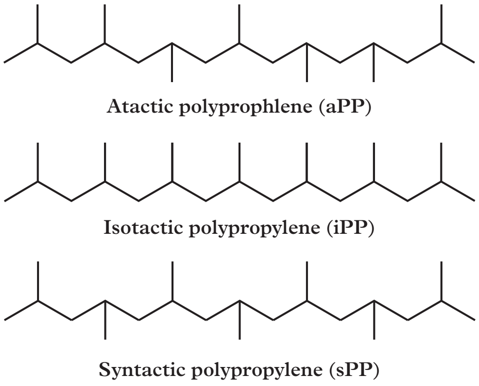


FIGURE 12 Types of polypropene

chiral centre
a carbon atom bonded to four different substituents

condensation polymer
a polymer formed when monomers undergo condensation and water is produced as a by-product

Study tip

The prefix "iso" means "equal" or "same"; think of other words with the prefix "iso".
The prefix "syn" means "along with", or "together".
"A" means "not"; think of other words with the prefix "a".

What are condensation polymers?

Condensation polymers form when monomers undergo condensation reactions to form polymers consisting of many monomers bonded end to end while also producing a small by-product (e.g. water). Each monomer of a condensation polymers needs to have at least two functional groups present. This is so the functional group of one monomer can react with the functional group of another, allowing covalent bonds to form between monomers and link together.

Polylactic acid

Polylactic acid (PLA) can be synthesised from lactic acid monomers and has the structure shown in Figure 13.

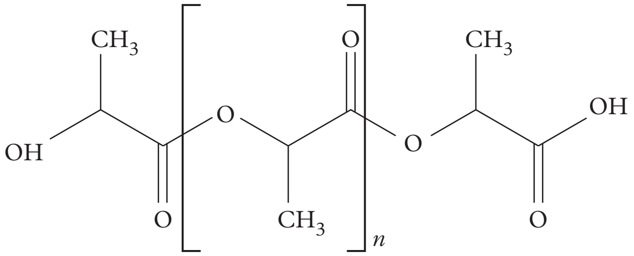


FIGURE 13 Polylactic acid is made from lactic acid monomers.

The lactic acid monomer can produced from renewable sources such as fermented plant starch from corn, cassava, sugar cane or sugar beet. It is a more environmentally friendly polymer than the many polymers that are synthesised from fossil fuels. Because it originates in plant material, its structure resembles organic molecules found in nature. Enzymes in decomposer organisms such as bacteria can break down the long polymer molecules into small molecules. This means that PLA is biodegradable.

PLA is chiral, so several forms of this polymer exist. The physical properties are different for PLA that contains a mixture of stereoisomers and PLA that contains a single stereoisomer. The mixture of stereoisomers produces an amorphous solid, where the molecules are arranged randomly, without any regular crystalline regions. In contrast, if the chirality of all sections of the polymer molecule is the same, the resulting PLA forms a solid in which the molecules align in a regular way, that exhibits crystallinity, is stronger and has a much higher melting point and thus is more heat resistant.

Because it is thermoplastic, PLA is used in 3D printers to fabricate objects. With both polar and non-polar regions in the molecule, PLA is soluble in a range of solvents such as ethyl ethanoate, allowing 3D printer extrusion tips to be cleaned. PLA is biodegradable, which makes it useful for medium-term medical implants such as plates, screws, rods and pins. It breaks down into harmless lactic acid over a period of months, as the body gradually heals.

What are polyamides?

Polyamides include natural substances such as enzymes and proteins, as well as synthetic polymers. A variety of synthetic polyamides exists, including nylon, first patented in the 1930s. The structure of a polyamide depends on whether it is made from a single monomer having a carboxyl group and an amino group, or whether it is made from two monomers, one being a diamine and the other a diacid. Some forms of polyamides incorporate a benzene ring in the monomer and are part of a class of compounds called **aromatic**, although nylon is **aliphatic** (Figure 14). In a benzene ring, each carbon atom is covalently bonded to three other atoms, and the fourth valence electron is delocalised, meaning it can move about and spread out around the ring.

aromatic
an organic compound containing at least one ring structure with delocalised electrons

aliphatic
an organic compound or group containing carbon and hydrogen joined together in straight chains, branched chains, or non-aromatic rings

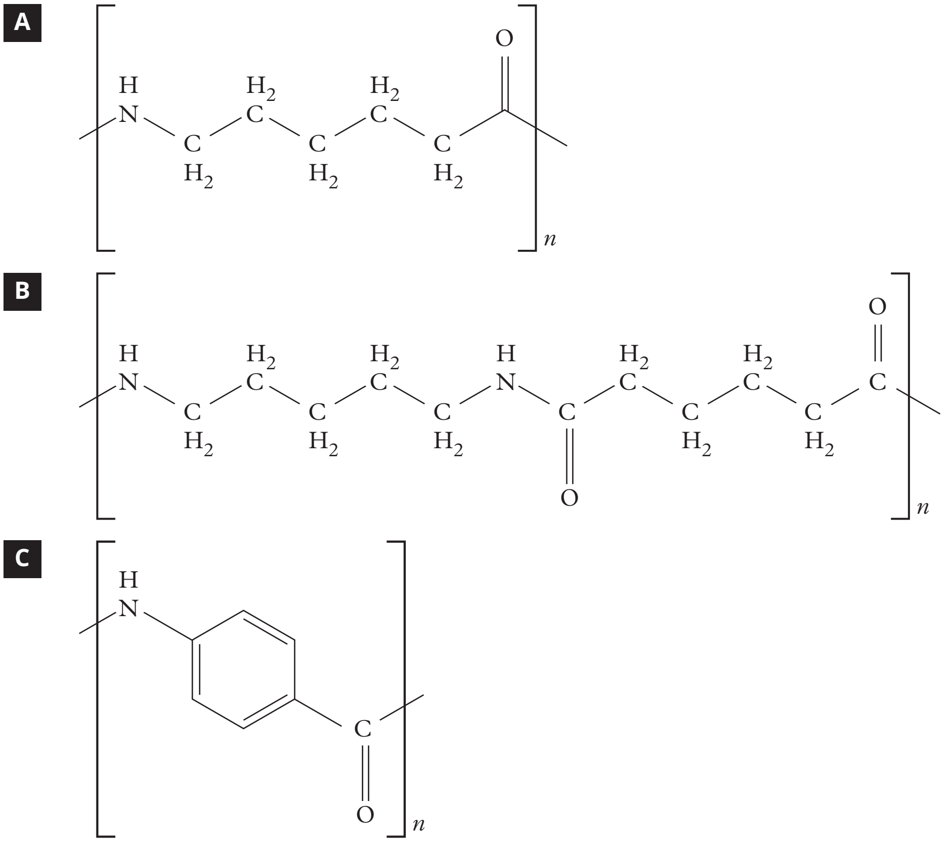


FIGURE 14 (A) Polyamide 6, a nylon formed from a single monomer with six carbon atoms; (B) polyamide 5.6, a renewable nylon formed from two different monomers, one with five carbon atoms, one with six carbon atoms; and (C) an aromatic polyamide

Polyamides are thermoplastic, allowing them to be **extruded** as fine filaments and fibres. Other desirable properties are toughness, high tensile strength and impact strength, low friction, wear resistance and corrosion resistance. These properties are due to the polar nature of the amide groups as neighbouring molecules are attracted to each other through both dipole–dipole forces and hydrogen bonding. Such properties make polyamides useful for carpets, as blends in clothing fabric, for parachutes, to protect cables, and other settings where high strength is desirable. Kevlar and Nomex are trademarked examples of polyamides with aromatic groups and have even higher strength than aliphatic polyamides.

extruded
push through a small opening

What are polyesters?

Polyesters are polymers made from alcohol and acid monomers. One of the most common and useful polyesters is polyethylene terephthalate (PET), with the structure shown in Figure 15. It is classed as an aliphatic-aromatic polyester.

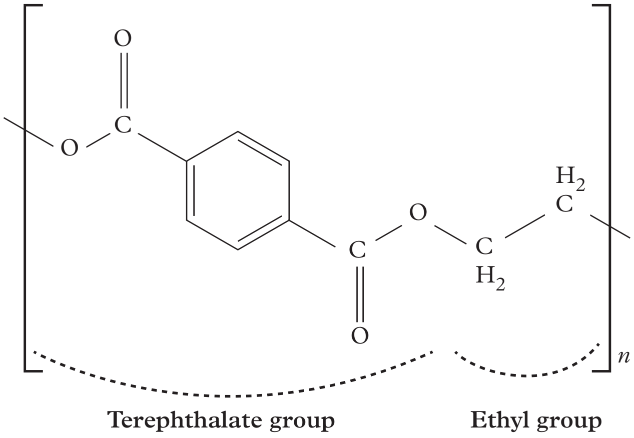


FIGURE 15 The structure of the polyester polyethylene terephthalate, commonly known as PET

The terephthalate section comes from a diacid monomer, and the ethyl group comes from the monomer ethane-1,2-diol. The monomers are joined through ester linkages. Because of the presence of polar bonds between C and O, the intermolecular forces between the polymer molecules are strong, although not as strong as in polyamides. PET is commonly used in soft-drink bottles, because it is thermoplastic, quite strong, and impervious to water and carbon dioxide. All raw materials and side products have low toxicity, and it is easily recycled to make new products.

The properties of polyesters depend on whether they are aliphatic, aromatic or both, as well as the chain length and degree of branching. This means polyesters are versatile and can be designed for many different applications. Table 1 summarises how the structure of polyesters affects their properties and applications.

TABLE 1 A summary of the structural features, properties and applications of polyesters

Structural features	Properties	Application
Linear (unbranched), aliphatic, high molecular mass, semicrystalline	• Low melting points (40–80°C) • Biodegradable • Thermoplastic	Useful where environmental impact is a concern, e.g. packaging, disposable items, agricultural use, biomedical and pharmaceutical uses
Highly branched polyesters	• Low viscosity (flows easily) • Soluble	Added to modify the properties of other polymers including coatings
Aliphatic-aromatic, semicrystalline (PET and others)	• High melting points (160–280°C) • Thermoplastic • Can be extruded	Fibres to make fabrics, films, containers; can be engineered into parts for automobiles and electrical and electronic devices
Wholly aromatic	• High strength • Heat resistant • Thermoplastic	Engineered into components for specialised high-performance applications
Unsaturated (contains unsaturated monomers and alcohol monomers with a number hydroxyl groups)	• Can form bonds that cross-link the polymer chains • Thermosetting	Resins that can be cast into shapes or used as high-strength coatings and fillers

Polyesters are biodegradable because microorganisms can break the ester linkages with hydrolysis reactions. Internal surgical sutures are biodegradable polyesters – the body can break them down within 90 days.

Real-world chemistry

Michelle Coote: leading polymer research scientist

Australian Professor Michelle Coote worked as an industrial chemist for a short time, before turning to research in polymer chemistry. Her early research focused on using neutron reflectivity to explore the properties of polymers. Later, Michelle focused on the potential of better control of free-radical polymerisation.

Free radicals are molecules with an unpaired electron and are used to initiate addition reactions between unsaturated monomers. Michelle developed computer-guided methods to design reagents to control the stereochemistry of free-radical polymerisation. Stereochemistry is the arrangement of the bonds and substituents of polymer molecules in space, and includes the different types of tacticity as well as mirror-image stereoisomers with chiral carbon atoms; this greatly affects the physical and chemical properties.

Her other research interests include methods for stabilising polymers to minimise degradation. Michelle and members of her research team were awarded the 2019 Eureka Prize for their discovery that static electric fields can be used instead of chemical catalysts for chemical reactions. This discovery has the potential to lead to safe green methods of chemical synthesis.

TABLE 2 Melting points of stereoisomers of polypropene with differing tacticity

Tacticity of polypropene	Melting point range (°C)
Isotactic	165–175
Syntactic	120–130
Atactic	Does not melt, softens above 100

Apply your understanding

1 **Compare** the melting points of isotactic and syntactic polypropene and **propose** a reason for the difference. (3 marks)

2 **Consider** why stabilisers to prevent degradation are important in some applications of polymer chemistry. (2 marks)

3 **Research** the 12 principles of green chemistry. **Consider** which of these principles would apply to the use of static electric fields in synthesis reactions. **Justify** your reasoning. (3 marks)

Skill drill

Developing a strong research question

Science inquiry skill: Preparing for your research investigation (Lesson 1.12)

In the first part of the report of your research investigation, you are required to have a

- considered rationale identifying clear development of the research question from the claim
- specific and relevant research question.

From a broad and general claim, you need to develop your specific and relevant research question.

FIGURE 16 What properties are important for a polymer used for fishing line?

Practise your skills

1 **Consider** the two research questions, **decide** which is the better research question and provide reasons for your choice. (2 marks)
  - Is nylon suitable for fishing lines due to the strength imparted by dipole–dipole forces and hydrogen bonding?
  - Is nylon better than polyethene for use in fishing lines, based on breaking strength, UV resistance and stretch?

2 The second research question could be altered by changing the variables. Other variables important when fishing are knot strength, castability, limpness, abrasion resistance and visibility. **Explain** whether it would be better to include more variables or different variables in a research question. (2 marks)

Check your learning 11.3

Check your learning 11.3: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain** how branching in polymers affects their properties. (2 marks)

2 **Explain** how bonding in synthetic polymers affects their properties. (2 marks)

3 **Explain** how the polarity of polymer molecules affects their properties. (3 marks)

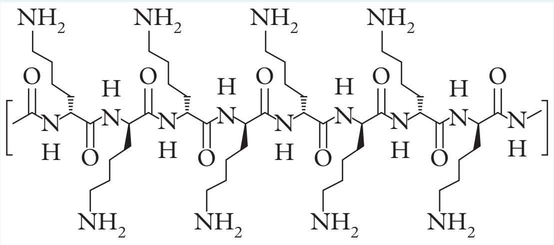
Analytical processes

4 **Compare** the structure and properties of polyethene with its substituted version polytetrafluoroethene. (4 marks)

5 **Compare** the structures and properties of the syntactic, isotactic and atactic versions of polypropene. (6 marks)

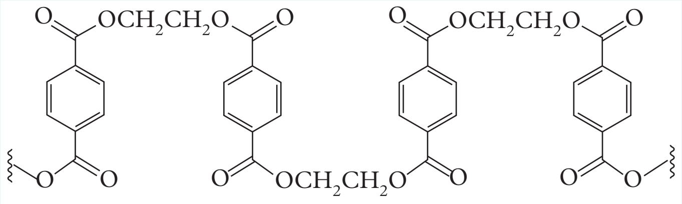
6 **Analyse** each polymer and identify the monomer(s) used.

a



(1 mark)

b



(1 mark)

MODULE 11

Lesson 11.4

Review: Organic materials: structure and function

Summary

11.1
- Monosaccharides are sugar monomers with three to seven carbon atoms and consist of a carbon chain with several hydroxyl groups, and either an aldehyde or a ketone.
- In aqueous solution, all but the smaller monosaccharides exist as two or three forms in dynamic equilibrium – a straight chain and two different ring forms, called alpha and beta, with 5- or 6-membered rings.
- Disaccharides are dimers of monosaccharides that are joined by glycosidic linkages.

11.2
- Sucrose is an example of a disaccharide.
- Amino acids have both amino and carboxyl functional groups. They have acid–base properties and can act as proton donors and proton acceptors.
- At a pH known as their isoelectric point, amino acids undergo internal transfer of a proton from the carboxyl group to the amino group to form a zwitterion.
- At pH values above the isoelectric point, amino acids donate a proton and become a negative ion, whereas at pH values below the isoelectric point, they accept a proton and become a positive ion.
- Peptides form when amino acid monomers bond through a peptide bond.
- Tripeptides consist of three amino acids bonded together.

11.3
- Synthetic polymers can be formed by either condensation or addition reactions.
- Synthetic polymers formed by addition include polyethene, polypropene and polytetrafluoroethene (Teflon).
- Synthetic polymers formed by condensation include polylactic acid (PLA), polyamides such as nylon, and polyester.
- Synthetic polymers can be designed with properties to suit different purposes, such as strength, density, lack of reactivity, plasticity and biodegradability.
- The properties of synthetic polymers are related to the structure of the materials, including variables such as the chain length, the nature, size and arrangement of substituents, the degree of branching and the mix of stereoisomers, if applicable.

Review questions 11.4A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

1 The structure of amino acids is a

A central nitrogen atom with a carboxyl group and two different R groups.

B carbon chain, which can vary in length, with a carboxyl group at one end and an amino group at the other end.

C carboxyl group, an amino group and a hydrogen atom on the second carbon, and an R group, which has at least one carbon atom, as a side chain.

D carboxyl group, an amino group and a hydrogen atom on the second carbon, and a side chain, which can be another hydrogen atom or contain carbon atoms.

2 What is the empirical formula of monosaccharides?

A CHO

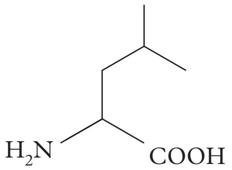
B CH_2O

C CH_3O

D CH_4O

3 Identify the structure of the amino acid tryptophan.

A



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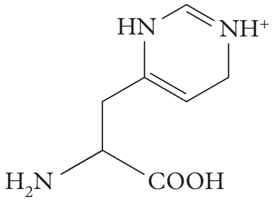
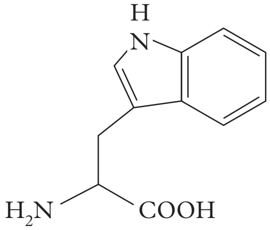
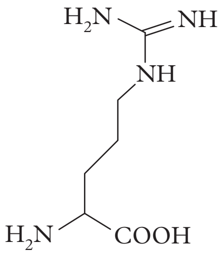


C



D



4 Amino acids bond to each other by

A ester links.

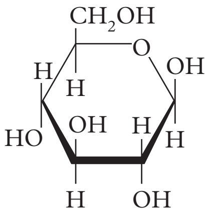
B peptide bonds.

C ionic attractions.

D hydrogen bonding.

5 Identify the chair conformation of the β-glucose molecule.

A



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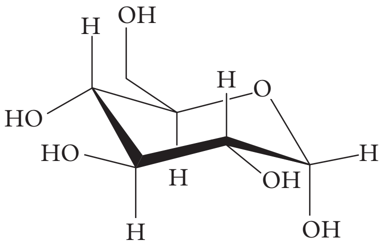

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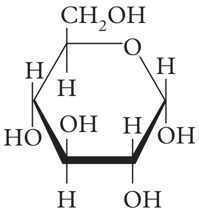

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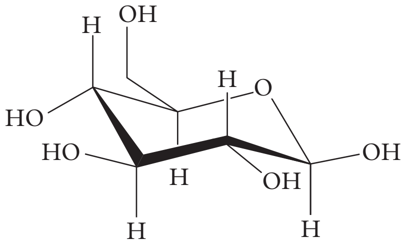


6 A zwitterion contains

A NH_2 and COO^-

B NH_2 and COOH

C NH_3^+ and COO^-

D NH_3^+ and COOH.

7 Which of the following describes the side chain (R group) of amino acids?

A It is identical for all amino acids.

B It always contains a carboxyl group.

C It does not affect the structure of tripeptides.

D It determines the amino acid's properties and classification.

8 Which of the following properties is a characteristic of polytetrafluoroethene?

A Water soluble

B High thermal conductivity

C High electrical conductivity

D Non-stick surface properties

9 What is the primary structural difference between LDPE and HDPE?

A LDPE is made from different monomers than HDPE.

B LDPE has a cyclic structure, whereas HDPE is linear.

C LDPE has a linear structure, whereas HDPE has a branched structure.

D LDPE has a highly branched structure, whereas HDPE has a more linear structure.

10 Polyamides (e.g. nylon) have which one of the following properties?

A Elasticity

B Chemical reactivity

C Electrical conductivity

D Low strength for weight

Review questions 11.4B Short response

Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

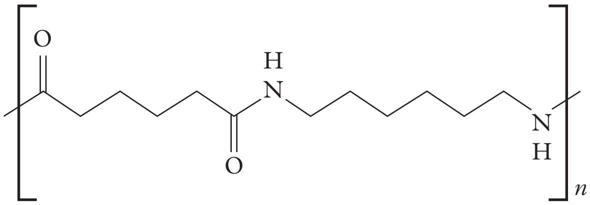
11 **Describe** the structure and bonding of a tripeptide. (2 marks)

12 **Define** the disaccharide sucrose by its molecular formula, bonding and structural features. (3 marks)

13 **Explain** how amino acids can form either a positive ion or a negative ion, depending on the pH of the surroundings. (4 marks)

14 **Describe** what is meant by crystalline and amorphous regions in a polymer. (2 marks)

15 The polyamide nylon 66 has the structure shown below. Nylon 66 is strong and abrasion resistant.



- **a** Nylon 66 takes its name from the two monomers. By considering the structural features, **explain** why it has this name. (2 marks)
- **b** **Describe** the type of bonding between the monomers that form nylon 66 and circle the bond on a diagram of the polymer. (2 marks)
- **c** **Describe** the types of intermolecular forces that will be exerted between nylon polymer molecules, with reference to the different polarities of the covalent bonds in the molecules. (3 marks)
- **d** **Explain** why nylon has high strength and abrasion resistance by considering the structure and the nature of the intermolecular forces. (4 marks)

16 Polyester is frequently made into a fine thread and combined with cotton to make clothing fabrics. It is known for being strong, durable and resistant to chemicals.

- **a** **Describe** the general structure of a polyester, including a sketch. (2 marks)
- **b** **Describe** the types of intermolecular forces that are present in polyester, based on the structure. (2 marks)
- **c** Based on the structure and intermolecular forces, **explain** why polyester has the properties listed above. (3 marks)

Analytical processes

17 Benedict's solution is a mild oxidising agent and is often used to detect the presence of glucose. **Analyse** the structure of glucose to discuss how this is possible. (2 marks)

18 **Compare** the structures and charges of the amino acids glycine and threonine at pH 6.1. (4 marks)

19 For LDPE and HDPE, **compare**

- **a** their individual molecules (2 marks)
- **b** a bulk sample of each polymer, and how the molecules are aligned in the solid, because of the different structures in part **a** (2 marks)
- **c** their properties, and relate the different properties to the structures considered in parts **a** and **b**. (4 marks)

20 Polypropene exists in three different structural forms, depending on the geometric arrangement of the methyl side groups. Copy and complete the table below to **compare** the three different forms of polypropylene. (9 marks)

Type of polypropene	Syntactic	Isotactic	Atactic
Sketch of geometric arrangement of several side groups in a section of polypropene			
Physical properties			
Explanation for physical properties			

21 The synthetic polyester used in fabrics is made from fossil fuels, whereas polylactic acid (PLA) is made from renewable biological sources. **Compare** the molecular structures and physical properties of polyesters made from fossil fuels and PLA. (4 marks)

Knowledge utilisation

22 **Determine** and **sketch** the general structure of an amino acid in the zwitterion form, clearly showing all bonds and ionic charges. (2 marks)

Data drill

Analysing polymer properties

Polymers are designed with many different properties to suit varied uses. Polyethene, both LDPE and HDPE, is among the most widely used polymers in the world. By blending LDPE and HDPE, the properties can be further modified for specific purposes.

FIGURE 1 HDPE is strong and widely used for pipes.

TABLE 1 Properties of blends of HDPE and LDPE

HDPE/LDPE blend: Sample number	HDPE/LDPE percentage by weight ratio	Density (g cm^{-3})	Average molar mass (kg mol^{-1})	Crystallinity (%)
1	100/0	0.950	Not provided	69
2	80/20	0.945	Not provided	63
3	70/30	?	610	60
4	60/40	0.940	Not provided	58
5	50/50	0.936	510	53
6	40/60	0.933	Not provided	49
7	20/80	0.928	Not provided	45
8	0/100	0.918	Not provided	41

Apply understanding

1 **Identify** the sample that is pure LDPE, not blended with HDPE. (1 mark)

2 **Identify** the percentage by weight ratio of the sample that has a density of 0.933 g cm^{-3}. (1 mark)

Analyse data

3 **Identify** the trend in crystallinity as the proportion of LDPE increases. (1 mark)

4 Density shows a similar trend to crystallinity. **Identify** the sample in which the density is somewhat lower than expected. (1 mark)

Interpret evidence

5 **Predict** the density of sample 3. **Justify** your reasoning. (2 marks)

6 **Deduce** whether the HDPE or the LDPE has a higher molar mass. **Justify** your reasoning. (2 marks)

Module 11 checklist: Organic materials: Structure and function

MODULE 12 Analytical techniques

Introduction

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 they do know the structure, they can predict how a compound may react and how to synthesise it. Several analytical techniques are available to help chemists with this task. Each technique reveals different kinds of information about the compound. Electrophoresis is one such technique and can be used for small molecules such as amino acids as well as larger molecules such as proteins.

Prior knowledge

Prior knowledge quiz

Check your understanding of concepts related to analytical techniques before you start.

Subject matter

Science understanding

→ Explain how amino acids can be separated and identified by paper/TLC chromatography, including intermolecular forces/solubility in mobile and stationary phase and retention (R_f) values.

→ Explain how amino acids can be separated and analysed by electrophoresis, including pH of buffer, isoelectric points, and movement of charged ions.

→ Analyse data, including paper/TLC chromatograms and electrophoresis to determine the identity of amino acids and retention factors.

$$\left(\text{Formula: } R_f = \frac{\text{distance moved by the amino acid}}{\text{distance moved by the solvent}}\right)$$

→ Analyse data from spectra, including mass spectroscopy and infrared to determine the identity and structure of organic molecules.

Science inquiry

→ Investigate:
  - paper/TLC chromatography to separate amino acids
  - electrophoresis to separate amino acids
  - mass spectroscopy and infrared spectra.

Source: *Chemistry 2025 v1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

Practicals

These lessons are available on Oxford Digital.

Lesson 12.2	Identifying amino acids using paper chromatography
Lesson 12.4	Identifying amino acids using electrophoresis
Lesson 12.6	Identifying organic compounds using mass spectrometry and infrared spectroscopy

Lesson 12.1
Chromatography for amino acids

Key ideas

→ Amino acids can be separated and analysed by paper chromatography and thin-layer chromatography (TLC).

→ The movement of an amino acid during chromatography depends on the relative strengths of the intermolecular forces between the amino acid and the mobile phase and the amino acid and the stationary phase.

→ Comparison of retention factors (R_f) of known and unknown amino acids allows unknown amino acids to be identified.

How are amino acids analysed using chromatography?

Recall from Unit 2 that **chromatography** is a technique that uses molecular properties (e.g. polarity and intermolecular forces) to separate the components of a mixture. This separation depends on the relative attractions of the molecules being analysed to both the **stationary phase** (the substance that stays still) and the **mobile phase** (the solvent that moves through the stationary phase) (Figure 1).

As the mobile phase or solvent moves across the stationary phase, the component molecules being analysed are continually **adsorbed** onto the stationary phase, then **desorbed** and released into the mobile phase. While in the mobile phase, they are carried along. Molecules that are more strongly attracted to the solvent (mobile phase) move further, whereas molecules that are more strongly attracted to the substrate (stationary phase) move shorter distances.

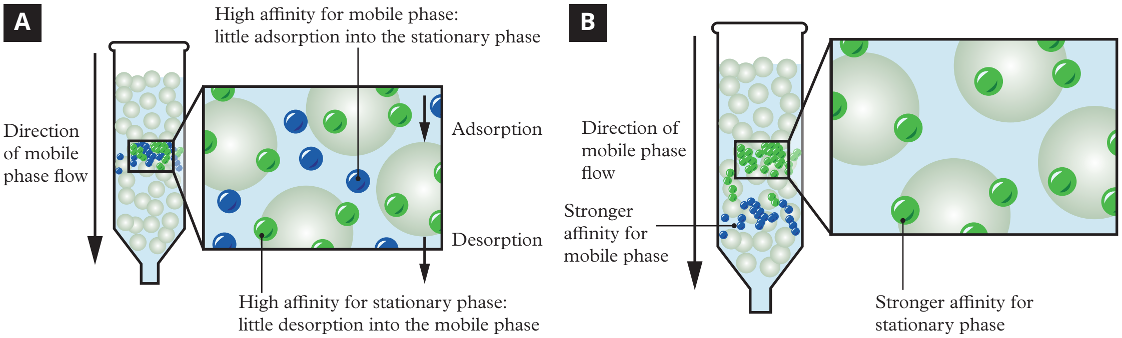


FIGURE 1 (A) The blue components have a stronger affinity for the mobile phase and the green components have a stronger affinity for the stationary phase. (B) This means the green components will travel less distance than the blue components.

Learning intentions and success criteria

chromatography
an analytical technique that depends on the different rates at which molecules are carried along with a mobile phase (solvent) across a stationary phase (chromatography medium)

stationary phase
the phase that remains fixed in place while the solvent moves through it

mobile phase
the phase that moves across the stationary phase, i.e. the solvent

adsorb
the process of the component sticking onto the solid surface of the stationary phase (not the same as absorb)

desorb
the release of the compound being analysed from the solid surface of the stationary phase

The retention factor (R_f) is the ratio of the distance travelled by the solute (component) to the distance travelled by the solute. It is calculated by using:

$$R_f = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent}}$$

In this lesson, you will look at how paper chromatography and thin-layer chromatography (TLC) can be used to separate and identify amino acids.

What is paper chromatography?

paper chromatography
a chromatography technique that uses chromatography paper as the stationary phase and a solvent (e.g. water) as the mobile phase

Paper chromatography uses chromatography paper as the stationary phase. The paper is made of cellulose, which is a natural polymer from plants and contains many saccharide units. Because of the presence of hydroxyl groups and carbon-oxygen bonds within cellulose, it is a polar molecule. Typically, some water is held within the cellulose as well. The paper is a polar stationary phase. A solvent (e.g. water, alcohol or another organic solvent or combination of solvents) is used as the mobile phase. The solvent may be polar or non-polar.

The movement of each amino acid as measured by R_f depends on the overall polarity of the amino acid and the solvent being used. This is because different amino acids experience different strengths of intermolecular attractions to both the paper and the solvent. To analyse an unknown sample of amino acids, known amino acids are used as standard in the process. Because of this, of their R_f values can be compared after separation.

For some solvents, it may not be possible to separate two amino acids and a different solvent may be required. Two-dimensional chromatography can also be used – the sample is run with one solvent in one direction, removed, dried thoroughly, and then turned 90° and allowed to proceed in another direction with a different solvent. This enables two different R_f values to be calculated, one for each direction.

Chromatography is allowed to run until the solvent front has almost reached the end of the paper, to allow for maximum distances and separation. The paper is then removed and allowed to dry. Amino acids are colourless so the paper is treated with ninhydrin, which reacts with amino acids to form coloured compounds.

To analyse an unknown mixture of amino acids by paper chromatography, the steps shown in Figure 2 are followed.

1. The paper (stationary phase) is cut to fit the container that will hold the mobile phase, and a straight line or "origin" is drawn at the bottom of the paper.
2. A drop of the sample is placed on the origin along with drops of the known amino acids (the standards A, B and C in Figure 2).
3. The mobile phase is added to the container to a level just below the origin.
4. The paper is added to the container.
5. The paper is left in the container to adsorb the mobile phase; the sample travels up the paper adsorbing and desorbing to separate the mixture.
6. The paper is removed when the solvent is close to the top of the paper (the "solvent front").
7. The paper is left to dry and then treated with ninhydrin. The separation shown is called a chromatogram.

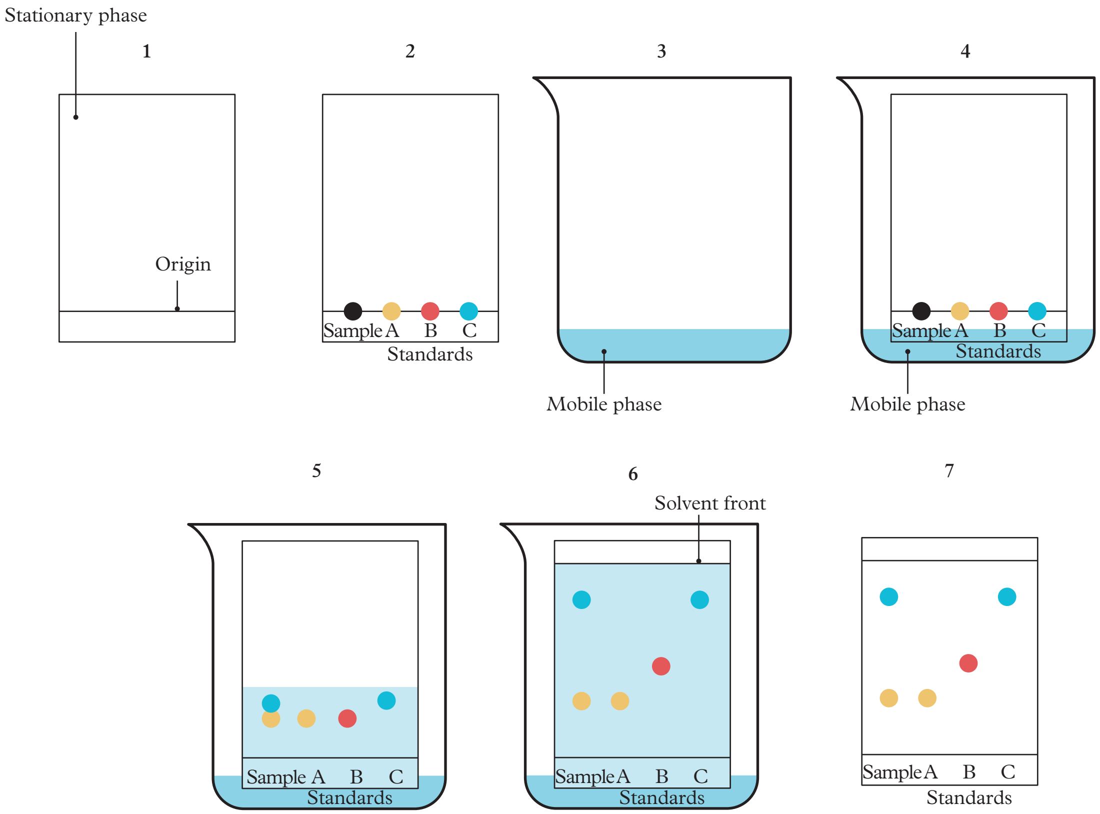


FIGURE 2 The process of separating a mixture of unknown amino acids using paper chromatography; the chromatogram shows that the mixture contained amino acids A and C but not B.

What is thin-layer chromatography (TLC)?

Thin-layer chromatography (TLC) is a chromatography technique in which the stationary phase is a thin layer of one of the following: aluminium oxide, cellulose or silica gel. The thin layer is a coating on a rigid material such as glass, plastic or aluminium. For the separation and analysis of amino acids, silica gel is a good choice as it is quite polar. An organic solvent is usually used. The amino acids will have different attractions to the silica gel stationary phase and the solvent mobile phase depending on the polarity and size of the variable R group. As a result, amino acid molecules will be adsorbed onto the silica gel stationary phase and desorbed into the solvent mobile phase. Amino acids that are more strongly attracted to the polar silica gel spend more time adsorbed onto the surface and less time moving. They will travel a shorter distance and have a smaller R_f value.

The chromatography chamber should be closed to prevent the solvent evaporating. As in paper chromatography, the solvent front should be allowed to reach almost to the end before stopping the process. Ninhydrin is used to react with the amino acids to produce a visible compound, for measurements.

thin-layer chromatography
a chromatography technique that uses a thin layer of aluminium oxide, cellulose or silica gel as the stationary phase and an organic solvent as the mobile phase

Study tip

For amino acids, O–H and N–H bonds are very polar and C–O bonds are polar. C–C and C–H bonds can be considered to be non-polar.

Paper chromatography has the advantage of having almost no preparation time, whereas TLC takes time if the plate with the stationary phase is being prepared in the laboratory. However, TLC has several advantages over paper chromatography. It generally has faster run times for the process. It provides better chromatograms because it has greater sensitivity and produces better separation of the components. This makes the results more reproducible. Both methods are relatively easy to conduct and quite inexpensive. In TLC, a fluorescent silica gel can be used that glows under a UV lamp, making spots visible on the background.

In all cases, for accurate identification, the R_f of an unknown amino acid should be compared with the R_f of known amino acids run under the same conditions. Both methods of chromatography are suited to determining if a sample is pure and contains only one amino acid, or if it contains a mixture. A mixture is likely to produce more than one spot. However, some amino acids can have almost identical R_f values for a particular solvent, so this needs to be taken into consideration. What steps could you take to overcome this problem?

Worked example 12.1A

Calculating retention factors and determining the identity of amino acids

A TLC chromatogram is shown in Figure 3. The bottom of the paper is represented by –0.1, the origin of the spots is the lower horizontal line (at 0), and the solvent front is the upper horizontal line (at 1.0).

TABLE 1 The amino acids and their associated spots in the chromatogram

Amino acid	Spot number
Glutamic acid	1
Leucine	2
Methionine	3
Serine	4
Proline	5
Unknown mixture of amino acids	6, multiple spots

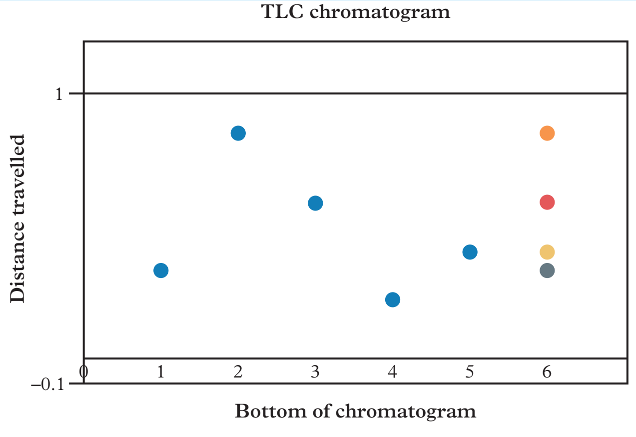


FIGURE 3 A TLC chromatogram of amino acids. The solvent is a 12:3:5 mixture of butan-1-ol, ethanoic acid and water. The colours of the spots are not significant; they are just a way to distinguish the spots.

a **Calculate** R_f for each spot in the unknown mixture of amino acids. (4 marks)

b Use the data in Table 1 to **identify** which amino acids are in the unknown mixture and which spot(s) cannot be identified. (4 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Calculate" means determine or find (e.g. a number, an answer) by using mathematical processes. We need to measure the distance travelled by the solvent, and each of the four spots present in the unknown. We need to use the rule for R_f. "Identify" means distinguish; locate, recognise and name. We need to state the name for each spot that we can ascertain, and state any spots that cannot be identified. Each question is worth 4 marks, so we must express four separate answers for each part.
Step 2: Select the appropriate formulas and gather the required data.	For each spot, use the rule: $R_f = \frac{\text{distance moved by amino acid}}{\text{distance moved by solvent}}$
Step 3: Answers only for part **a** are shown. Allow for measurement uncertainty in your answers.	**a** The four amino acid spots in the unknown mixture have retention factors of: 0.27 (1 mark) 0.40 (1 mark) 0.50 (1 mark) 0.71 (1 mark)
Step 4: Finalise your answer to part **b** by identifying the amino acid that produced each spot and stating any molecule that could not be identified.	**b** The mixture consists of: 0.27 is glutamic acid (1 mark) 0.40 cannot be identified (1 mark) 0.50 is methionine (1 mark) 0.71 is leucine (1 mark)

Your turn

A TLC chromatogram is shown in Figure 4. The bottom of the paper is represented by −0.1, the origin of the spots is the lower horizontal line (at 0) and the solvent front is the upper horizontal line (at 1.0).

TABLE 2 The amino acids and their associated spots in the chromatogram

Amino acid	Spot number
Glutamic acid	1
Leucine	2
Alanine	3
Cysteine	4
Asparagine	5
Unknown mixture of amino acids	6, multiple spots

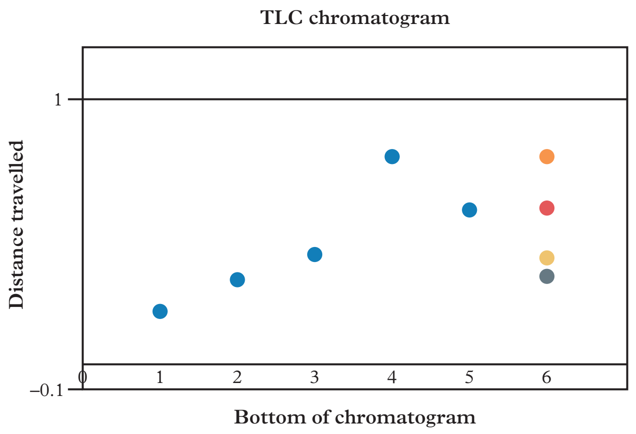


FIGURE 4 A TLC chromatogram of amino acids. The solvent is water-saturated phenol.

a **Calculate** R_f for each spot in the unknown mixture of amino acids. (4 marks)

b Use the data in Table 2 to **identify** which amino acids are present in the unknown mixture and which spot(s) cannot be identified. (4 marks)

Check your learning 12.1

Check your learning 12.1: Complete these questions online or in your workbook.

Retrieval and comprehension

1 All amino acids contain a polar amino group and a polar carboxyl group. However, their side chains may be polar or non-polar and vary in size. Use the structures shown in the QCAA *Formula and data book* to **identify** whether the side chains are polar or non-polar for each of the following amino acids.

  a Arginine (1 mark)
  b Isoleucine (1 mark)
  c Phenylalanine (1 mark)
  d Threonine (1 mark)

2 **Explain** how chromatography can separate a mixture of amino acids. (3 marks)

Analytical processes

3 **Compare** paper chromatography and thin-layer chromatography. (2 marks)

4 Aspartic acid and glutamic acid are both acidic amino acids. **Compare** the structures of these amino acids from the QCAA *Formula and data book* to **determine**

  a why they are described as acidic amino acids (1 mark)
  b which would be more polar. Provide reasons. (2 marks)

5 Butan-1-ol is mixed with pyridine to form a solvent that is less polar than silica gel. This solvent is used to separate arginine, isoleucine, phenylalanine and threonine by silica gel TLC. The R_f values are 0.63, 0.56, 0.36 and 0.15. By considering the relative polarity of the side chains, **infer** which amino acid is associated with which R_f value. Provide reasons for your decisions and indicate if there is any uncertainty. (5 marks)

Practical

Lesson 12.2

Identifying amino acids using paper chromatography

Learning intentions and success criteria

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Lesson 12.3

Electrophoresis for amino acids

Key ideas

→ Electrophoresis is a technique that can separate amino acids by mass and the size and sign of their charge.

→ In electrophoresis, the ionic forms of amino acids move through a gel towards the electrode of opposite charge.

→ Amino acids can be positively charged, negatively charged or uncharged (zwitterions) depending on the pH of the electrophoresis gel and the isoelectric point of each amino acid.

→ Amino acids with smaller masses move more rapidly than amino acids with larger masses, so the distance moved is inversely proportional to the mass.

→ Some amino acids form ions with a 2+ or 2– charge and move faster than similar-sized amino acids with a single charge.

How can amino acids be analysed using electrophoresis?

Electrophoresis is a technique that can be used to analyse and identify amino acids and other biological molecules. The electrophoresis tank, shown in Figure 1, contains a gel buffered at a known pH and has electrodes at either end with a high voltage difference. In the electrical circuit, the cathode is negatively charged and the anode is positively charged. Polyacrylamide gel is most commonly used to separate amino acids. This solid is mixed with the gel-buffering solution and set. The gel thus consists of the solid polymer matrix and the pH-buffered solution. Charged particles such as amino acids can move slowly through the pores in the solid component of the gel towards the oppositely charged electrode. Similarly to chromatography, to identify the unknown samples, they are compared with known amino acids separated under the same conditions.

Learning intentions and success criteria

electrophoresis
a separation technique that involves the movement of charged particles, such as amino acids, along an electric field

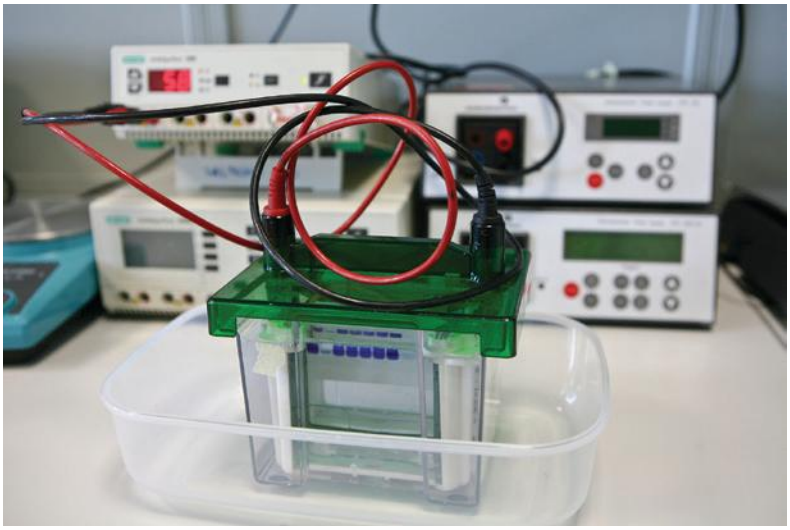


FIGURE 1 A gel electrophoresis tank. An electrical field is applied across a gel to separate charged biomolecules such as amino acids.

The known standards and the samples are placed in wells in the gel. For amino acids, the wells are in the middle of the tank, halfway between the electrodes. This is because amino acids can be in the form of positive ions or negative ions, depending on the pH.

Recall from Module 11 that amino acids have both acidic and basic properties. At the isoelectric point, the amino acid is in the form of a zwitterion. Although the zwitterion has a positive charge and a negative charge, overall it is neutral. At pH values lower than the isoelectric point, the amino acid accepts a proton and gains a positive charge. At pH values higher than the isoelectric point, the amino acid donates a proton and gains a negative charge.

An electrophoresis comb is used to make a series of wells, one for each sample, in the gel. Each amino acid sample is mixed in an ethanol/glycerol solvent. The glycerol increases the density of the solution. This ensures that the amino acid sample sinks to the bottom of the well, rather than “floating” out into the buffer solution. Future movement is thus restricted to movement between the pores of the gel rather than across the surface. Once the electrophoresis process has been finished, the plate is sprayed with ninhydrin. As in the chromatography technique, the ninhydrin enables the amino acids to be visible.

Once the samples are loaded into the wells, and the current is switched on, positively charged amino acids move towards the negatively charged cathode, and negatively charged amino acids move towards the positively charged anode. Any amino acids present as zwitterions will not move. The direction in which each sample amino acid migrates depends on the pH of the gel and the isoelectric points of the amino acids.

The gel is a solid acrylamide/bisacrylamide cross-linked polymer mixed in a solution and the technique is often referred to as polyacrylamide gel electrophoresis (PAGE). When set, the solid polymer forms a matrix with tiny pores that the amino acids can move through. Smaller, less massive amino acids more easily find a path through the pores and so move more quickly than larger, heavier amino acids. The distance that each sample amino acid moves is related to the molar mass of the amino acid.

The rate of movement is also affected by the electrical charge of the amino acid. Most amino acids have a 1+ or a 1– charge. This means the electrical force on them will be the same in size but can differ in direction. However, a few amino acids have additional acidic or basic groups on their side chain or R group. If the buffer pH is significantly different from the isoelectric point, these amino acids form ions with a 2+ or a 2– charge, doubling the attraction to the oppositely charged electrode. This greatly increases the rate at which these amino acids move. In this case, charge as well as mass needs to be considered.

Study tip

When analysing electrophoresis data, always check the pH, in order to assign charges to the amino acids being studied, and accordingly determine the direction of migration. Use the QCAA *Formula and data book* rather than another source of isoelectric points.

To find the rate of migration:

$$\text{Rate of migration} = \frac{\text{distance component migrated}}{\text{time of electrophoresis}}$$

Amino acids are colourless. Typically, a stain such as ninhydrin is added to the loading buffer to colour the amino acid bands so that distance and direction can be measured. Alternatively, UV light can be used to detect the final position of the amino acid.

Worked example 12.3A

Analysing electrophoresis data to determine the identity of amino acids

The four amino acids listed in Table 1 undergo electrophoresis in a gel that is buffered at pH 6.0. The results are shown in Figure 2. (Simplifying assumption to use: Amino acids at the isoelectric point are overall electrically neutral zwitterions, whereas amino acids at a pH above their isoelectric point are negatively charged and amino acids at a pH below their isoelectric point are positively charged.)

TABLE 1 Amino acids and their pH at isoelectric point

Amino acid	pH at isoelectric point
Asparagine	5.4
Leucine	6.0
Proline	6.3
Glutamine	5.7

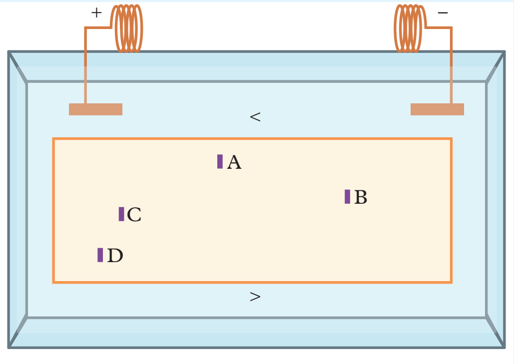


FIGURE 2 The positions of the amino acids at the end of the electrophoresis run

a **Determine** the charge of each amino acid at pH 6.0. (4 marks)

b **Identify** the position of each amino acid at the end of the electrophoresis run. Use the letters A to D from the Figure 1. **Explain** your reasoning. (8 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Determine" means establish, conclude or ascertain after consideration, observation, investigation or calculation. We need to consider each amino acid and whether it will have accepted a proton, donated a proton or neither, at pH 6.0, to determine its charge. "Identify" means distinguish; locate, recognise and name. We must look at the location of each amino acid (A to D) in Figure 1, and name the amino acid associated with it. "Explain" means make an idea or situation plain or clear by describing it in more detail or revealing relevant facts. We must use relevant facts about the charge and size of each amino acid and link this to the distance moved and direction of movement. The questions are worth 4 marks and 8 marks, so we must express the relevant answers and explanations.
Step 2: Select the appropriate formulas and gather the required data.	Recall that at the pH of the isoelectric point, amino acids are uncharged (zwitterion form). At pH values below their isoelectric point, amino acids accept H^+ and form a 1+ ion. At pH values above their isoelectric point, amino acids donate H^+ and form a 1– ion.
Step 3: List the four amino acids and their charges at a pH of 6.0	**a** Asparagine, 1– (1 mark) Leucine, uncharged (1 mark) Proline, 1+ (1 mark) Glutamine, 1– (1 mark)
Step 4: Consider the direction of movement due to charge, and the rate of movement, due to molecular size.	**b** Leucine will not have moved, which can be explained by it being uncharged. (1 mark) Proline will have moved towards the negative electrode on the right, due to it having a 1+ charge. It is the smallest and will have moved the furthest. (1 mark) Asparagine and glutamine will have moved towards the positive electrode on the left, due to having a 1– charge. Glutamine is larger than asparagine and has an isoelectric point closer to the pH of the buffer so it will not have moved as far as asparagine. (2 marks)
Step 5: Finalise your answer by rounding the numbers to an appropriate number of significant figures and include the units.	A = leucine (1 mark) B = proline (1 mark) C = glutamine (1 mark) D = asparagine (1 mark)

Your turn

The four amino acids listed in Table 2 undergo electrophoresis in a gel that is buffered at pH 5.4. The results are shown in Figure 3.

TABLE 2 Amino acids and their pH at isoelectric point

Amino acid	pH at isoelectric point
Alanine	6.1
Asparagine	5.4
Cysteine	5.1
Methionine	5.7

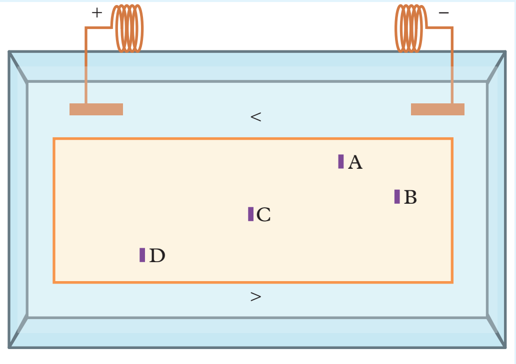


FIGURE 3 The positions of the amino acids at the end of the electrophoresis run

a **Determine** the charge of each amino acid at pH 5.4. (4 marks)

b **Identify** the position of each amino acid at the end of the electrophoresis run. Use the letters A to D from the Figure 3. **Explain** your reasoning. (8 marks)

Real-world chemistry

A Nobel Prize from studying pond scum!

As a child, Carol Greider battled dyslexia. Her struggles led to her developing unique ways of learning and thinking, which paid off throughout her career as a researcher. Her next struggle was to be accepted into postgraduate studies. Eventually, she was accepted into the University of California, Berkeley, and researched under the supervision of Elizabeth Blackburn. Elizabeth had described telomeres, pieces of DNA at the end of chromosomes that protect the chromosomes from being shortened during cell division. Carol set out to discover what protected telomeres themselves from being shortened.

Carol chose to study extracts from *Tetrahymena*, single-celled organisms in pond scum that have huge numbers of telomeres. She hypothesised that there was an enzyme that would re-lengthen any shortened telomeres. She subjected her cell extracts to many different experimental conditions to discover if telomeres could be lengthened. To obtain the necessary data from these experiments, she used gel electrophoresis, which separates molecules by size.

On Christmas Day 1984, Carol discovered that telomere lengthening was caused by an enzyme, which she named telomerase. Telomere shortening is implicated in cell ageing and cancers, so her discovery had far-reaching implications. In 2009, she shared the Nobel Prize in Physiology or Medicine for this discovery.

Apply your understanding

1 **Explain** how gel electrophoresis would have enabled Carol Greider to determine the size of telomeres and if any had been lengthened after subjecting them to various experimental treatments. (2 marks)

2 In the course of her work, Carol discovered that extracts in which the telomeres had been lengthened did not produce a single well-defined spot after electrophoresis. Rather, they produced a smeared blob. **Deduce** what this meant about the length of the telomeres in those extracts. **Explain** reasoning. (3 marks)

FIGURE 4 Carol Greider (left) and Elizabeth Blackburn (right) at a news conference in Stockholm after sharing the Nobel Prize with Jack Szostak.

Challenge

Alanine vs aspartic acid

The amino acid alanine can exist in three different forms; namely, neutral or with +1 or 1– charge. The amino acid aspartic acid can exist in four different forms. By considering the structure of the side chain of aspartic acid, **determine** the charges of these four forms, and **explain** how aspartic acid differs from alanine. (3 marks)

Check your learning 12.3

Check your learning 12.3: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain** the role of the electrodes during electrophoresis. (1 mark)

2 When conducting electrophoresis of many biological molecules, the samples are placed at one end of the gel strip. However, for amino acids, the samples are placed halfway along the gel strip midway between the two electrodes. **Explain** the reason for placing amino acid samples in this position. (1 mark)

Analytical processes

3 At pH 6.3, **determine** the
  - **a** electrical charge of isoleucine (1 mark)
  - **b** electrode isoleucine would move towards during electrophoresis. (1 mark)

4 Many amino acids form only three charged species (1+, 0 and 1–). However, arginine and cysteine are two amino acids that can form four charged species. **Compare** the structures of the side chains of both these amino acids to
  - **a** **identify** groups that can donate or accept protons (2 marks)
  - **b** **determine** the charges of the ions that arginine and cysteine can form. (2 marks)

Practical

Lesson 12.4

Identifying amino acids using electrophoresis

oxforddigital **This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.**

Learning intentions and success criteria

Lesson 12.5

Mass spectrometry and infrared spectroscopy

Key ideas

- → Mass spectrometry is a technique used to determine the molar mass of organic molecules and give information about their composition.
- → 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 ratios (*m*/*z*).
- → Isotopic masses of the elements in an organic compound allow for the analysis of the *m*/*z* ratios in a mass spectrum to determine molar mass and the masses of major fragments.
- → In infrared spectroscopy, bonds in molecules absorb infrared radiation corresponding to the energy of vibrations. Different bonds in an organic compound absorb different frequencies of infrared radiation to produce characteristic peaks on the spectrum that allow functional groups to be identified.
- → A combination of analytical techniques is frequently used to analyse compounds. The mass spectrum and the infrared spectrum of a single compound together provide more evidence to determine the identity of a compound than either technique on its own.

Learning intentions and success criteria

mass spectrometry a technique used to determine the molecular mass of a compound

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

How is mass spectrometry used to analyse molecules?

You may recall from Unit 1 that **mass spectrometry** is used to determine the masses and abundances of the isotopes of elements. Mass spectrometry can also be used for whole molecules. This analytical technique 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 only requires very small amounts of a sample, which can be solid, liquid or gas. The sample is introduced into the mass spectrometer (Figure 1), where it is vapourised by heating or other techniques. There are many types of mass spectrometers, but all rely on creating charged particles. When the whole molecule becomes charged, it is called a **molecular ion**. Because of the large amount of energy transferred to the molecular ion, it can break apart into smaller fragments. These fragments also produce distinct peaks in the mass spectrum. The molecular ion and the ionised molecular fragments each produce distinct lines on the mass spectrum, corresponding to the mass/charge or *m*/*z* ratio.

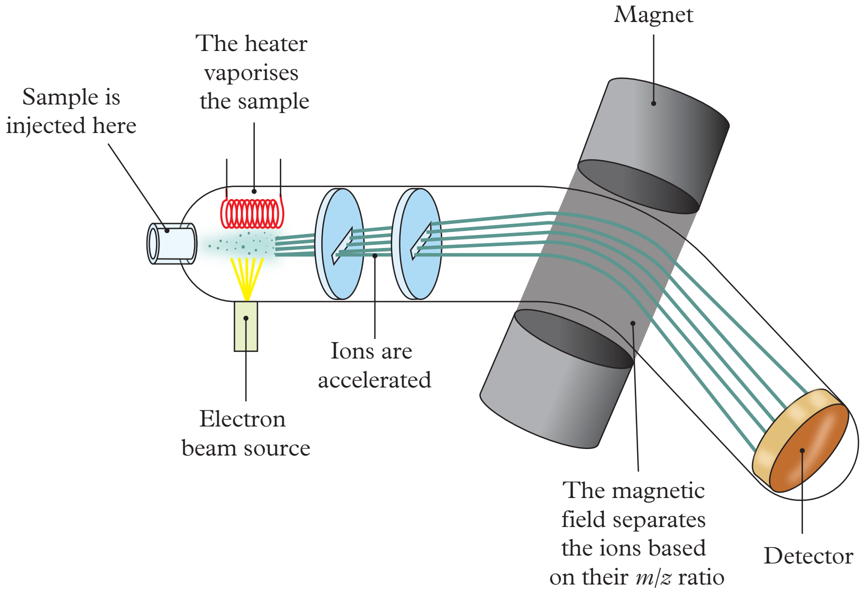


FIGURE 1 A mass spectrometer

The molecular ion is the heaviest ion produced with the largest m/z ratio and its mass represents the mass of the molecule being analysed. Because nearly all ions will have a charge of 1+, $z = 1$, the mass of each ion can easily be seen from the m/z value. The masses of the fragments provide additional information about how the molecule has broken up, which can help determine the composition.

Study tip

Remember, spectra is plural for spectrum.

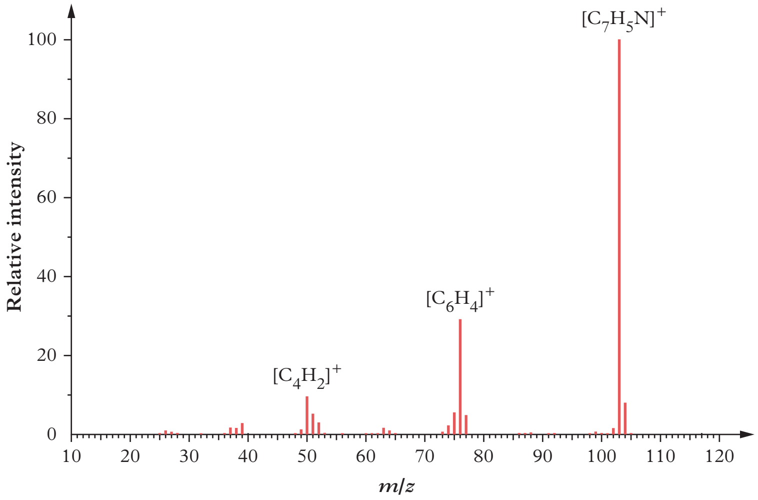


FIGURE 2 The mass spectrum of benzonitrile (C_7H_5N). The molecular ion is at m/z 103 and smaller fragment ions appear at around m/z 76, 50 and 39.

How can we interpret 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. There are a few guidelines to assist in analysis.

The "rule of 13" and base value

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

base value in mass spectrometry, the hydrocarbon molecular formula (C_xH_y) that matches the mass of a molecular ion the molecule would have if 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.

"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 3 and 5 in the worked examples include small peaks 1 m/z unit above the molecular ion peak. 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 summarises the natural abundance of selected isotopes found in organic compounds.

TABLE 1 The natural abundance of the main elements with isotopes and the patterns 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 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.

The peak at 89 in Figure 5 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. Due to the relatively small percentage of carbon-13, and other factors, the "rule of 13" together with the methods shown when other elements are present, is more useful to find the number of C atoms.

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

$$\text{Number of C atoms} = \frac{100}{1.1} \times \frac{\text{abundance M+1 ion}}{\text{abundance M}^{+}\text{ ion}}$$

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. Thus, 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. This use of M+12 and M+2 peaks is much more useful for compounds containing chlorine or other elements with a reasonably sized proportion of each isotope.

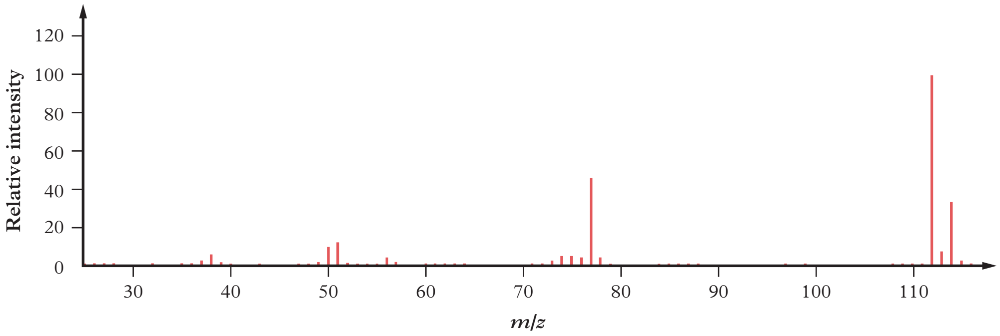


FIGURE 3 The mass spectrum of chlorobenzene (C_6H_5Cl)

Figure 7 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.

Study tip

Recall the most common isotopic masses of the isotopes of elements that occur in organic molecules.

Worked example 12.5A

Analysing the mass spectrum of a hydrocarbon

Analyse the mass spectrum in Figure 3 to **identify** the linear (straight chain) hydrocarbon. (3 marks)

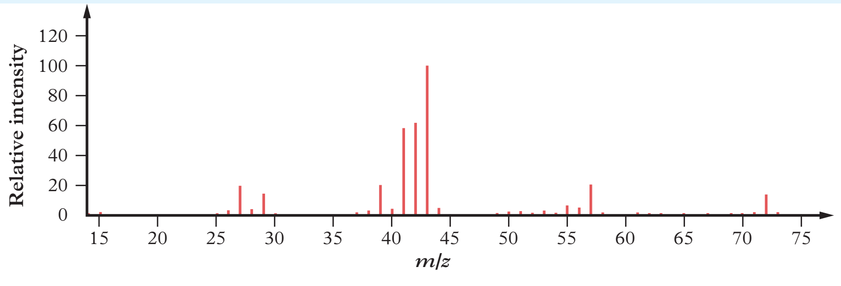


FIGURE 4 The mass spectrum of a hydrocarbon with a molecular ion of *m*/*z* 72

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the question is asking you to do.	“Analyse” means 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. “Identify” means locate, recognise and name. We need to examine the mass spectrum and interpret the relevant information and what it means for the composition and molecular mass of the compound. We need to name the compound. The question is worth 3 marks, so we must express the steps clearly and the correct name.
Step 2: Gather the required data, in this case *m*/*z* of the molecular ion.	The molecular ion is at *m*/*z* = 72
Step 3: Find the base value by dividing the m/z value of the molecular ion by 13.	$\frac{72}{13}$ = 5 remainder 7 The molecule contains a maximum of five carbon atoms. (1 mark)
Step 4: To work out the number of hydrogen atoms, add the remainder to the number of carbon atoms.	5 + 7 = 12, which means there are 12 hydrogen atoms. (1 mark)

Think	Do
Step 5: Finalise your answer by writing a formula, checking that the molar mass = *m*/*z* of the molecular ion, and naming the compound.	The compound has a base value of C_5H_{12}. Mass $C_5H_{12} = 5 \times 12 + 12 \times 1 = 72$ amu The linear hydrocarbon with five carbon atoms and 12 hydrogen atoms is pentane. (1 mark)

Your turn

Analyse the mass spectrum in Figure 4 to **identify** the linear (straight chain) hydrocarbon. (3 marks)

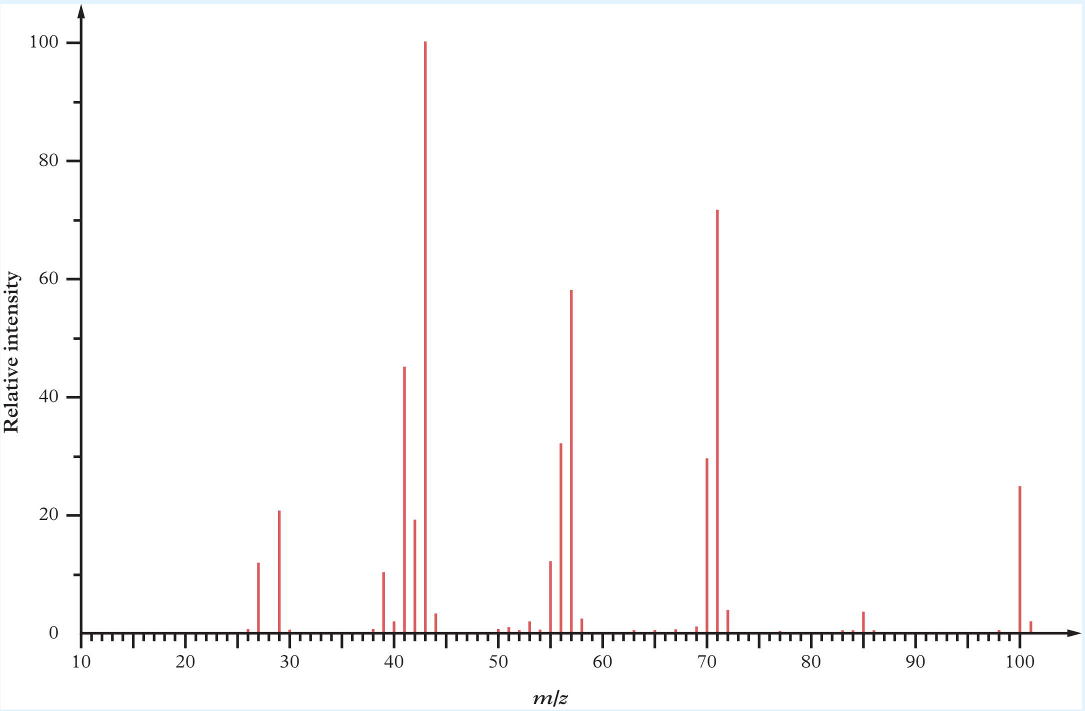


FIGURE 5 The mass spectrum of a hydrocarbon with a molecular ion of *m*/*z* 100

Worked example 12.5B

Analysing a mass spectrum to identify an organic compound containing oxygen

Analyse the mass spectrum of the ester shown in Figure 5 to

a **deduce** possible structures of the molecule (3 marks)

b **identify** and name it. (2 marks)

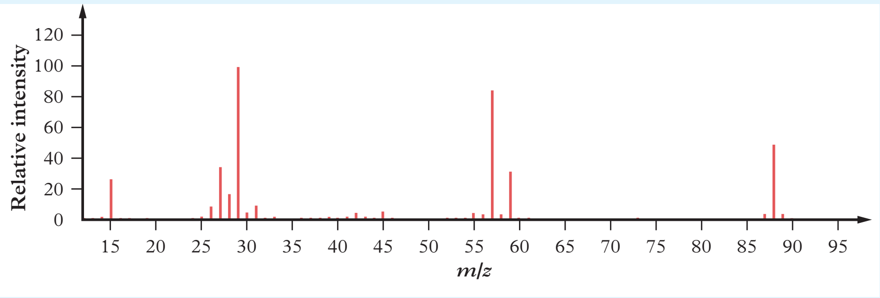
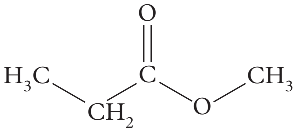
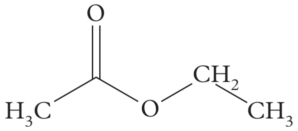
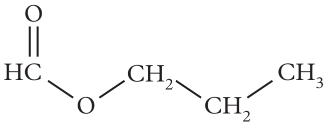


FIGURE 6 The mass spectrum of an unknown ester

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Analyse" means examine or consider something to explain and interpret it, for the purpose of finding meaning or relationships and identifying patterns, similarities and differences. "Deduce" means to draw a logical conclusion from reasoning and the information given. "Identify" means locate, recognise and name. We need to examine the mass spectrum and interpret the relevant information and what it means for the composition and molecular mass of the compound and list structures of possible esters. We need to identify one possible structure for the ester. The question is worth 5 marks, so we must express the steps clearly and draw a possible structural formula.
Step 2: Gather the required data, in this case *m*/*z* of the molecular ion.	**a** The molecular ion is at *m*/*z* 88.
Step 3: Find the base value by dividing the *m*/*z* value of the molecular ion by 13.	$\frac{88}{13} = 6$ remainder 10 The molecule contains a maximum of 6 carbon atoms. (1 mark)
Step 4: To work out the maximum number of hydrogen atoms, add the remainder to the number of carbon atoms.	$6 + 10 = 16$ The maximum number of hydrogen atoms is 16. (1 mark)
Step 5: Determine the molecular formula. Given that this is an ester, it must contain at least two oxygens. The base value will need to be adjusted to allow for two oxygens. Each oxygen atom has an amu of 16, which is equal to the mass of 1 carbon atom (12 amu) plus 4 hydrogen atoms (4 × 1 amu). So to add 2 oxygens, you need to subtract 2 carbon atoms and 8 hydrogens.	Molecular formula is: $C_{(6-2)}H_{(16-8)}O_2$, which gives $C_4H_8O_2$ (1 mark) (Check that it is correct. $4 \times 12 + 8 \times 1 + 16 = 72$, which is correct.)
Step 6: Propose some possible structures and then look at the fragmentation pattern to help determine which is more likely. Show reasoning. (This could be done in a diagram form, showing masses of possible fragments.)	**b** There are three esters that have this molecular formula and have a molar mass of 88 g mol^{-1}.  **Methyl propanoate**  **Ethyl ethanoate**  **Propyl methanoate** (3 marks)
Step 7: Analyse the fragmentation pattern by considering which structural formula could produce fragments with the *m*/*z* ratios shown in the spectrum.	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). (1 mark for reasoning)
Step 8: Propose a structure that matches the information about molecular mass as well as the composition based on possible fragments.	The mass spectrum is that of methyl propanoate.

Your turn

Analyse the mass spectrum shown in Figure 6 to

a **deduce** possible structures of the molecule (4 marks)

b **identify** and name it. (2 marks)

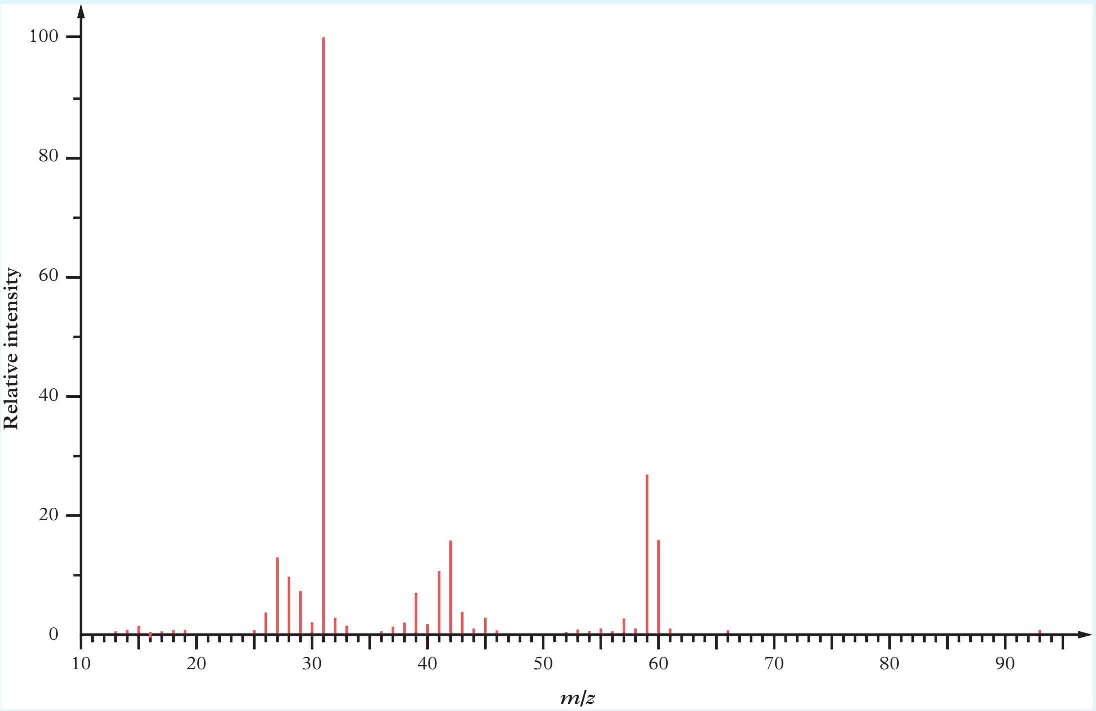


FIGURE 7 The mass spectrum of a molecule containing oxygen

What is infrared spectroscopy?

infrared radiation electromagnetic radiation in the region between visible light and microwave radiation

wavenumber the reciprocal of wavelength (where wavelength is measured in centimetres)

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

Infrared radiation is the part of the electromagnetic spectrum between the visible and microwave regions. It is often measured in **wavenumbers** ($\tilde{v}$) (the reciprocal of wavelength, λ) in units of reciprocal centimetres (cm^{-1}):

$$\tilde{v}\ (cm^{-1}) = \frac{1}{\lambda (cm)}$$

In 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 (2.998×10^{8} m s^{-1}), and:

$$E = hv = \frac{hc}{\lambda}$$

where E is energy (J) and h is Planck's constant (6.626×10^{-34} 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**.

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 4,000 to 1,400 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 1,400 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 1,780–1,650 cm^{-1}, which is in the infrared region of the electromagnetic spectrum (Figure 8). Stretching vibrations are the most useful for working out the functional groups in a compound.

Many types of peaks, or absorption bands can appear on an IR spectrum. They can be described as strong, medium or weak in relation to the depth of the band. Absorption bands are also described as broad or narrow in relation to the width of the band. Figure 8 shows the different types of peaks. Figure 9 shows the stretching and the bending peaks for carbon dioxide and why the stretching peak is more useful.

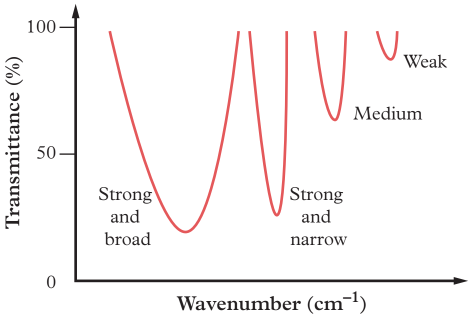


FIGURE 8 Different types of peaks that appear on an IR spectrum

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

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.

Study tip

The QCAA *Formula and data book* shows other characteristic infrared regions with different bond types.

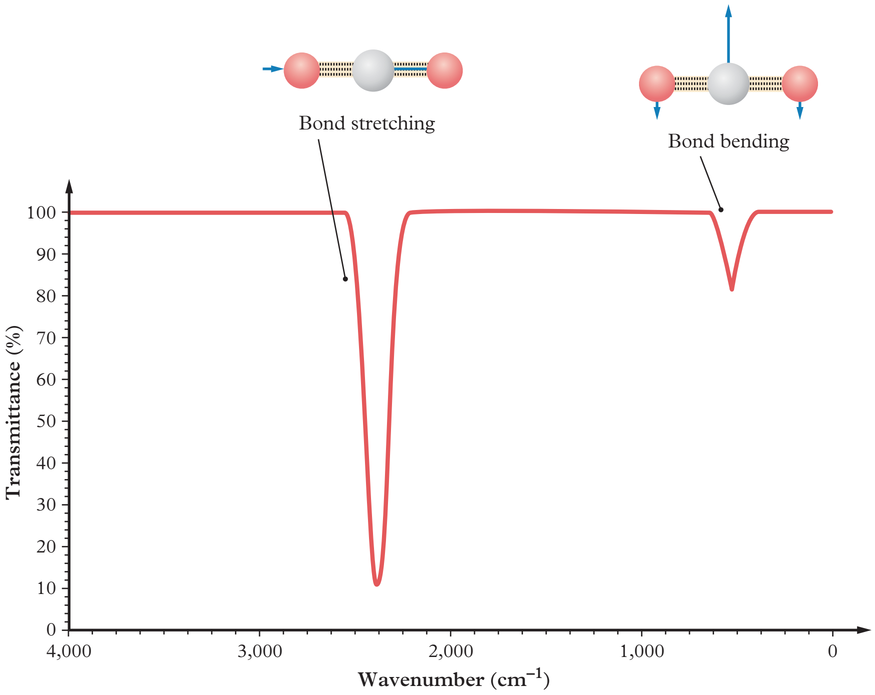


FIGURE 9 Vibrations of carbon dioxide and the accompanying infrared absorptions

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.

TABLE 2 Characteristic infrared regions for different stretching vibrations

Bond	Organic molecules	Wavenumber (cm^{-1})
C–I	Iodoalkanes	490–620
C–Br	Bromoalkanes	500–600
C–Cl	Chloroalkanes	600–800
C–F	Fluoroalkanes	1,000–1,400
C–O	Alcohol, ester	1,050–1,410
C=C	Alkenes	1,620–1,680
C=O	Aldehydes, carboxylic acids, ester, ketones	1,700–1,750
C≡C	Alkynes	2,100–2,260
O–H	Carboxylic acids (hydrogen bonded)	2,500–3,000
C–H	Alkanes, alkenes, alkynes, aldehydes, amides	2,720–3,100
O–H	Alcohol (hydrogen bonded)	3,200–3,600
N–H	Amines	3,300–3,500

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 10). More strongly absorbing bands will have lower transmittance (%) values.

The relationship between transmittance and absorbance is:

$$\text{Absorbance} = 2 - \log_{10}(\text{transmittance (\%)})$$

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 11 and 12 show the infrared spectra of propanone (which contains a C=O group) and 2-methylprop-1-ene (which contains a C=C group). You can see that the band due to the C=C bond (about 1,650 cm^{-1}) is much smaller than the band due to the C=O bond (1,750 cm^{-1}).

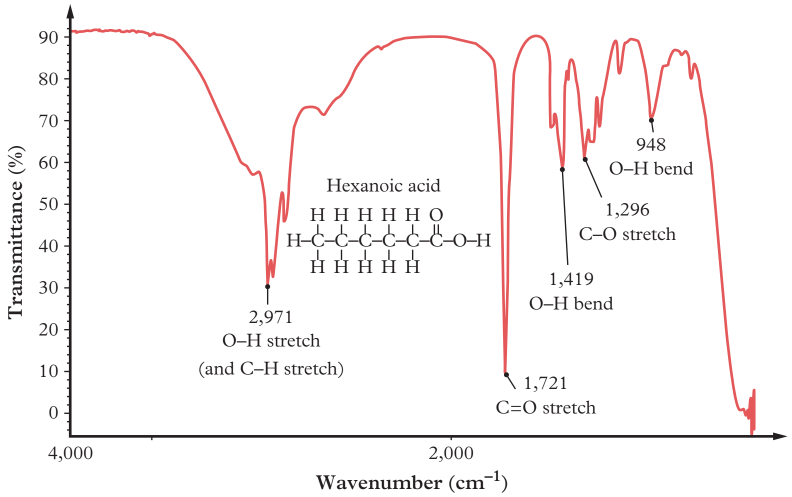


FIGURE 10 The infrared spectrum of hexanoic acid

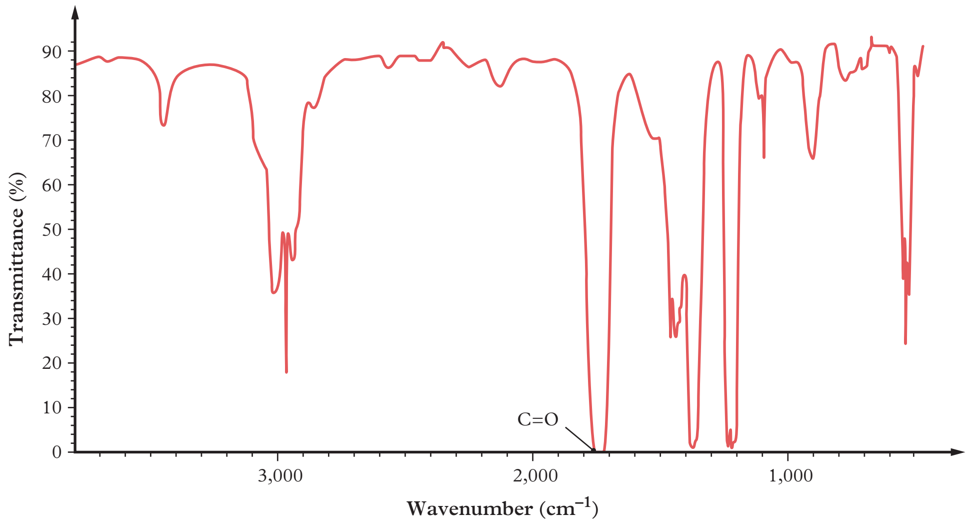


FIGURE 11 The infrared spectrum of propanone (acetone) ($(CH_3)_2C{=}O$)

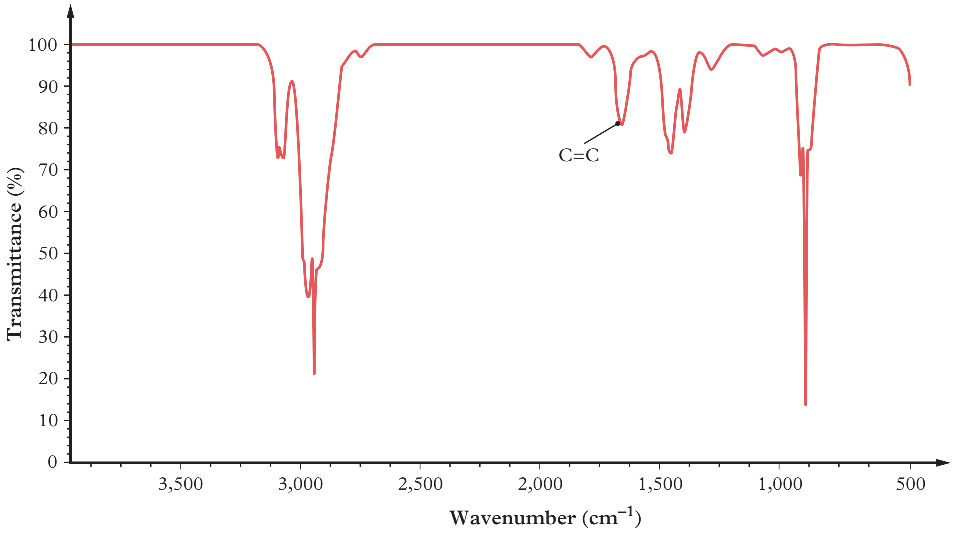


FIGURE 12 The infrared spectrum of 2-methylprop-1-ene ($H_2C{=}C(CH_3)_2$)

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 usually show the expected intensity of peaks as strong (s), medium (m) or weak (w). The strongest peaks have the lowest percentage transmittance values.

How can we interpret 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 4,000–1,300 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 1,870–1,540 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 3,700–3,580 cm^{-1}, as a narrow peak.

Hydrogen bonding shifts this to 3,550–3,200 cm^{-1} and broadens the peak considerably. You can see this in the infrared spectrum of ethanol in Figure 12. O–H bending vibrations occur in the region 1,420–1,330 cm^{-1}. Figure 13 shows the infrared spectrum of liquid ethanol with an O–H stretching vibration around 3,360 cm^{-1}.

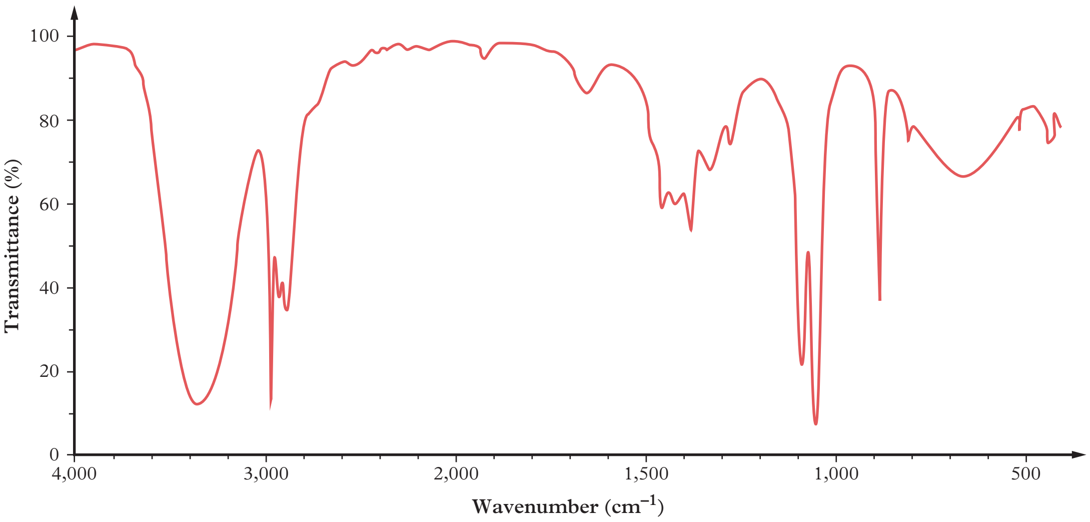


FIGURE 13 The infrared spectrum of liquid ethanol

There is a characteristic broad O–H stretching vibration around 3,360 cm^{-1}. The C–O stretch is also strongly absorbing at 1,050 cm^{-1}. The C–H stretching vibrations are at a slightly lower wavenumber than the O–H stretching vibration for alcohols.

For carboxylic acids when hydrogen bonded, the O–H stretch is also broad and strong. It appears at a lower wavenumber than the O–H stretch in alcohols and partly overlaps the C–H stretching vibration, as shown in Figure 14. This produces several sharp peaks superimposed on the right-hand side of the broad O–H band.

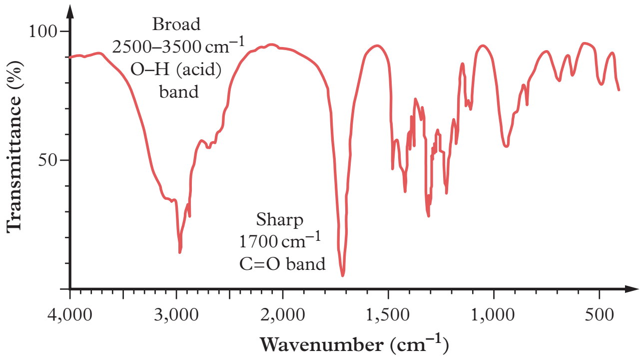


FIGURE 14 An infrared spectrum of a carboxylic acid

NH groups

N–H stretching vibrations are also affected by hydrogen bonding, which shifts their peaks to lower wavenumbers. Aliphatic primary amines give bands at 3,400–3,300 and 3,330–3,250 cm^{-1}. Aromatic primary amines give bands at slightly higher wavenumbers. N–H bending vibrations occur at 1,650–1,580 cm^{-1} as a medium-to-strong-intensity band.

Along with the N–H stretch, amines also exhibit a C–N stretch. The infrared stretch for a C–N bond depends on the type of amine, with aromatic amines appearing at 1,200–1,350 cm^{-1} and aliphatic amines appearing at 1,000–1,250 cm^{-1}. Primary amines show an $-NH_2$ scissoring bend at 1,550–1,650 cm^{-1}. Neither of these are listed in the QCAA *Formula and data book* but can be useful.

Figure 15 shows the infrared spectrum of an amine. You can see that the bands for N–H stretching at 3,370 and 3,290 cm^{-1} are much less intense and narrower than the O–H stretch in Figures 12 and 13.

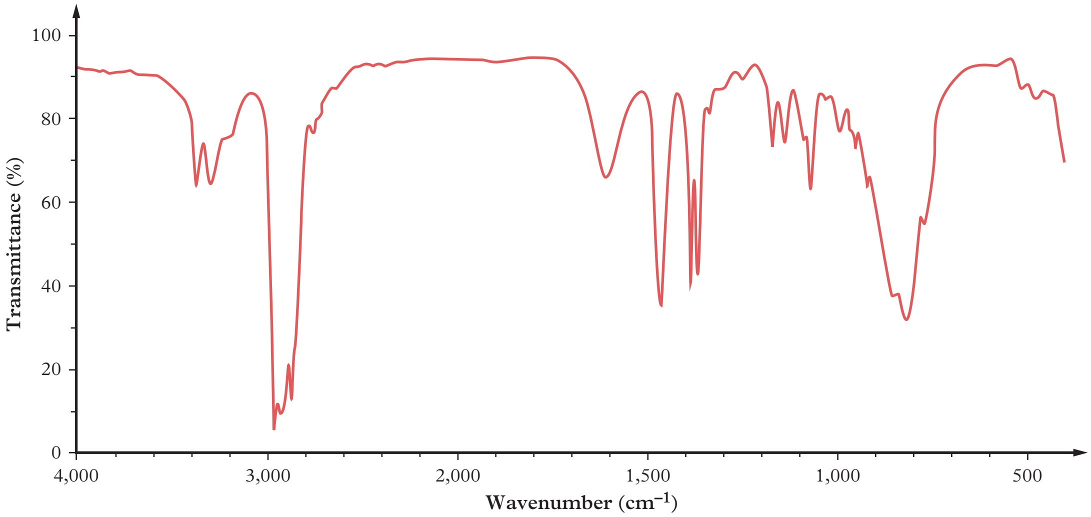


FIGURE 15 The infrared spectrum of an amine. The N–H stretches show as a doublet at 3,370 and 3,290 cm^{-1}. The NH_2 absorption gives the peak around 1,600 cm^{-1}

How do we interpret 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 but narrow stretching band at 1,870–1,540 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 in aldehydes, ketones, carboxylic acids, esters, amides and other carboxylic acid derivatives. Table 3 outlines some indicators that will help you distinguish these different carbonyl-containing groups.

TABLE 3 Distinguishing carbonyl (C=O) groups

Functional group	Carbonyl stretching vibration	Other notable bands
Aldehyde	1,740–1,720 cm^{-1} aliphatic aldehydes	2,830–2,695 cm^{-1} C–H stretch, two moderately intense bands
Ketone	About 1,715 cm^{-1} saturated ketone 1,685–1,665 cm^{-1} neighbouring phenyl group (conjugation)	1,300–1,100 cm^{-1} bending vibration involving the carbonyl group may also be observed, moderate absorption 1,230–1,100 cm^{-1} aliphatic ketones, with aromatic ketones at higher wavenumbers
Carboxylic acid	More intense than ketones 1,720–1,706 cm^{-1} aliphatic carboxylic acids	3,300–2,500 cm^{-1}, usually centred on 3,000 cm^{-1}, very broad intense OH stretch
Carboxylate salt	1,650–1,550 cm^{-1} strong stretching band About 1,400 cm^{-1} weaker band	No OH band present
Ester	1,750–1,735 cm^{-1} aliphatic esters 1,730–1,715 cm^{-1} benzoate esters	1,210–1,160 cm^{-1} stretching vibration for saturated esters 1,240 cm^{-1} ethanoate (acetate) esters for simple alcohols 1,300–1,250 cm^{-1} aromatic acid esters
Amide	Occurs at lower wavenumbers than most other carbonyl groups. Amide band – position depends on hydrogen bonding About 1,650 cm^{-1} primary amides as solid sample 1,640 cm^{-1} secondary 1,680–1,630 cm^{-1} tertiary	1,650–1,515 cm^{-1} a second amide band for primary and secondary amides 3,520 and 3,400 cm^{-1} N–H stretches for primary amides

How do we interpret alkane, alkene and alkyne stretching vibrations?

C–H stretching vibrations in alkanes are generally observed at 3,000–2,840 cm^{-1}. In alkanes, methyl groups often give rise to bands at 2,962 and 2,872 cm^{-1}, with bending vibrations for methyl groups seen at 1,375 and 1,450 cm^{-1}.

Methylene groups ($-CH_2-$) are seen at 2,926 and 2,853 cm^{-1}. A bending vibration is observed around 1,465 cm^{-1}, which often overlaps with the bending vibration of methyl groups.

Alkenes give a moderate absorption around 1,667–1,642 cm^{-1} due to a C=C stretching vibration, with the more substituted alkenes absorbing near 1,680 cm^{-1} for *trans*-substituted alkenes and 1,650 cm^{-1} for *cis*-substituted alkenes. C–H stretching bands above 3,000 cm^{-1} are evidence of unsaturation.

Alkynes give rise to a weak stretching band at 2,260–2,100 cm^{-1}. You do not usually observe a C≡C band if the alkyne is symmetrical (e.g. $CH_3CH_2C{\equiv}CCH_2CH_3$). The H–C≡C– stretch of terminal alkynes is a strong and narrow band, seen between 3,330 and 3,270 cm^{-1}. It is narrower than O–H or N–H 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}.

Figure 16 shows where peaks for different functional groups appear on an infrared spectrum.

Study tip

Know your cognitive verbs precisely. The QCAA syllabus uses the cognitive verb "determine" for questions such as Worked example 12.5C. However, in previous external examinations, the cognitive verb "deduce" has been used. Both verbs involve reaching a conclusion. "Deduce" has the additional aspect that the conclusion is "necessarily true" or "logical", so it would be the only possible conclusion for the information provided.

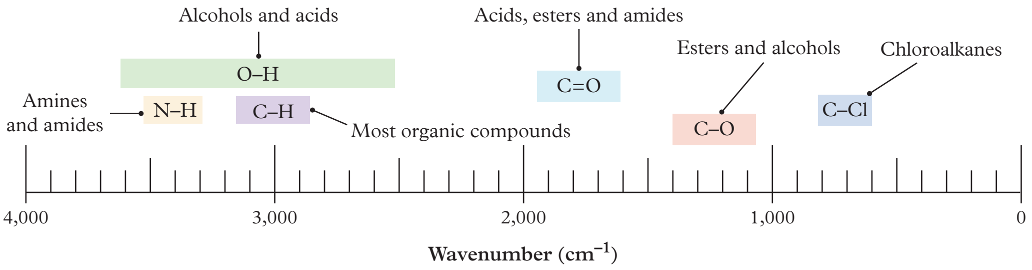


FIGURE 16 Different functional groups and where they appear on infrared spectra

Worked example 12.5C shows how infrared spectra can be used. Worked example 12.5D presents a much more complex infrared spectral analysis.

Worked example 12.5C

Analysing data from an infrared spectrum to determine the identity and structure of an organic molecule

A compound has the empirical formula of $C_3H_6O_2$ and the infrared spectrum shown in Figure 17.

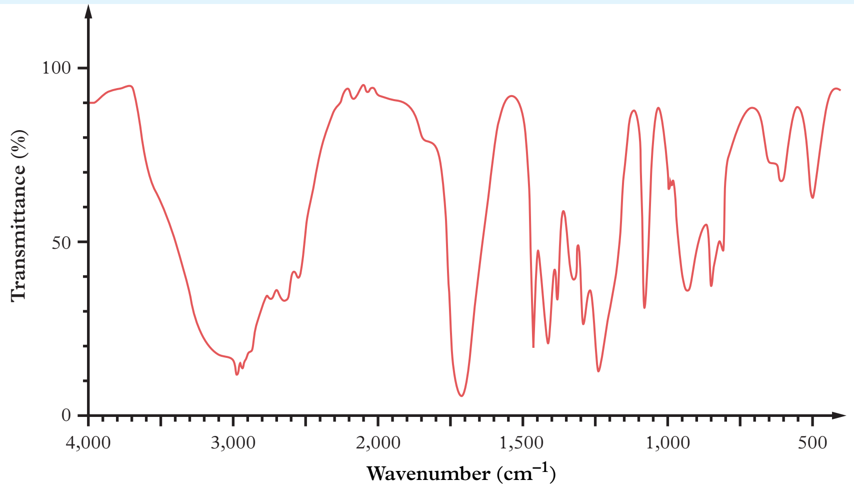
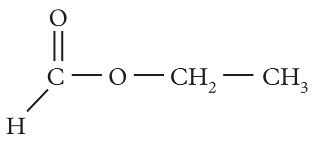
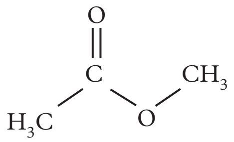
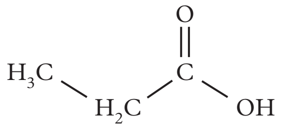


FIGURE 17 The infrared spectrum of the unknown compound

a **Determine** three possible structural formulas for the isomers of $C_3H_6O_2$. (3 marks)

b **Deduce** the structure and name of the compound. **Explain** your reasoning. (5 marks)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the questions are asking you to do.	"Determine" means establish, conclude or ascertain after consideration, observation, investigation or calculation. We need to consider which classes of compounds we have studied and how this could lead to the molecular formula provided. Part **a** is worth 3 marks, so we must express three structural formulas. "Deduce" means arrive at, reach or draw a logical conclusion from reasoning and the information given. We need to use the information provided in the spectrum to conclude which isomer could have produced it. Part **b** is worth 5 marks, so we must deduce which of the structures produces this spectrum, name the structure, and clearly explain the reasoning.
Step 2: Select the appropriate formulas and gather the required data.	The molecular formula is $C_3H_6O_2$.

Think	Do
Step 3: Draw three structural formulas. Carboxylic acids and esters both have two carbon atoms in their molecular formula.	**a**  (1 mark)  (1 mark)  (1 mark)
Step 4: Finalise your answer by explaining clearly which compound produced the spectrum, selecting the structural formula and providing the name.	**b** The IR spectrum has a strong relatively narrow peak at about 1,700 cm^{-1} which is characteristic of C=O bonds. This bond is present in all three compounds. (1 mark) There is a broad strong peak at about 3,000 cm^{-1}, which corresponds to an O–H functional group. (1 mark) There are other narrow peaks ranging between 2,600 and 3,000 cm^{-1} superimposed on the broad absorbance. This is typical of the O–H group in carboxylic acids. (1 mark) The compound must have the third structure shown above. (1 mark) The name of the compound is propanoic acid. (1 mark)

Your turn

A compound containing carbon, hydrogen and oxygen has the infrared spectrum shown in Figure 18. It has the molecular formula of $C_4H_{10}O$.

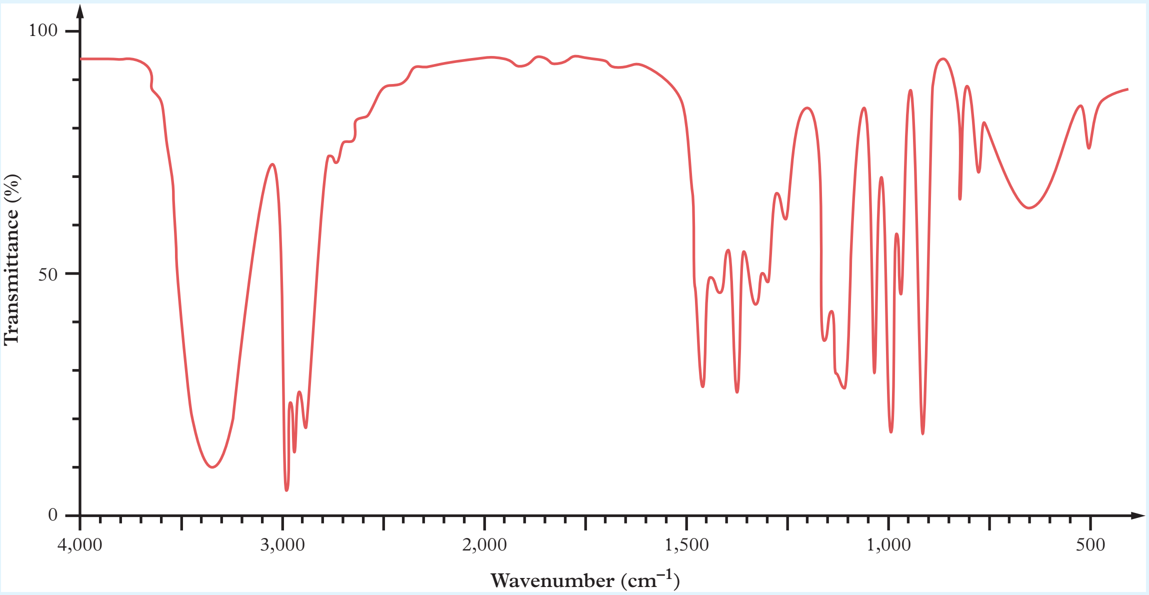


FIGURE 18 The infrared spectrum of a compound

a **Deduce** the class of compound. **Explain** all reasoning. (3 marks)

b **Determine** the structural formulas of four possible structural isomers that belong to the class of compound in part **a**. (4 marks)

c **Compare** the four isomers in part **b** and **identify** additional chemical tests that could be done to assist in identifying which of the four compounds has produced the spectrum? (2 marks)

Worked example 12.5D

Analysing an infrared spectrum to deduce which functional groups are present in a molecule

Consider the infrared spectrum in Figure 19. **Analyse** the spectrum to **deduce** which functional groups are present in the molecule. (8 marks)

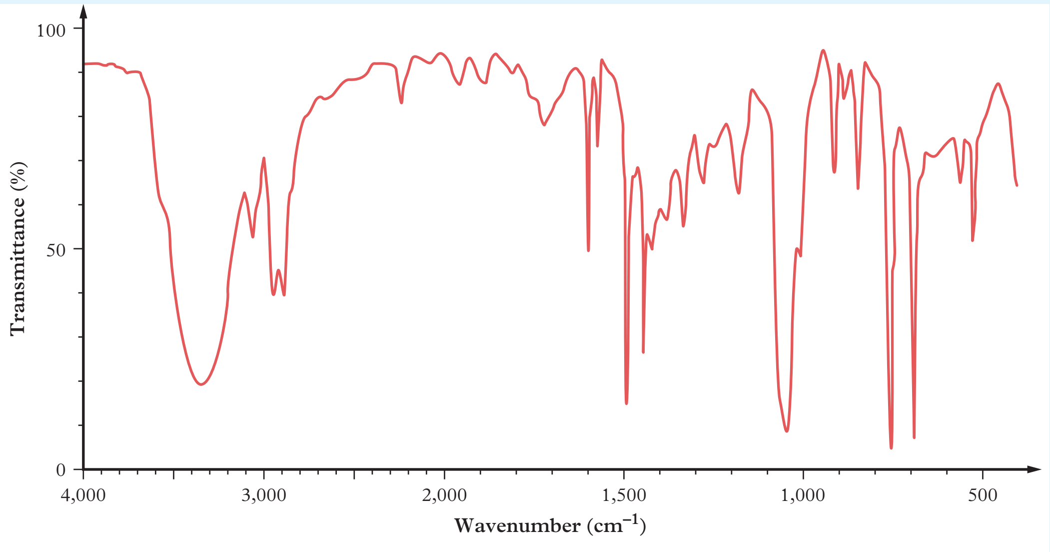


FIGURE 19 The infrared spectrum of an unknown compound

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the question is asking you to do.	"Analyse" means break down or examine in order to identify the essential elements, features, components or structure. "Deduce" means arrive at, reach or draw a logical conclusion from reasoning and the information given. We need to sequentially analyse the features of each of the peaks in the left and middle of the infrared spectrum to determine which functional groups are present and which functional groups are absent. The question is worth 8 marks, so we must express whether there is evidence or not for particular functional groups.
Step 2: Look for the presence of oxygen and nitrogen as O–H, N–H, C–O and C=O.	Evidence: The broad, intense peak around 3,330 cm^{-1} matches what would be expected for an OH group. It would be less intense if an NH group was present instead. (1 mark) A carbonyl group would give an intense peak in the region 1,870–1,540 cm^{-1}. There is a strong peak at 1,491 cm^{-1}, but this is outside the expected range. (1 mark) A C–O stretching vibration would appear as a strong peak in the region of 1,250–1,050 cm^{-1} and of strong intensity. This is consistent with the peaks at about 1,168 and 1,045 cm^{-1}. (1 mark) Therefore, there is an OH group present, a C–O group present but no NH or C=O groups. (1 mark)
Step 3: 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 1,598 and 1,442 cm^{-1} confirm this. (1 mark) The peaks to the left of 3,000 cm^{-1} look like C–H stretches in aromatic molecules. (1 mark)

Think	Do
Step 4: Look for other important peaks.	The peak at 2,239 cm^{-1} could easily be overlooked, but this is in a region of the spectrum that tends to be 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 3,330–3,270 cm^{-1}. This suggests an internal alkyne, not a terminal alkyne. (2 marks)
Step 5: Finalise your answer by listing the conclusions made.	The compound contains an OH group, a C–O bond, an internal C≡C triple bond, and an aromatic group (e.g. benzene ring/phenyl group).

Your turn

Consider the infrared spectrum in Figure 20. **Analyse** the spectrum to **deduce** which functional groups are present in the molecule. (5 marks)

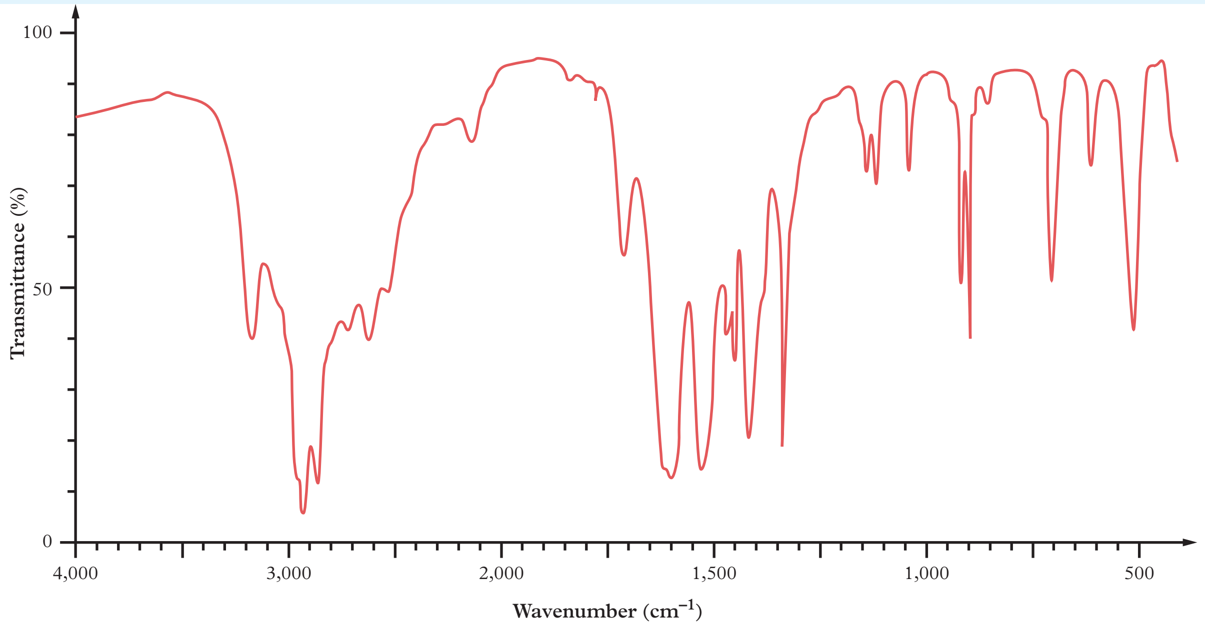


FIGURE 20 The infrared spectrum of an unknown compound

Why are analytical techniques combined?

The analytical techniques studied in this module are rarely used alone because any one analytical technique provides some information but not enough to fully identify a compound. Frequently, mass spectrometry and infrared spectroscopy results are combined. Additionally, the chemical reactions and tests studied in Module 10 provide further information about unknown compounds.

Skill drill

Evaluating the quality of evidence

Science inquiry skill: Evaluating evidence (Lesson 1.8) and Preparing for your research investigation (Lesson 1.12)

The research investigation in Unit 4 requires students to identify relevant evidence by researching scientifically credible sources to answer the research question. The ISMG section "Evaluating" shows that marks are awarded for the evaluation of the quality of evidence.

What is a scientifically credible source? An acronym to remember criteria for evaluating sources is CRAP. The four letters stand for four aspects to be considered for each source.

C: Currency – How recently was this information published? Recency can somewhat depend on your topic due to rapid research in some topics.

R: Reliability – Is the information supported by evidence? Can it be confirmed by other sources?

A: Authority – Who wrote the information? Are they an expert or knowledgeable in their field?

P: Purpose/Point of view – Why was it written? To sell? To convince? To entertain? To inform?

The analytical techniques summarised in this module can be used in many industries, including

- forensic analysis
- manufacturing of polymers (for measuring the degree of polymerisation)
- food industry, pesticide testing and allergen testing (for quality control)
- space industry (for tracking hydrocarbons in the universe, Figure 21).

Practise your skills

1 **Select** one analytical technique for one of the industries mentioned and **identify** one credible resource and one non-credible resource on the use of the analytical technique. Use the acronym CRAP to evaluate each source. **Summarise** why they were or were not credible.
   - a Resource 1 evaluation (4 marks)
   - b Resource 2 evaluation (4 marks)

FIGURE 21 The space industry uses mass spectrometry to track hydrocarbons in space.

Check your learning 12.5

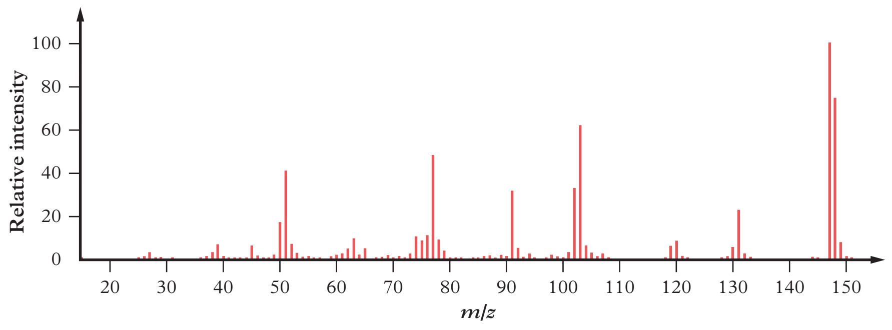
Check your learning 12.5: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** the information that can be obtained about a compound from mass spectrometry and infrared spectroscopy. (2 marks)

2 **Explain** why infrared spectroscopy can identify the presence of functional groups but not determine the complete structure of a molecule without other information. (2 marks)

3 Copy and annotate the mass spectrum of *trans*-cinnamic acid shown and label the positions of the base peak and the molecular ion. **Explain** what information can be determined from particular parts of the spectrum. (4 marks)



4 **Describe** the different wavenumber and appearance of the O–H peak for alcohols and the O–H peak for carboxylic acids. (2 marks)

Analytical processes

5 The spectroscopic techniques mentioned in this lesson are complementary because of their relative strengths and weaknesses. **Determine** two disadvantages of each technique. (4 marks)

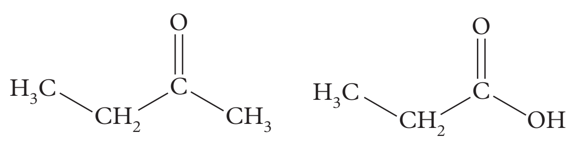
6 **Determine** the most appropriate technique for identifying

  a polymers in drink containers at a recycling station (1 mark)

  b traces of an accelerant fuel at a suspected arson site. (1 mark)

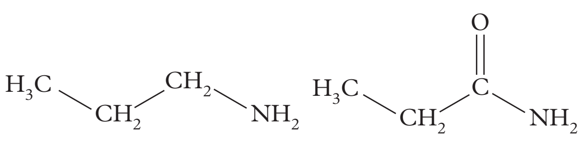
7 **Consider** the following three pairs of compounds. **Analyse** which absorption band in the infrared spectrum could be used to distinguish between them.

  a

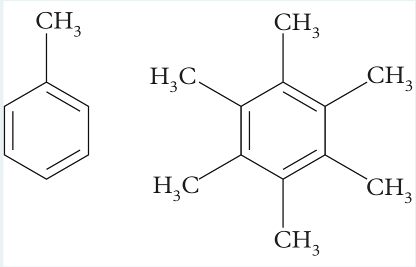


(2 marks)

  b



(2 marks)

c 

(2 marks)

Knowledge utilisation

8 **Determine** the relative intensities of peaks related to the molecular ion for 1,2-dibromoethane. **Construct** a diagram of the pattern that you would expect. (3 marks)

Practical

Lesson 12.6

Identifying organic compounds using mass spectrometry and infrared spectroscopy

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Learning intentions and success criteria

MODULE 12

Lesson 12.7

Review: Analytical techniques

Summary

12.1
- Amino acids can be separated and analysed by paper chromatography and thin-layer chromatography (TLC).
- The movement of an amino acid during chromatography depends on the relative strengths of the intermolecular forces between the amino acid and the mobile phase and the amino acid and the stationary phase.
- Comparison of retention factors (R_f) of known and unknown amino acids allows for the identification of unknown amino acids.

12.2
- Practical: Identifying amino acids using paper chromatography

12.3
- Electrophoresis is a technique that can separate amino acids by mass and the size and sign of their charge.
- In electrophoresis, the ionic forms of amino acids move through a gel towards the electrode of opposite charge.
- Amino acids can be positively charged, negatively charged or uncharged (zwitterions) depending on the pH of the electrophoresis gel and the isoelectric point of each amino acid.
- Amino acids with smaller masses move more rapidly than amino acids with larger masses, so the distance moved is inversely proportional to the mass.
- Some amino acids form ions with a 2+ or 2– charge and will move faster than similarly sized amino acids with a single charge.

12.4
- Practical: Identifying amino acids using electrophoresis

12.5
- Mass spectrometry is a technique used to determine the molar mass of organic molecules and their composition.
- 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 ratios (m/z).
- Isotopic masses of the elements in an organic compound allow for analysis of the m/z ratios in a mass spectrum to determine molar mass, and the masses of major fragments.
- In infrared spectroscopy, bonds in molecules absorb infrared radiation corresponding to the energy of vibrations. Different bonds in an organic compound absorb different frequencies of infrared radiation to produce characteristic peaks on the spectrum that allow functional groups to be identified.
- A combination of analytical techniques is frequently used to analyse compounds. Compared to either technique on its own, the mass spectrum and the infrared spectrum of a single compound together provide more evidence to identify a compound.

12.6
- Practical: Identifying organic compounds using mass spectrometry and infrared spectroscopy

Key formulas

Retention factor	$R_f = \dfrac{\text{distance travelled by component}}{\text{distance travelled by solvent}}$

Review questions 12.7A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

1 In paper chromatography of amino acids, the amino acid that travels the furthest is the one

A with the smallest molecular mass.

B with the greatest charge at the pH used.

C that is most easily adsorbed by the paper.

D that experiences only weak intermolecular forces to the paper.

2 A mass spectrometer separates ions based on which of the following factors?

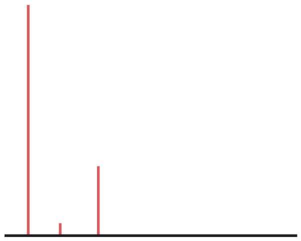
A Mass

B Charge

C Atomic mass

D Mass-to-charge ratio

3 A halogen-containing compound gives the molecular ion pattern shown.



From the pattern, what can we conclude that the compound contains?

A Iodine

B Fluorine

C Chlorine

D Bromine

4 Identify the bond that would show the strongest absorption in the infrared region.

A C=C

B H–C

C H–N

D H–O

5 Which of the following is a limitation of paper chromatography of amino acids?

A The procedure is inconvenient because it takes a long time to carry out.

B Water is the only solvent that can be used and both it and paper are polar.

C Amino acids are colourless, so it is not possible to determine their final position with any method.

D Some amino acids experience equal attractions to the paper and the solvent therefore have the same R_f values.

6 In electrophoresis, the speed of migration of amino acids in an electric field depends on the

A shape and size of molecules.

B magnitude (size) and sign (+ or –) of the charge.

C magnitude of the charge and shape of molecules.

D magnitude and sign of the charge and the size of molecules.

7 The technique of infrared spectroscopy is based on the

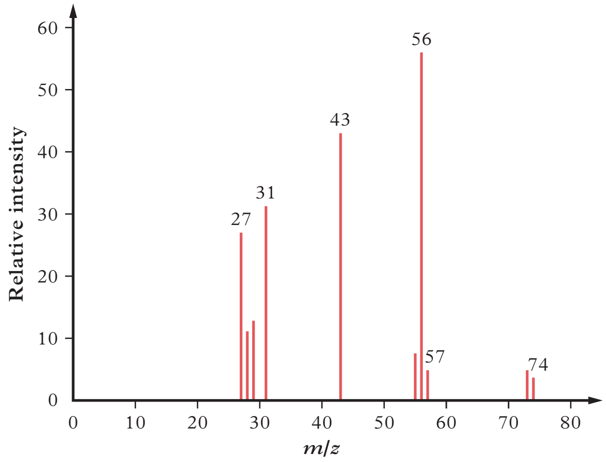
A nuclei of different atoms being affected by the nuclei of adjoining atoms.

B bonds between different atoms in molecules absorbing different wavelengths.

C bonds between different atoms in a molecule emitting different wavelengths when excited.

D bonds between different hydrogen atoms in a molecule absorbing different wavelengths.

8 The mass spectrum of a pure sample is shown.



Deduce which one of the following pure samples is most likely to produce this spectrum.

A Ethanol

B Butan-1-ol

C Propan-1-ol

D Pentan-1-ol

9 Why is electrophoresis of amino acids conducted using wells at the centre of the gel plate?

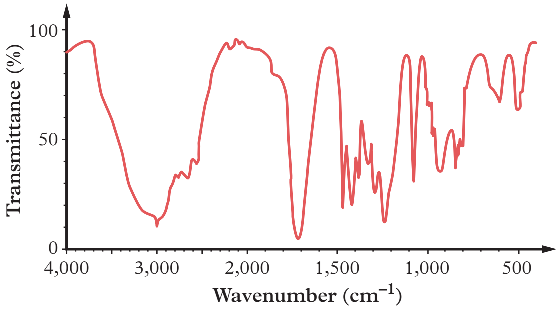
A To ensure that amino acids are separated based on their masses

B To ensure all amino acids carry a single positive or negative charge

C To ensure all the amino acid molecules migrate towards the same electrode

D Because amino acid molecules migrate towards the oppositely charged electrode

10 The infrared spectrum of a compound is shown.



Classify the type of compound that produced this infrared spectrum.

A Ketone

B Alcohol

C Aldehyde

D Carboxylic acid

Review questions 12.7B Short response

Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

11 **Explain** why when interpreting an infrared spectrum, you should first look for peaks attributable to O–H, N–H or C=O stretches. (2 marks)

12 **Explain** how the charge of an amino acid at a particular pH can be determined. (3 marks)

13 **Explain** why a few amino acids can accept or donate two protons and get a 2+ or a 2– charge, while most amino acids do not. (3 marks)

14 When loading amino acids into wells in gel electrophoresis, they are mixed with a mixture of solvents that includes glycerol. After electrophoresis, the gel plate is sprayed with ninhydrin. **Explain** the purpose of the

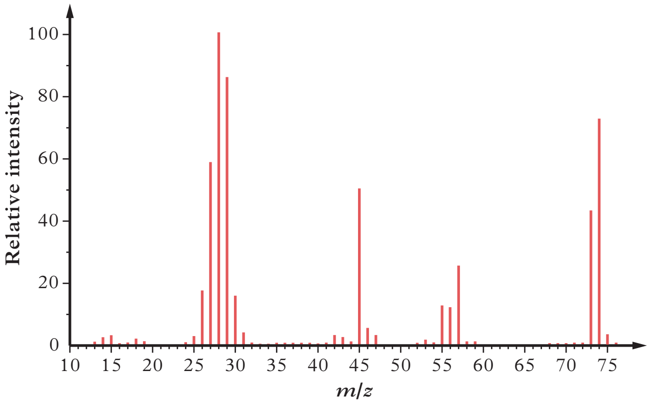
- **a** ninhydrin (1 mark)
- **b** glycerol. (1 mark)

15 **Describe** two characteristic absorption bands (wavenumber range, bond that produced them and strength) that would be present on an infrared spectrum for the following classes of compounds.

- **a** Amine (2 marks)
- **b** Carboxylic acid (2 marks)
- **c** Alcohol (2 marks)
- **d** Ester (2 marks)

Analytical processes

16 An organic compound was analysed and found to contain 48.6% carbon, 8.2% hydrogen and 43.2% oxygen. The mass spectrum of the compound is shown.



- **a** **Deduce** the empirical formula of this compound. (3 marks)
- **b** **Identify** the species of the molecular ion and the ionic fragments suggesting formulas that correspond to
  - **i** *m*/*z* 29
  - **ii** *m*/*z* 45
  - **iii** *m*/*z* 73
  - **iv** *m*/*z* 74. (4 marks)
- **c** **Deduce** the molecular formula of the compound. (2 marks)

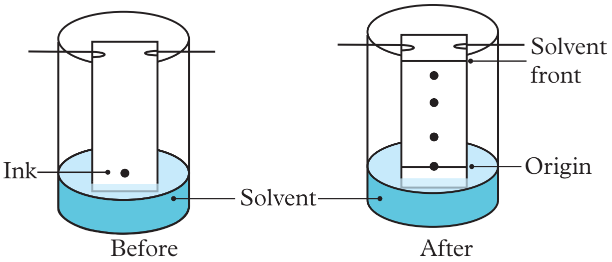
17 Amino acids can be separated and analysed by paper chromatography, thin-layer chromatography and electrophoresis. Copy and complete the table to **contrast** how each method works, and the advantages and disadvantages of each method. (9 marks)

	Paper chromatography	Thin-layer chromatography	Electrophoresis
How the method works			
Advantages			
Disadvantages			

18 A buffer with pH 6.3 was used for electrophoresis of amino acids. Use the simplifying assumption about charges of amino acids at different pH values. For cysteine, glycine, histidine and proline, **determine** the

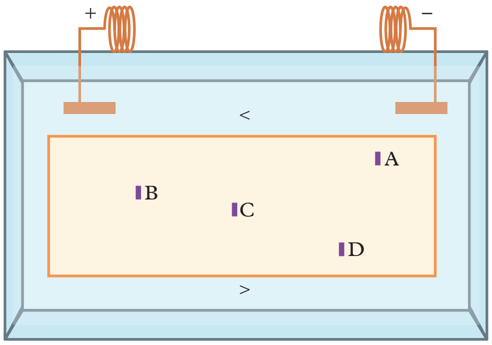
- **a** sign of their charge (4 marks)
- **b** electrode each amino acid will move towards. (4 marks)

19 A mixture of amino acids underwent paper chromatography, and the result is shown in below.

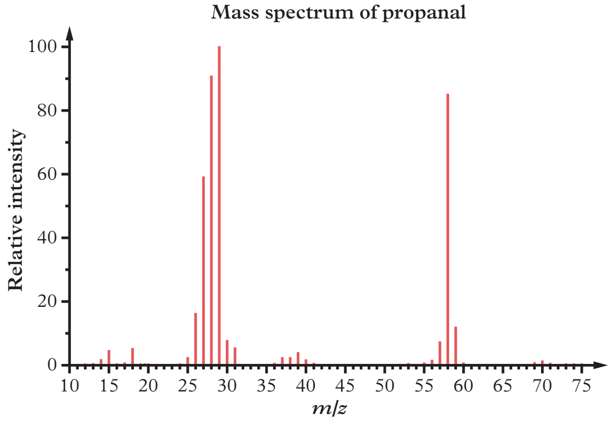


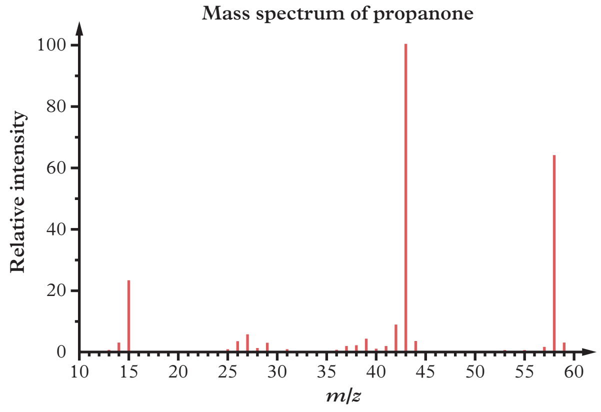
Determine the R_f values for each of the amino acids. (6 marks)

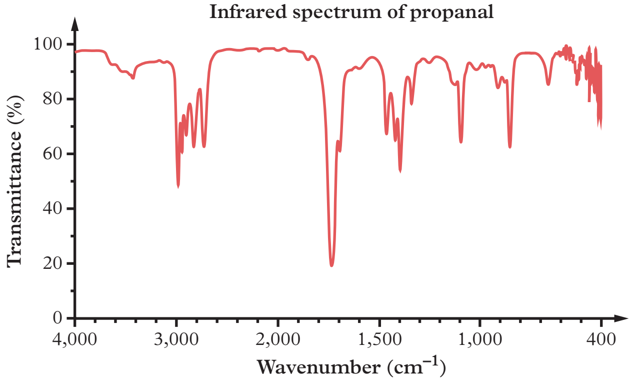
20 Electrophoresis of the amino acids arginine, asparagine, valine and proline is carried out at pH 6. The results are shown below. **Analyse** the results to **determine** the identity of A–D. Use the simplifying assumption, as well as whether the side chain is acidic or basic or neutral in nature. Consider the masses and size and sign of all charges to provide evidence of your reasoning. (5 marks)

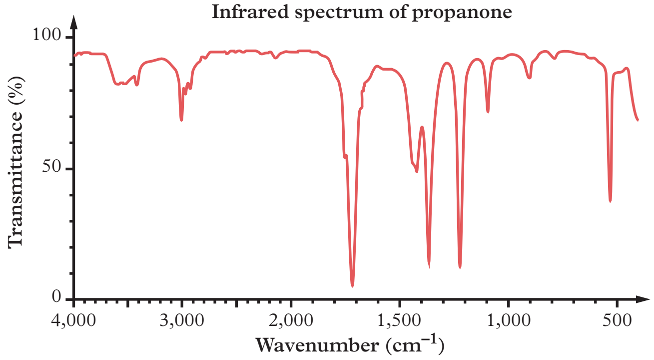


21 Propanone and propanal are isomers and have the same molecular formula but different structures. **Compare** the mass spectra and the infrared spectra of these two compounds, accounting for the main fragments and peaks to **determine** which aspects of each spectrum are most useful for distinguishing these isomers from each other. (6 marks)

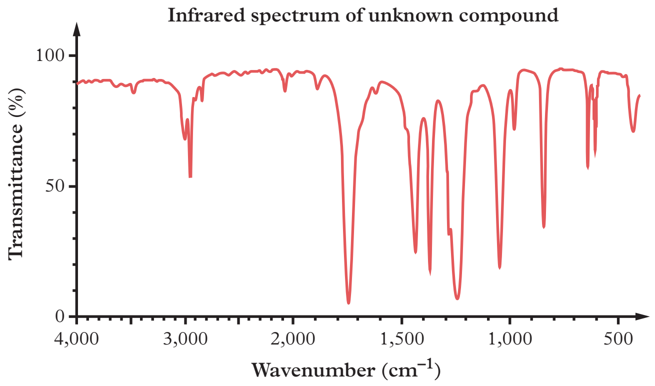


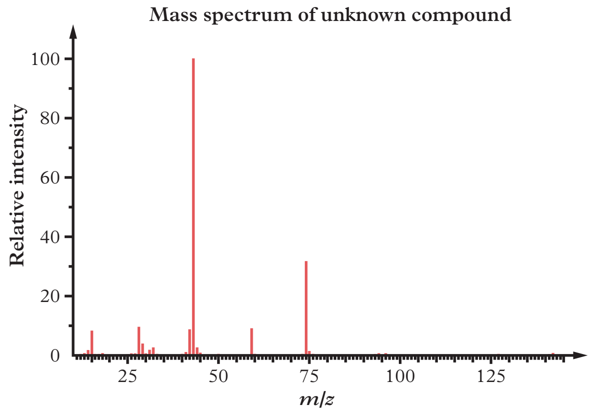






22 While cleaning out a laboratory shelf labelled "Carboxylic acids and esters", a chemist discovers a bottle simply labelled "$C_3H_6O_2$". To identify the molecular structure of the contents of the bottle, a sample is submitted for analysis by infrared spectroscopy and mass spectrometry. The spectra are shown.





a **Contrast** the structural formula for the possible acid or ester isomers of $C_3H_6O_2$. (3 marks)

b **Identify** the three compounds from part **a**. (3 marks)

c **Analyse** the two spectra and **deduce** the identity of the unknown compound. Provide reasons. (2 marks)

Knowledge utilisation

23 **Create** a flow chart of the sequence of steps used to analyse an infrared spectrum. (4 marks)

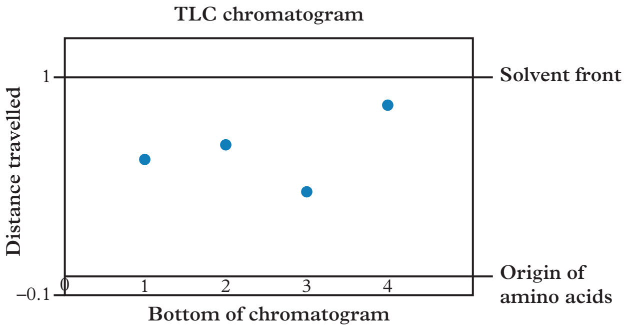
24 The R_f values found from TLC for several amino acids using three different solvents is shown in the table. Use these to answer the following questions.

Amino acid	Butan-1-ol + ethanoic acid + H_2O	Water-saturated phenol	Butan-1-ol + cyclohexamine + H_2O
Alanine	0.30	0.58	0.37
Valine	0.51	0.78	0.48
Histidine	0.11	0.65	0.24
Glycine	0.23	0.42	0.29
Leucine	0.70	0.85	0.60
Tryptophan	0.50	0.77	0.62

a **Determine** if it is possible to distinguish the valine and tryptophan by chromatography. (2 marks)

b Chromatography was performed on alanine, histidine, glycine and leucine, placed in order from left to right along the chromatography plate. The solvent was a mixture of butan-1-ol, ethanoic acid and water. **Construct** a drawing of the plate at the end of the process, showing the solvent front, and the origin and the final position of each amino acid. (5 marks)

c Four unknown amino acids were separated by TLC using water-saturated phenol. The chromatogram is shown below. **Determine** the identity of each one. (8 marks)



Data drill

Analysing data from a variety of analytical techniques

In conducting an analysis of one of more organic chemicals, chemists generally use multiple analytical techniques to obtain information about compounds. Chemical tests for functional groups include testing for saturation, primary, secondary and tertiary alcohols and tests to see if a compound is an acid or a base. Physical properties such as melting points, boiling points and solubility are useful. The analysis of the products of complete combustion allows the empirical formula to be determined. Instrumental techniques used include mass spectrometry and infrared spectroscopy.

Data from a variety of techniques for a group of related compounds is presented in Figures 1 and 2 and Table 1.

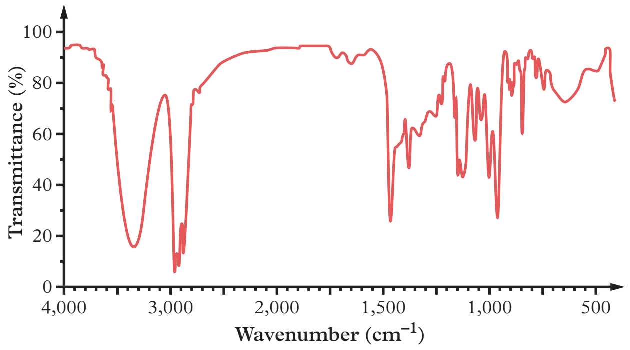


FIGURE 1 Infrared spectrum of compound B

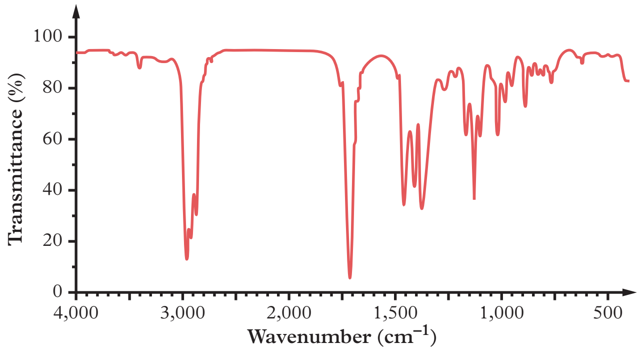


FIGURE 2 Infrared spectrum of compound C

TABLE 1 Data about compounds A, B and C

Property or test	Compound A	Compound B	Compound C
Solubility in water (g L^{-1})	Insoluble	Slightly soluble, 16	Slightly soluble, 14.7
Boiling point (°C)	67	135	Not provided
Bromine water test	Rapidly decolorised. Formed a single product	Reacted slowly in the presence of UV light to form multiple products	Reacted slowly in the presence of UV light to form multiple products
Reaction with water	Reacted with water, at high temperatures and pressures, and phosphoric acid catalyst to form one product, B	No reaction	No reaction
Complete combustion	100 mg of A undergoes complete combustion to produce 313 mg of CO_2 and 128 mg of H_2O	Not provided	Not provided
Oxidation test with acidified dichromate solution	Unable to be oxidised	Oxidised to form one product only, product C.	Unable to be oxidised
Mass spectrum	Mass of molecular ion = 84	Mass of molecular ion = 102	Mass of molecular ion = 100
Infrared spectrum	Not provided	Figure 1: Significant peaks 3,366 (s broad), 2,961, 2,933, 2,876 group (all s narrow), 1,466, 1,460 (both s narrow) cm^{-1}.	Figure 2: Significant peaks 2,965, 2,939, 2,907, 2,878 group (all s to m and narrow), 1,715 (s narrow), 1,460, 1,414, 1,377 group (all m and narrow) cm^{-1}.

Apply understanding

1 **Identify** which one of the three compounds is most soluble in water. (1 mark)

2 **Calculate** the ratio between carbon atoms and hydrogen atoms in compound A. (3 marks)

Analyse data

3 **Compare** the carbon-to-hydrogen ratio for compound A to the mass of its molecular ion to **identify** the molecular formula of compound A. (2 marks)

4 **Identify** the class of compound for compounds B and C. Provide two pieces of supporting evidence for each compound. (4 marks)

Interpret evidence

5 **Deduce** the structural formula of compounds A and B. Provide reasoning. (4 marks)

6 **Predict** the boiling point of compound C and **justify** your prediction. (3 marks)

Module 12 checklist: Analytical techniques

UNIT 4

Topic 1 review

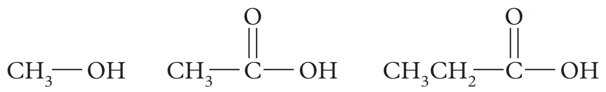
Multiple choice

(1 mark each)

1 Which one of the following groups of compounds is a homologous series?

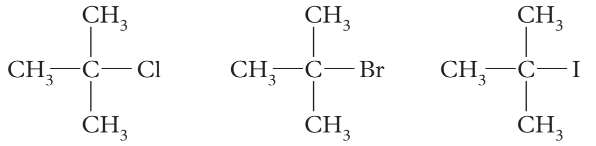
A CH_3CH_2Cl, CH_3CHCl_2, CH_3CCl_3

B



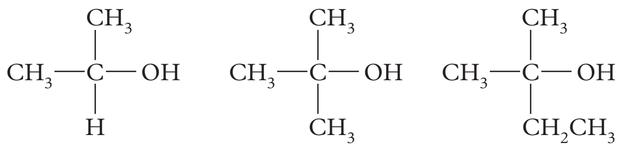
$CH_3{-}OH \quad CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH \quad CH_3CH_2{-}\overset{\overset{O}{\|}}{C}{-}OH$

C



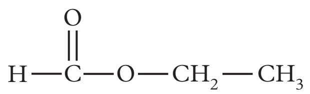
$CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}Cl \quad CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}Br \quad CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}I$

D



$CH_3{-}\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}OH \quad CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}OH \quad CH_3{-}\underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}OH$

2 What is the name of the compound with the following structural formula, according to IUPAC nomenclature rules?



$H{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}CH_3$

A Ethyl formate

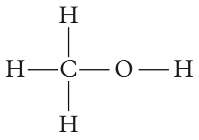
B Methyl acetate

C Ethyl methanoate

D Methyl ethanoate

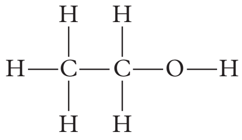
3 Which of the following substances is the least soluble in water?

A



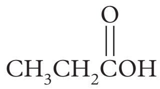
$H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}O{-}H$

B



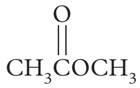
$H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}O{-}H$

C



$CH_3CH_2\overset{\overset{O}{\|}}{C}OH$

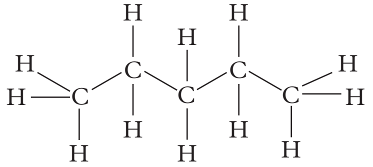
D



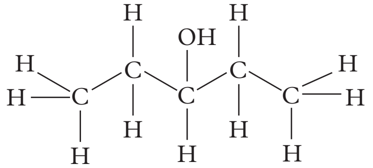
$CH_3\overset{\overset{O}{\|}}{C}OCH_3$

4 Which of the following molecules is a structural isomer of pentene?

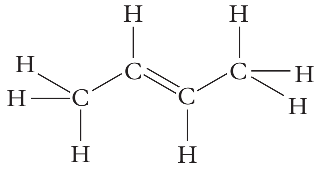
A



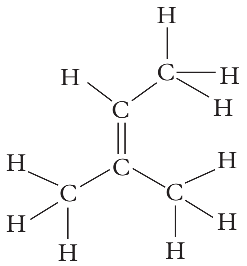
B



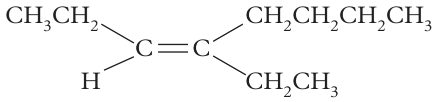
C



D



5 The IUPAC name for the following compound is



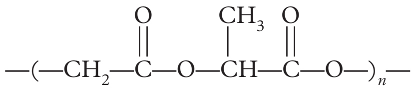
A *cis*-4-ethyloct-3-ene.

B *cis*-butylhex-3-ene.

C *trans*-5-ethyloct-5-ene.

D *trans*-4-ethyloct-3-ene.

6 A polymer, used to stitch wounds, has the general formula:



$$-(-CH_2-\overset{\overset{\Large O}{\|}}{C}-O-\overset{\overset{\Large CH_3}{|}}{CH}-\overset{\overset{\Large O}{\|}}{C}-O-)_n-$$

The formulas of the two monomers are

A $HOCH_2CH_2OH$ and $HOCH_2CH_2COOH$.

B $HOCH_2COOH$ and $(HOCH)(CH_3)COOH$.

C $HOOCCH_2CH_2OH$ and $HOCH_2CH_2COOH$.

D $HOOCCH_2COOH$ and $(HOCH)(CH_3)COOH$.

7 Bromine (Br_2) dissolves in water. When this solution is added to an unsaturated hydrocarbon, it reacts immediately. Which statement best describes this process?

A Bromine is polar and reacts by adding bromine atoms across the double bond.

B Bromine is polar and reacts by substituting hydrogen atoms with bromine atoms.

C Bromine is non-polar and reacts by adding bromine atoms across the double bond.

D Bromine is non-polar and reacts by substituting hydrogen atoms with bromine atoms.

Use the following information to answer questions 8 and 9.

Reaction 1:

$X + KOH(aq) \rightarrow CH_3CH_2OH(l) + KCl(aq)$

Reaction 2:

$CH_3CH_2OH(l) \xrightarrow{Y} CH_3COOH(l)$

Reaction 3:

$CH_3COOH(l) + CH_3OH(l) \rightarrow Z + H_2O(l)$

8 Which of the following shows the formulas of species X, Y and Z?

A $X = CH_3CH_2Cl$, $Y = H_2O/H^+$, $Z = CH_3COCH_3$

B $X = CH_2ClCH_2Cl$, $Y = H_2O/H^+$, $Z = CH_3COOCH_3$

C $X = CH_3CH_2Cl$, $Y = K_2Cr_2O_7/H^+$, $Z = CH_3COOCH_3$

D $X = CH_2ClCH_2Cl$, $Y = K_2Cr_2O_7/H^+$, $Z = CH_3COCH_3$

9 Which of the following correctly identifies each reaction type?

A Reaction 1, addition. Reaction 2, oxidation. Reaction 3, reduction

B Reaction 1, substitution. Reaction 2, elimination. Reaction 3, reduction

C Reaction 1, addition. Reaction 2, elimination. Reaction 3, condensation

D Reaction 1, substitution. Reaction 2, oxidation. Reaction 3, condensation

10 Predict which of the following chemical reactions would form more than two products.

A The acid-catalysed hydration of but-2-ene

B The condensation of methanol and ethanoic acid

C The chlorination of ethane in the presence of sunlight

D The catalysed addition of hydrogen bromide to ethene.

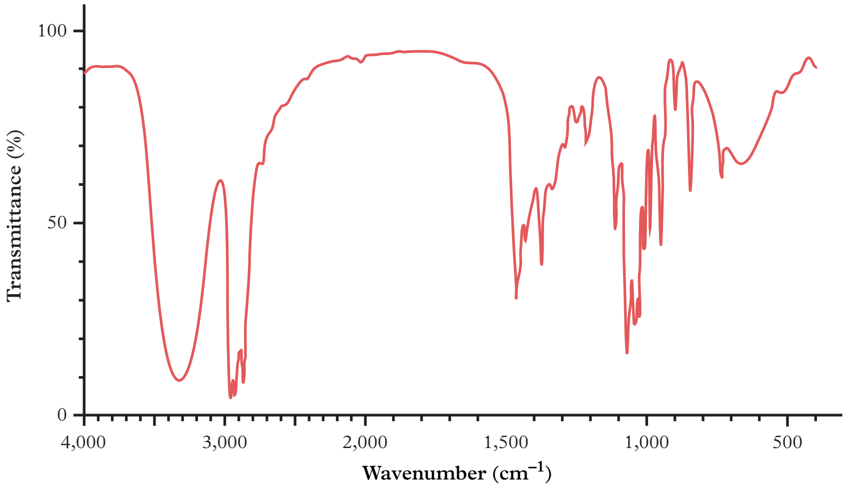
11 Determine the class of the compound that produced this infrared spectrum.

A Ester

B Alcohol

C Aldehyde

D Carboxylic acid



12 Infrared spectra are produced when the

A electrons in molecules transition to a lower energy level and emit infrared radiation.

B bonds between atoms in molecules absorb infrared radiation, causing them to vibrate.

C bonds between atoms in molecules lose vibrational energy and emit infrared radiation.

D electrons in molecules absorb infrared radiation and transition to a higher energy level.

13 During electrophoresis of amino acids, the amino acids

A are attracted to the positively charged anode.

B are attracted to the negatively charged cathode.

C move towards the electrode with the same charge as their ions.

D move towards the electrode with the opposite charge as their ions.

14 An amino acid was found to have a retention factor (R_f) of 0.85 during a paper chromatography process. This amino acid was

A adsorbed by the paper most of the time.

B not adsorbed by the paper during the process.

C adsorbed by the paper for approximately half the time.

D adsorbed by the paper for relatively short periods of time.

15 An organic compound contains one chlorine atom. The mass spectrum of this compound will show for the molecular ion

A pairs of peaks of equal height but a difference of m/z 2.

B trios of peaks with the middle peak being taller than the outside two peaks.

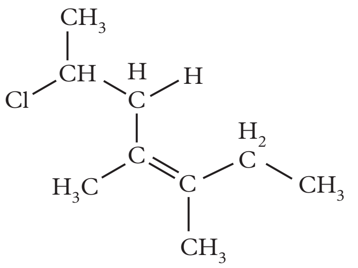
C pairs of peaks with the taller peak having m/z 2 smaller than the shorter peak.

D pairs of peaks with the shorter peak having m/z 2 smaller than the taller peak.

Short response

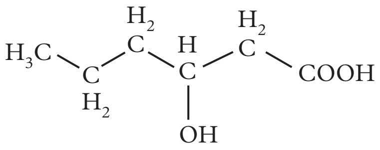
16 **Identify** the following compounds.

a



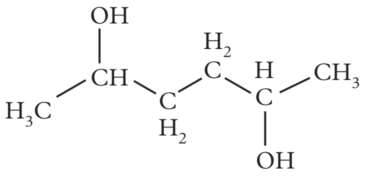
(1 mark)

b



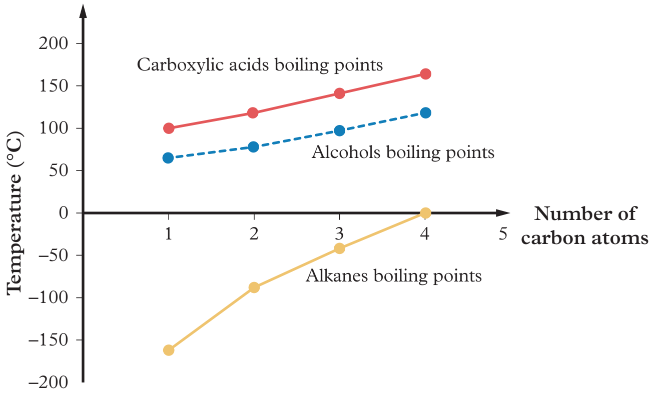
(1 mark)

c



(1 mark)

17 The following graph shows the boiling points of alkanes, alcohols and carboxylic acids with one to four carbon atoms.



a **Explain** why the boiling points of the alkanes are much lower than the boiling points of the alcohols and the carboxylic acids. (3 marks)

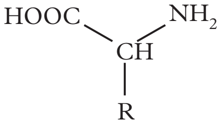
b **Explain** why the boiling points of all three series of compounds increase with increasing numbers of carbon atoms. (2 marks)

18 The experimental results of the solubility in water for some substances are shown in the following table.

Explain these observations. (3 marks)

Substance	Observations
Hexane (C_6H_{14})	Did not dissolve
Hexene (C_6H_{12})	Did not dissolve
Ethanol (CH_3CH_2OH)	Did dissolve
Propanoic acid (CH_3CH_2COOH)	Did dissolve

19 An amino acid with the general structural formula shown has a pH at isoelectric point of 6.3.



Sketch the most prevalent structures present at a pH of

- **a** 2.0 (1 mark)
- **b** 6.3 (1 mark)
- **c** 9.0. (1 mark)

20 Polypropene exists as three different structural forms, each with different physical properties.

- **a** **Describe** the structural features and distinguishing properties of each of the three forms of polypropene. (3 marks)
- **b** **Explain** why the properties of each form differ, depending on its structure. (3 marks)

21 From the starting reagents of ethene ($CH_2=CH_2$) and propane ($CH_3CH_2CH_3$), **construct** a reaction pathway diagram to form ethyl propanoate ($CH_3CH_2COOCH_2CH_3$). (5 marks)

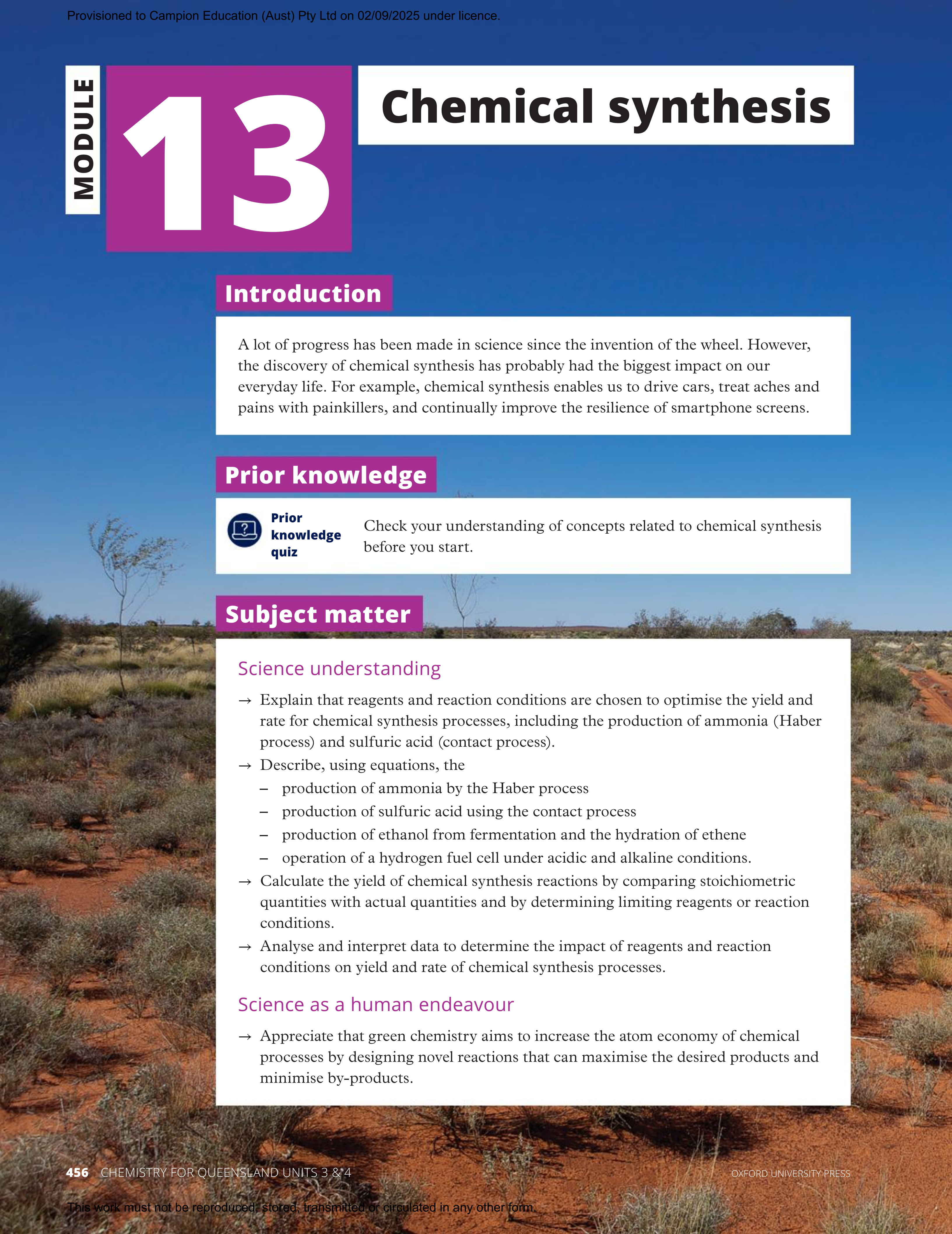
22 A sample of compound A, with the molecular formula C_3H_8O, is mixed with acidified $KMnO_4$ and heated. The product, B, is separated and purified. When B is mixed with water, the solution is found to have a pH 3.0. A and B are mixed with a small amount of concentrated H_2SO_4 and heated under reflux to produce C.

- **a** **Determine** the balanced chemical equation for the reaction of A to form B. (2 marks)
- **b** **Determine** the balanced chemical equation to form C from A and B. (2 marks)
- **c** **Describe** an observation for each of the reactions in parts **a** and **b**, and state why that observation occurs. (2 marks)

23 A linear hydrocarbon has the formula C_5H_{10}. The compound decolourises bromine water. To determine the position of the double bond and the name of the compound, it is reacted with HBr.

- **a** **Identify** the possible structural formulas of the products of the reaction with HBr for all positions of the double bond in the possible isomers of the original compound. (4 marks)
- **b** **Explain** how the position of the double bond in the original compound can be identified by knowing the product or products of the reaction with HBr and the proportions with which they are produced. (2 marks)

TOTAL MARKS
/52 marks



MODULE 13 Chemical synthesis

Introduction

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.

Prior knowledge

Prior knowledge quiz

Check your understanding of concepts related to chemical synthesis before you start.

Subject matter

Science understanding

→ Explain that reagents and reaction conditions are chosen to optimise the yield and rate for chemical synthesis processes, including the production of ammonia (Haber process) and sulfuric acid (contact process).

→ Describe, using equations, the
  - production of ammonia by the Haber process
  - production of sulfuric acid using the contact process
  - production of ethanol from fermentation and the hydration of ethene
  - 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 or reaction conditions.

→ Analyse and interpret data to determine the impact of reagents and reaction conditions on yield and rate of chemical synthesis processes.

Science as a human endeavour

→ Appreciate that green chemistry aims to increase the atom economy of chemical processes by designing novel reactions that can maximise the desired products and minimise by-products.

- → Explore important developments in sustainable chemical industries, such as new synthetic schemes that can simplify operations in chemical productions and greener solvents that are inherently environmentally and ecologically benign.
- → Consider the principles of green chemistry, including the design of chemical synthesis processes that use renewable raw materials, limiting the use of potentially harmful solvents and minimising the amount of unwanted products.
- → Appreciate that dwindling supplies of economically viable sources of fossil fuels and concerns related to carbon emissions have prompted research into the synthesis of biofuels.
- → Explore the development of biofuels from plant feedstocks such as algae, oil seeds and wood waste, or from waste materials such as food industry waste oils.
- → Explain how 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.

Science inquiry

- → Investigate the Haber and contact processes.* (*Simulations may be used.)

Source: *Chemistry 2025 v1.2 General Senior Syllabus* © State of Queensland (QCAA) 2024

Practicals

These lessons are available on Oxford Digital.

Lesson 13.2 Simulating the Haber process
Lesson 13.3 Simulating the contact process

Lesson 13.1

Synthesis of ammonia and sulfuric acid

Key ideas

→ 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.

→ Chemical synthesis involves designing reaction pathways and selecting reagents and conditions to form a product with desirable properties.

→ Ideal reagents and reaction conditions need to be selected to achieve optimal outcomes.

Why is chemical synthesis important?

Learning intentions and success criteria

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.

FIGURE 1 The front of a smartphone is typically a synthetic glass-ceramic material.

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 it to form a material that endures much more stress than its original components.

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 added to a system to cause a chemical reaction or test for the presence of another substance

yield
the amount of product obtained from a chemical reaction

Why is it important to select the reagents 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". It can refer to all the reactants, but sometimes it refers to a reactant other than the main reactant. For example, you saw in Module 10 that oxidising agents react with alcohols; the main reactant is the alcohol and the oxidising agent is the reagent.

Chemical synthesis processes involve selecting specific reagents and reaction conditions to optimise the rate and yield 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.

FIGURE 2 Fritz Haber (1868–1934), one of the inventors of the ammonia synthesis process, working in his laboratory in Karlsruhe, Germany

Haber process – the production of ammonia

Ammonia (NH_3) exists naturally in the environment and the human body but it is also manufactured for many industrial applications. Ammonia is used to produce fertilisers, refrigeration gases, explosives and many household and industrial cleaning products. Today in large-scale manufacturing plants, almost 190 million tonnes of ammonia is produced annually. To understand just how large a scale this is, assume that the average sedan car weighs approximately 2,000 kg. This would mean that 180 billion kilograms would be the equivalent of 900 million cars! That's an enormous amount of mass of one product to be made each year.

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:

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

The Haber process is typically conducted under high pressure (approximately 20 MPa) 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. As such, this is an artificial nitrogen-fixation process rather than biological nitrogen fixation (where bacteria use an enzyme to convert nitrogen into ammonia at ordinary pressures and temperatures).

Haber process
the production of ammonia by a nitrogen-fixation process

contact process
the production of very concentrated sulfuric acid

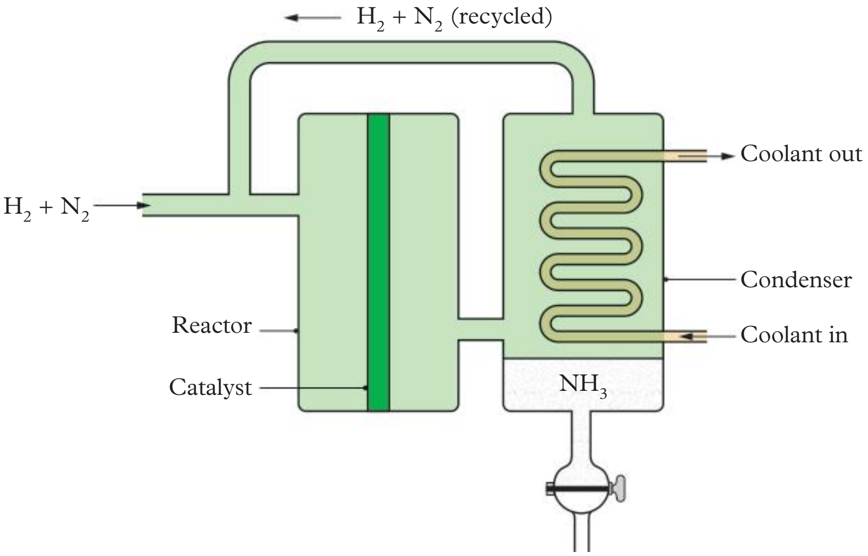


FIGURE 3 The Haber process for producing ammonia

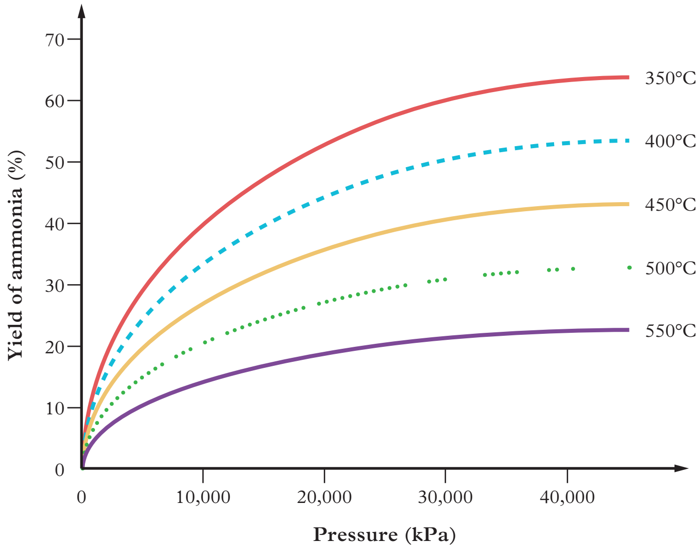


FIGURE 4 The yield of ammonia (%) (see Lesson 13.5) at different pressures and temperatures

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 back into its reactants: N_2 and H_2. Consequently, in order to increase yield, lower temperatures are optimal; however, at temperatures lower than 200°C, the rate of ammonia production is very slow and the reaction is not efficient. Hence, the reaction conditions of 20,000 kPa and 400–500°C is a compromise. Despite these modifications to the production conditions, the yield of ammonia does not seem to be very high (about 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).

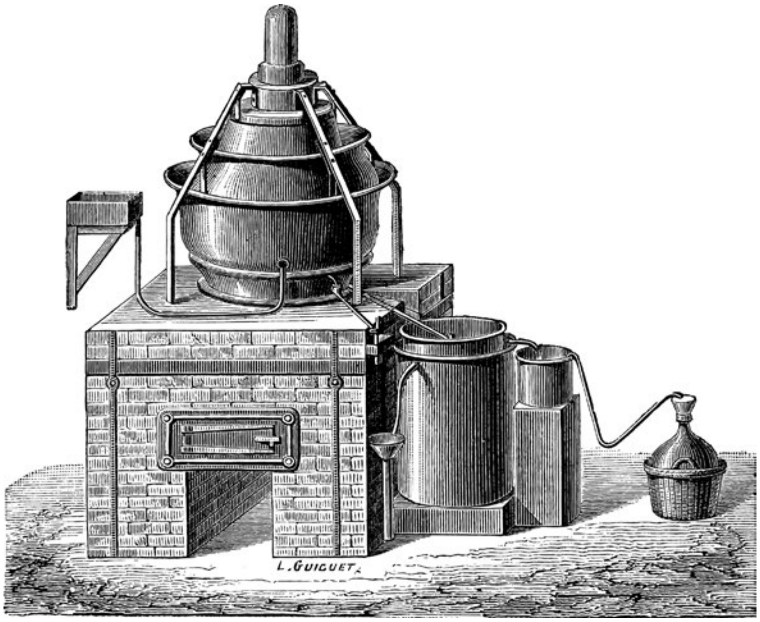


FIGURE 5 The equipment that was used in the early production of highly concentrated sulfuric acid

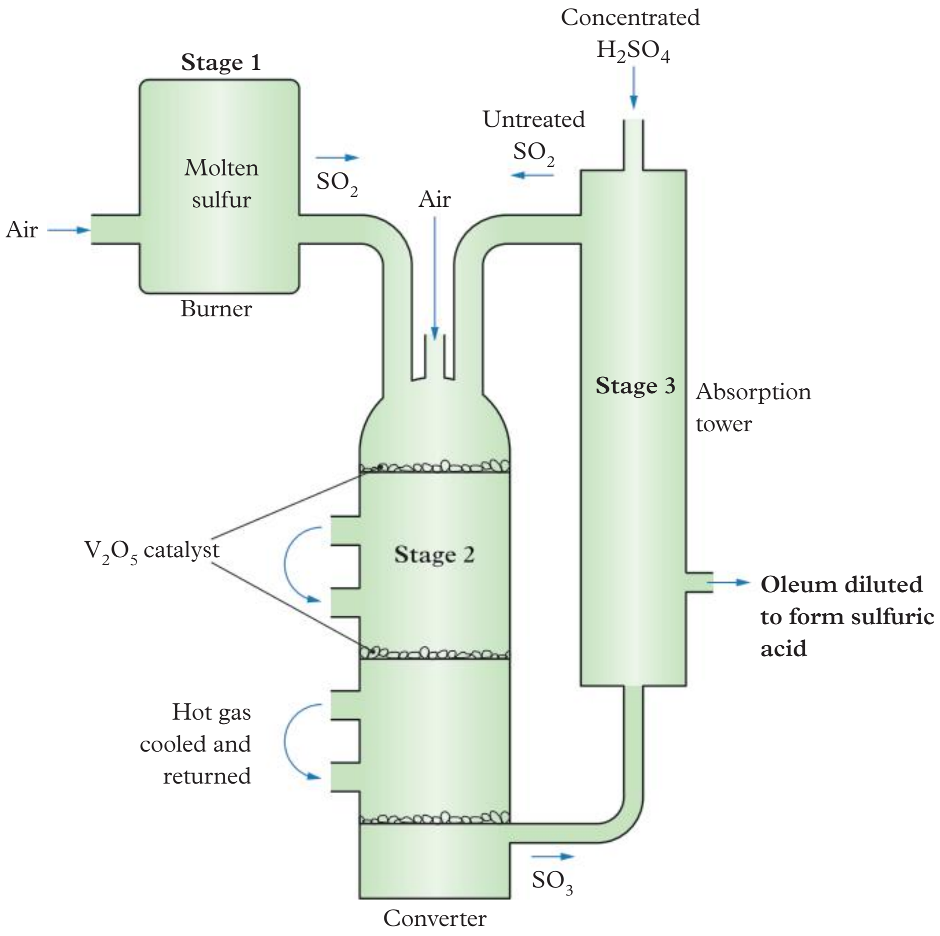


FIGURE 6 The contact process for producing sulfuric acid

There are three main stages in the contact process (Figure 6).

1 Sulfur or materials containing sulfur are burnt to produce sulfur dioxide:

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

The ratio of sulfur to oxygen must be 1:1 and molten sulfur is sprayed as a mist into the reaction chamber to enable the combustion with the oxygen gas. Although theoretically an excess of oxygen would increase the yield of sulfur trioxide, it would also make the conversion of sulfur trioxide in the presence of the excess oxygen gas ineffective for processing through to Step 2.

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):

$$2SO_2(g) + O_2(g) \xrightleftharpoons{V_2O_5} 2SO_3(g)$$

At low temperatures, the equilibrium lies far to the left, so only a small amount of SO_3 is formed. This reversible step of the contact process is identified as the rate-limiting step, or the slowest step of the entire process. It determines the rate at which the final product (H_2SO_4) is made and is why a catalyst is required for this stage of manufacture. To improve the yield, the reaction is conducted at 400–500°C and 100–200 kPa. The reasons for this will be discussed next.

oleum
a solution of sulfur trioxide in sulfuric acid, also called fuming sulfuric acid

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:

$$H_2S_2O_7(l) + H_2O(l) \rightarrow H_2SO_4(l)$$

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 reverse reaction is favoured, which reduces the yield of SO_3. However, at lower temperatures, SO_2 reacts with O_2 very slowly. At about 450°C, the rate of SO_3 formation is high and the rate of decomposition is minimal, which is why this temperature is considered a compromise, since it is at this temperature that the rate of production of product is balanced by the yield of the desired product SO_3 in the equilibrium mixture. This is also why in this step of the process, the vanadium oxide catalyst is used to increase the rate of production. By improving the rate, the total production of an industrial plant can be maximised.

When SO_3 is formed, there is a decrease in the number of moles of the gaseous components. Manufacturers can then decrease the volume of the reaction chamber. This is done to increase the pressure, which favours the forward reaction, and therefore leads to a further 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 of 1500–1700 kPa are used.

Real-world chemistry

"A greener ammonia for a greener fertiliser"

Researchers in a number of countries, including Australia, are working on the development of "greener" ammonia that can be manufactured by small facilities and farmers as opposed to large centralised chemical plants. Globally, the production of ammonia uses up to 1% of non-renewable fossil fuels and also produces 1% of all carbon dioxide emissions, making it a major contributor to climate change.

Currently, two main areas are being researched to produce ammonia in a more environmentally friendly way. The first employs renewable energy sources such as solar to produce the major reactant hydrogen gas and then to produce ammonia. This is a sustainable method of splitting water, unlike the more conventional method of obtaining hydrogen from the decomposition of natural gas or methane.

The second method is designing novel catalysts as alternatives to the iron oxide catalyst currently used. These include solid metal-organic frameworks (MOFs). MOFs are highly porous with extremely large surface areas. They are tuneable, meaning they can be adapted to bind to particular substances more than to others. MOFs can be designed to selectively bind to the reactants and more easily release ammonia. They function at lower temperatures and pressures, which saves energy in the process. Incorporating these modifications into the Haber process ensures ammonia manufacturing is more environmentally friendly; it also allows economically disadvantaged areas of the world to have easy access to nitrogenous fertilisers.

Apply your understanding

1 **Identify** the two areas that are currently being researched to improve the ammonia production process by making it more environmentally friendly. (2 marks)

2 **Explain** why ammonia production is currently a concern in terms of its environmental impact. (2 marks)

3 **Identify** the advantages of using MOFs as catalysts in place of the conventional iron(II) oxide catalyst. (2 marks)

Check your learning 13.1

Check your learning 13.1: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** the Haber process. (2 marks)

2 **Explain** the three stages in the contact process. (3 marks)

3 **Explain** the difference between a reagent and a reactant. (1 mark)

Analytical processes

4 **Analyse** and **compare** the percentage yields for ammonia from Figure 4 at 20,000 kPa and 350°C versus conditions at 20,000 kPa and 550°C. Which of the two conditions leads to a larger yield and why? (3 marks)

5 **Compare** the steps of the Haber process and the contact process. Consider three main categories based on their function: material preparation, reaction process and product collection and handling. Provide a brief description of each category for both processes. (12 marks)

Knowledge utilisation

6 **Distinguish** why temperature is often categorised as the compromise condition in the Haber process of ammonia production. **Justify** your response. (2 marks)

Practical

Lesson 13.2

Simulating the Haber process

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Learning intentions and success criteria

Practical

Lesson 13.3

Simulating the contact process

Learning intentions and success criteria

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Lesson 13.4

Synthesis of fuels

Key ideas

→ There are many alternatives to fossil fuels. Some of the important ones are biofuels, which include biodiesel, ethanol and hydrogen.

→ The production of ethanol can be achieved by fermentation or by hydration of ethane.

Learning intentions and success criteria

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

How can fuel production become more sustainable?

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.

Biofuels include biodiesel and ethanol when it is made from renewable sources. They 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 not all biofuels generally are a green alternative to fossil fuels because large areas of land are required to produce only a small amount of fuel.

What are biofuels?

Biofuels are fuels that are obtained from materials such as plants and animal matter. Assisting with reducing carbon emissions, the main two renewable biofuels produced in Australia that serve as possible replacements for petrol and diesel are biodiesel and bioethanol respectively. E10 (Figure 1) is a blend of unleaded petrol with 9–10% ethanol and is available at petrol stations. Biofuels have been promoted as being able to reduce carbon emissions by up to 85%.

What is ethanol and how is it produced?

Ethanol (C_2H_6O) (Figure 2) is one of the most common types of alcohol. There are two main methods used to produce ethanol: fermentation and the hydration of ethene.

Ethanol 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) and starch from grains, mainly wheat. Researchers are also currently trialling the use of cellulose from wood. Ethanol produced from such renewable raw materials not only has the potential to reduce automobile emissions, but its high oxygen content also helps petrol burn more cleanly. It can do so while behaving similarly to conventional fuels such as petrol. As it has a high octane rating, is volatile and burns well, it is a viable substitute in petrol blends without requiring car engines to be modified.

Perhaps the main disadvantage that reduces the functionality of bioethanol is that it has a low volumetric energy density when used in its most pure form (E100 blend). While this may translate to vehicles requiring more bioethanol per kilometre than petrol fuels, it is not always the case; the higher-octane rating can counteract this. Bioethanol can also increase the degradation of certain metals inside older vehicle engines, manufactured prior to the year 2000. Lower percentage bioethanol blends (e.g. E10) are currently incorporated into petrol and are used by most conventional engines without the need for further modification (Figure 1).

FIGURE 1 E10 is unleaded petrol blended with 9–10% ethanol.

Alternatively, ethanol can be produced by the **catalytic hydration** of ethene. Ethene is sourced from petroleum, which is a fossil fuel. Combustion of ethanol from ethene produces carbon dioxide and water in the same way as the combustion of ethanol from fermentation. The carbon dioxide causes an increase in atmospheric carbon dioxide levels as this carbon was removed from the atmosphere when the fossil fuel first formed. Fossil fuels are also a finite, non-renewable resource.

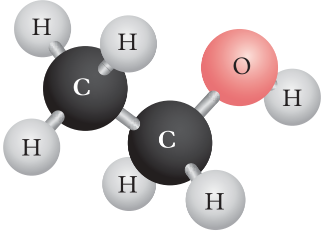


FIGURE 2 The structure of an ethanol molecule

How is fermentation used to produce ethanol?

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 (e.g. amylase) and go through a process called saccharification. This is the hydrolysis of polysaccharides to turn them into soluble sugars such as glucose and sucrose. Yeast, a fungal organism, is added. The sugars are then slowly decomposed by an enzyme produced by yeast called zymase during the fermentation. The reaction occurs in **anaerobic** conditions (without the presence of oxygen) and results in glucose reacting to form ethanol and carbon dioxide. The bubbles seen in Figure 3 are CO_2 and the chemical reaction is:

$$C_6H_{12}O_6 \xrightarrow{\text{yeast enzyme}} 2C_2H_6O + 2CO_2$$

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.

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

anaerobic
the absence of air, which normally supplies oxygen

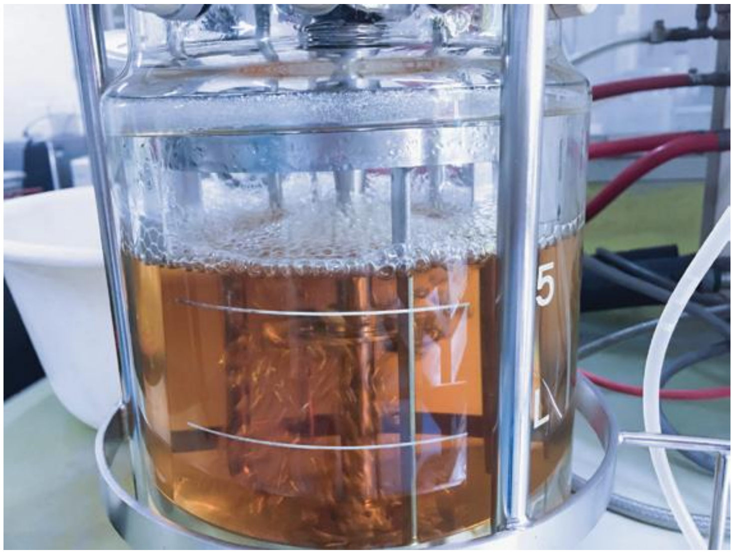


FIGURE 3 Fermentation of ethanol aided by yeast respiration

How is the hydration of ethene used to produce ethanol?

Most ethanol is produced by the direct hydration of ethene, under typical conditions of 300°C and 7,000 kPa. Phosphoric acid is used as a catalyst. The equation of the reaction is:

$$C_2H_4(g) + H_2O(g) \xrightarrow{H_3PO_4,\ 300°C,\ 6{,}000–7{,}000\ kPa} C_2H_5OH(g)$$

The reaction is reversible and reaches equilibrium, but the yield is quite high. To extract ethanol from the reaction mixture, it is cooled and condensed. Ethene remains as a gas and can be reused in the plant. Water and ethanol form a liquid mixture. Fractional distillation is then used to separate the ethanol and leave the water.

This process has the advantages over fermentation in that it is faster and can produce larger amounts of ethanol in less time. Some of the disadvantages are that it requires a catalyst with a low pH, which needs to be managed, the high pressures and temperatures involved in the process are costly and it uses a lot of energy. Both processes require distillation at the end, which is also an energy-using process.

$$CO + H_2O \xrightarrow{\text{nickel catalyst}} CO + 3H_2CO + H_2O \rightarrow CO_2 + H_2$$

Real-world chemistry

Can "dirty" diesel ever be clean and green?

Diesel made from petroleum is a mixture of hydrocarbons with 9–25 carbon atoms. As it is a fossil fuel, combustion of diesel increases atmospheric levels of CO_2. Diesel engines are known for producing particulates, tiny pieces of black soot that pollute surroundings and cause health problems. Can biodiesel help?

Biodiesel is produced from renewable sources such as waste vegetable oils and animal fats and oils. Renewable fuels, including biodiesel, do not contribute additional atmospheric CO_2. However, to switch fully from diesel to biodiesel would require large areas to plant oil crops, displacing farming for food. Because biodiesel is chemically similar to regular diesel in composition and carbon chain length (with the exception that regular diesel doesn't contain the ester functional group), diesel engines can combust biodiesel with minimal modification.

Two industrial processes are used to produce biodiesel; both rely on transesterification. They are the base-catalysed method and the lipase-catalysed method. Biological triesters (triglycerides), which are thick liquids or soft solids, are converted to esters with a single functional group. Transesterification reacts a triglyceride with three alcohol molecules to form three new esters and a triol. The chemical equation for the base-catalysed method is shown in Figure 4.

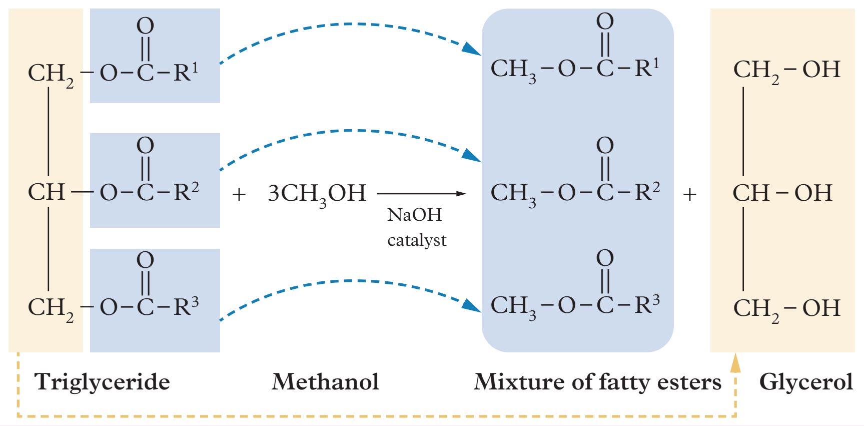


FIGURE 4 The base-catalysed transesterification reaction. The triglyceride molecule on the left reacts with methanol at a high pH to produce three esters and glycerol.

TABLE 1 A comparison of methods to produce biodiesel

Features	Base-catalysed method	Lipase-catalysed method
Raw material	Triglycerides	Triglycerides
Other reactant	Methanol or another small alcohol	None
Catalyst used	A proton-accepting base such as NaOH, which supplies the hydroxide ion	An enzyme
Conditions	Atmospheric pressure and 60–70°C High pH due to strong base	Atmospheric pressure and 30–60°C pH 7–9
Advantages	High yield, approximately 98%	Low temperatures and moderate pH No ingredients are harmful to engines or the environment Fewer unwanted by-products
Disadvantages	NaOH needs to be very dry, or saponification occurs to make soap and alcohol, not biodiesel Leftover base can corrode engines when not completely removed from the biodiesel Environmental problems due to the high pH	Longer reaction times: several hours to 1 day Enzymes destroyed if the temperature gets too high, affecting yield Yield is approx. 85–95% Costs slightly more

Apply your understanding

1 **Calculate** the percentage error for each fuel and comment on the validity of the experimental process used by the students. (3 marks)

2 **Discuss** potential sources of error that may have contributed to the errors obtained. (2 marks)

3 **Determine** the identity of the fuels combusted from trends and relationships that may exist between the fuels. **Justify** your response. (2 marks)

Skill drill

Investigating the properties of fuels

Science inquiry skills: Planning investigations (Lesson 1.4); Processing and analysing data (Lesson 1.7)

A group of students conducted an experiment measuring the energy yields of five colourless fuels, some of which were unidentified. It was known that the sample of fuels included ethanol, propanol, butanol, pentanol and biodiesel. The students recorded the boiling points and actual yield of energy for each fuel, while the theoretical yield of each fuel was noted on its label (Table 2).

TABLE 2 Theoretical yield, actual yield and boiling point of the five fuels in the sample

Fuels	Theoretical yield (kJ mol^{-1})	Actual yield (kJ mol^{-1})	Boiling point (°C)	% Error
Ethanol	–1,367	–960	78	
Fuel B	–2,021	–1,879	97	
Fuel C	–2,676	–2,290	118	
Fuel D	–11,000	–9,789	320–360	
Fuel E	–3,327	–3,098	138	

Practise your skills

1 **Calculate** the percentage error for each fuel and comment on the validity of the experimental process used by the students. (3 marks)

2 **Discuss** potential sources of error that may have contributed to the errors obtained. (2 marks)

3 **Determine** the identity of the fuels combusted from trends and relationships that may exist between the fuels. **Justify** your response. (2 marks)

Check your learning 13.4

Check your learning 13.4: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** what biofuels are. (1 mark)

2 **Explain** how ethanol is produced by fermentation. (2 marks)

3 **Explain** how ethanol can be produced by the hydration of ethene. (2 marks)

4 **Identify** the raw materials commonly used for producing ethanol by fermentation in Australia. (2 marks)

5 **Identify** three reasons for why small percentages of ethanol can be blended with petrol for use in modern cars. (3 marks)

Knowledge utilisation

6 **Investigate** the advantages and disadvantages of using fermentation compared to hydration of ethene for the production of ethanol. (3 marks)

7 The catalytic hydration of ethene is commonly employed in ethanol manufacturing. **Predict** how the use of fermentation to produce ethanol might affect the cost and environmental footprint of biodiesel production if it becomes more widely adopted in the industry. (2 marks)

Lesson 13.5

Hydrogen fuel cells

Key ideas

- → Hydrogen fuel cells can be used to power engines and generate electricity for other purposes.
- → There are two different types of fuel cells – one runs under acidic conditions and the other one runs under alkaline conditions.
- → Hydrogen fuel cells operate by continually supplying the hydrogen fuel at one electrode and oxygen (usually air) at the other electrode.
- → Diagrams and half-equations can be used to describe the processes occurring in a fuel cell.

Learning intentions and success criteria

What are hydrogen fuel cells?

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 water vapour; this powers their engines (Figure 1). The same reaction is used in **hydrogen fuel cells** to produce electricity. Fuel cells, including hydrogen fuel cells can achieve an efficiency of more than 75%, whereas combustion engines only have an efficiency of 25–30% due to the large amount of wasted heat energy involved. 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, depending on how the hydrogen is produced, pollutants may be released at the site of the hydrogen production; for example, if the hydrogen is derived from reformed natural gas, and while transporting and storing hydrogen. Fuel cells are still considered to be environmentally friendlier than combustion engines.

Fuel cells can operate with a continuous supply of fuel at the anode and oxygen at the cathode. This overcomes a disadvantage of galvanic cells where the chemicals reach chemical equilibrium, and the battery goes flat. Even rechargeable galvanic cells will go flat in this way.

FIGURE 1 Hydrogen is used to power space shuttles.

How do hydrogen fuel cells function under acidic conditions?

phosphoric acid fuel cell
a fuel cell that uses liquid phosphoric acid as an electrolyte, producing water, heat and electricity

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.

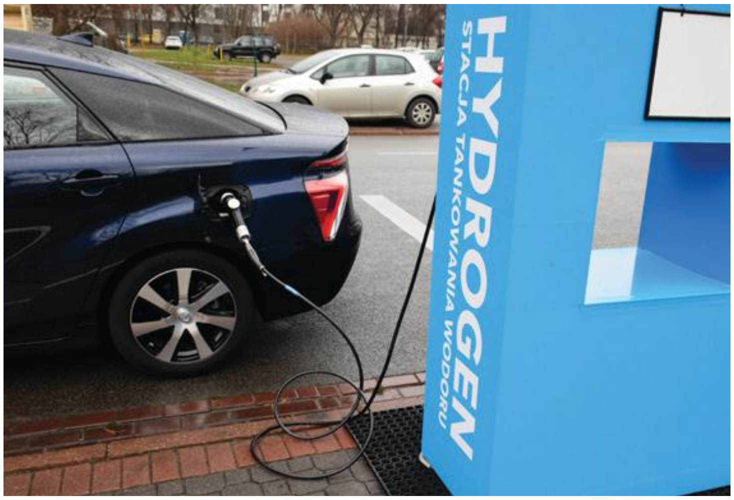


FIGURE 2 A hydrogen fuel cell car with zero emissions

The function of the fuel cell is as follows. Hydrogen molecules (H_2) enter at the anode, where they lose their electrons in a chemical reaction (Figure 3). So, the oxidation half-reaction is:

$$2H_2(g) \rightarrow 4H^+(aq) + 4e^- \quad 0.00\,V$$

The ionised hydrogen travels through the electrolyte, while the electrons travel through an external circuit, providing electricity. Oxygen enters the fuel cell at the cathode and combines with the electrons and protons to form water. This is represented in the half-reaction:

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(g) \qquad 1.23\,V$$

The net chemical reaction is:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \qquad 1.23\,V$$

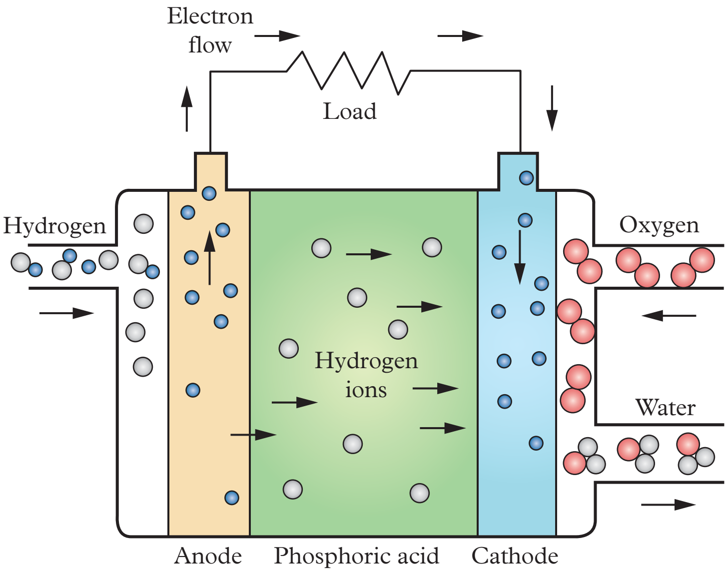


FIGURE 3 A phosphoric acid fuel cell

How do hydrogen fuel cells function under alkaline conditions?

Alkaline fuel cells have been used by NASA since the mid-1960s in the *Apollo* missions. Like the acid-based fuel cells, electrical energy 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 facilitates the reduction of oxygen. An alkaline fuel cell consumes hydrogen, which is oxidised at the anode side (Figure 4), producing water and releasing electrons. This is represented in the half-reaction:

alkaline fuel cell
a fuel cell that consumes hydrogen and oxygen, producing water, heat and electricity

$$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(g) + 2e^- \qquad 0.83\,V$$

The electrons flow through an external circuit and return to the cathode, where oxygen is reduced and hydroxide ions are produced:

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \qquad 0.40\,V$$

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.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \qquad 1.23\,V$$

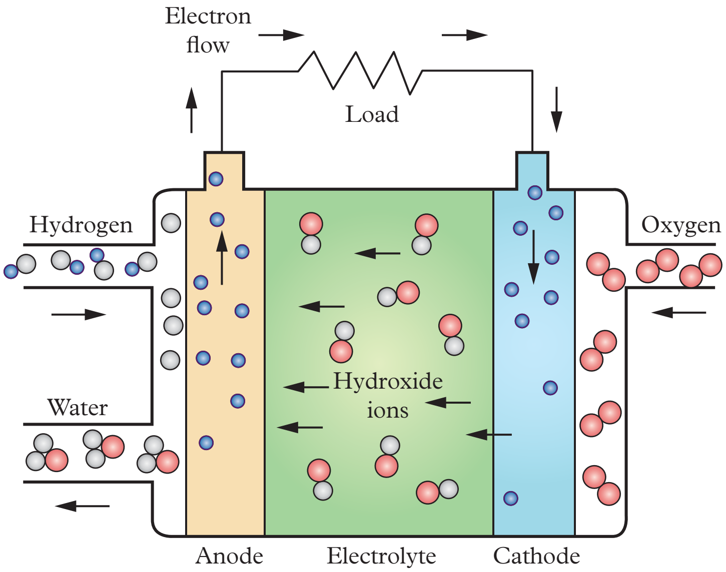


FIGURE 4 An alkaline fuel cell

Study tip

For hydrogen fuel cells in acidic or basic conditions, the half-equations can easily be identified from the table of reduction potentials. Hydrogen gas is always oxidised at the anode, whether H^+ or OH^- is involved. Oxygen is always reduced at the cathode, whether H^+ or OH^- is involved.

Challenge

Calculating the maximum efficiency of a hydrogen fuel cell

Given that the maximum efficiency of the hydrogen fuel cell when water is a product is approximately 83%, **calculate** the maximum efficiency of the hydrogen fuel cell if steam is produced as a product instead of water. **Explain** why there is a decrease in efficiency. (4 marks)

Real-world chemistry

Splitting water to get renewable fuel!

Imagine a future where green chemistry was the main means by which all industries operated, and non-renewable fuel was a thing of the past. The main challenges facing such a future is the high cost of converting renewable energy sources such as solar, wind and hydro energy into fuel.

Ethiopian-American chemist Sossina Haile is tackling these challenges and helping us reduce our reliance on fossil fuels. Sossina has created a method for directly using solar energy to split water to make hydrogen. She has developed fuel cells that use hydrogen to efficiently generate electrical energy from hydrogen. She pioneered solid acid fuel cells (SAFCs), which are less costly than conventional fuel cells, and she has created high-performance solid oxide fuel cells (SOFCs) that can work like batteries – generating electrical power when it is needed and generating hydrogen when there is excess electrical power from renewable energy sources.

Fuel cells directly convert the chemical energy of fuels into electricity without having to burn the fuel in combustion. They are more efficient than combustion engines and release no carbon emissions. Sossina's research has resulted in better materials and catalysts to make SOFCs less costly and more durable. Her current research includes fuel cells designed to operate on fuels beyond hydrogen.

FIGURE 5 Sossina Haile

Apply your understanding

1 **Identify** the key features of SOFCs developed by Sossina Haile and **explain** how these features contribute to more efficient and durable energy conversion than conventional fuel cells. (4 marks)

2 **Explain** the environmental benefits of Sossina Haile's development of SOFCs. (2 marks)

3 **Identify** and **categorise** two renewable energy sources mentioned and **determine** one potential advantage and one challenge for each in the shift towards a future without non-renewable fuels. (4 marks)

Check your learning 13.5

Check your learning 13.5: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Describe** the steps involved in a hydrogen fuel cell under:
  a acidic conditions (2 marks)
  b alkaline conditions. (2 marks)

Analytical processes

2 **Identify** the key components of a hydrogen fuel cell and **compare** them with a traditional galvanic cell. (3 marks)

3 **Derive** the chemical equations for a hydrogen fuel cell that uses aqueous potassium hydroxide (KOH) as the electrolyte. (2 marks)

4 **Discriminate** between a hydrogen fuel cell under acidic conditions and one under alkaline conditions. (2 marks).

Lesson 13.6

Yield of chemical synthesis

Key ideas

→ 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, and it is typically lower than the theoretical yield because of factors such as spills or incomplete reactions; for example, those limited by equilibrium.

→ Yield involves comparing stoichiometric quantities with actual quantities.

→ The yield of chemical synthesis reactions is calculated by finding the fraction of actual yield over theoretical yield and converting to a percentage.

→ To calculate theoretical yield, the limiting reagent must be determined first.

Learning intentions and success criteria

What are excess and 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-cream cones 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

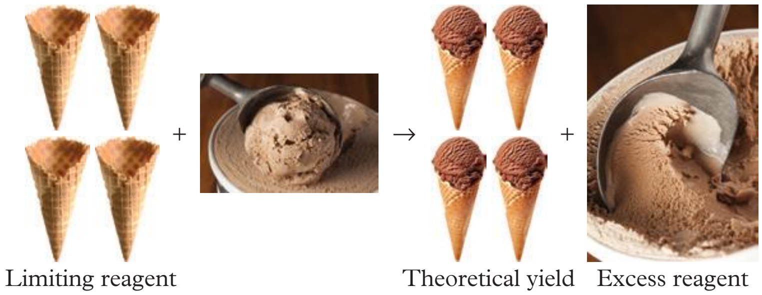


FIGURE 1 An analogy for understanding limiting reagents and theoretical yield

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.

What is the theoretical yield and how is it calculated?

The theoretical yield is the predicted quantity of a product obtained from the complete conversion of the limiting reagent. The expected quantity of product or theoretical yield can be calculated from a balanced chemical reaction assumed to be conducted under ideal conditions. Worked example 13.6A shows you how to calculate theoretical yield.

Worked example 13.6A

Calculating the theoretical yield

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, given that 5.0 g of each reactant was used. (5 marks)

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	“Calculate” means to determine or find a number or answer by using mathematical processes.
Step 2: Write a 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 (1 mark)
Step 3: Calculate the number of moles of each reactant and identify the limiting reagent.	$\frac{5.0\text{ g of } C_7H_6O_3}{138.13\text{ g mol}^{-1}} = 0.036\text{ mol of } C_7H_6O_3$ (1 mark) $\frac{5.0\text{ g of } C_4H_6O_3}{102.10\text{ g mol}^{-1}} = 0.049\text{ mol of } C_4H_6O_3$ (1 mark)
Step 4: Use the number of moles of the limiting reagent to calculate the number of moles theoretically produced of the product using the mole ratio from the balanced equation.	Since the mole ratio is 1:1 $C_7H_6O_3$:$C_4H_6O_3$ Hence, the species with the least number of moles = 0.036 mol of $C_7H_6O_3$. (1 mark)
Step 5: Calculate the theorical mass of product – this is the theoretical yield produced.	Mole ratio is 1:1 for limiting reagent : desired product $C_7H_6O_3$:$C_9H_8O_4$ Number of moles of aspirin = 0.036 mol $m(\text{aspirin}) = n \times M(\text{aspirin})$ $= 0.036\text{ mol} \times 180.17$ $= 6.5\text{ g}$ (1 mark)

Your turn

Calculate the theoretical yield of carbon dioxide gas produced from a reaction of 100 g of iodine (V) oxide (I_2O_5) when reacted with 25 g of carbon monoxide (CO), producing iodine gas (I_2) and CO_2 gas. (4 marks)

What is percentage yield and how is it calculated?

Because industry is regulated by profits, experimental conditions are often managed in order to maximise product. Under non-ideal experimental conditions, especially in large-scale operations, many factors can contribute to a reduced yield of products. This includes loss of products from reaction vessels and impurity of reactants.

Chemical issues that reduce yield include side reactions occurring that can reduce the amount of the specific product being manufactured, reactions occurring in reverse, and changes in temperature and pressure after yields. A measure of the efficiency of a chemical reaction or process is the percentage yield. The **experimental yield** of a product is typically less than the theoretical expected yield. Chemists can also calculate the percentage yield. The percentage yield serves as a measure of effectiveness of the synthesis:

experimental yield
the actual amount of the product

$$\text{Percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$$

Worked example 13.6B

Determining the percentage yield

When 39.75 g of magnesium carbonate decomposed in an experiment, 15 g of magnesium oxide was formed along with carbon dioxide (CO_2).

Determine the percentage yield of magnesium oxide, given that the theoretical yield for MgO was 19.00 g. (2 marks)

$MgCO_3 \rightarrow MgO + CO_2$

Think	Do
Step 1: Look at the cognitive verb and mark allocation to determine what the question is asking you to do.	“Determine” means to establish, conclude or ascertain after consideration, observation, investigation or calculation.
Step 2: Write the percentage yield formula.	$\text{Percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$
Step 3: Substitute the values for experimental and theoretical yields to calculate percentage yield. Ensure that the units are the same for the actual and theoretical yield.	$\text{Percentage yield} = \frac{15\text{ g}}{19\text{ g}} \times 100\%$ $= 78\%$ (1 mark) In this example, the percentage yield of MgO is 78%. (1 mark) Note: The percentage yield of CO_2 is also 78% and it is likely that this is due to 22% of the reactant having remained unreacted.

Your turn

In an experiment where 50.00 g of calcium carbonate ($CaCO_3$) was heated to produce calcium oxide (CaO) and carbon dioxide (CO_2), 22.5 g of calcium oxide was obtained. **Determine** the percentage yield of CaO, given that the theoretical yield was 28.00 g. (2 marks)

Check your learning 13.6

Check your learning 13.6: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain**

- **a** theoretical yield (1 mark)
- **b** percentage yield (1 mark)
- **c** excess reagent (1 mark)
- **d** limiting reagent. (1 mark)

2 In the synthesis of the insecticide DDT, 150 g of chlorobenzene C_6H_5Cl was reacted with 95 g of chloral (C_2HCl_3O):

$$2C_6H_5Cl + C_2HOCl_3 \rightarrow C_{14}H_9Cl_5 + H_2O$$

Calculate the percentage yield if 89 g of DDT ($C_{14}H_9Cl_5$) was obtained. (6 marks)

3 Another key intermediate in the insecticide industry is chlorobenzene, produced from the direct chlorination of benzene. 0.267 kg of benzene (C_6H_6) was reacted in excess chlorine gas (Cl_2) in the presence of a catalyst to produce 0.107 kg of chlorobenzene (C_6H_5Cl) and water (H_2O), **calculate** the percentage yield of chlorobenzene (C_6H_5Cl). (6 marks)

4 Tetraethyl lead ($Pb(C_2H_5)_4$) was used as an anti-knocking agent in petrol before this was stopped because of tetraethyl lead's environmental impact. It was synthesised from ethyl chloride (C_2H_5Cl) and sodium lead (NaPb) alloy. If 1,120 g of C_2H_5Cl was reacted with 678 g of NaPb alloy to produce 780 g of $Pb(C_2H_5)_4$ and sodium chloride (NaCl), **calculate** the percentage yield of tetraethyl lead. (6 marks)

5 Consider the synthesis of phosphorus trichloride (PCl_3) from phosphorus (P_4) and chlorine gas (Cl_2). **Calculate** the mass of phosphorus needed to produce 110 g of PCl_3 if the reaction has an 83.2% yield. (6 marks)

Analytical processes

6 **Derive** an analogy, similar to the ice-cream analogy, to describe theoretical yield, percentage yield, excess reagent and limiting reagent. (2 marks)

7 Consider the following synthesis reaction:

$$2K + Cl_2 \rightarrow 2KCl$$

1 g of each reagent is available.

- **a** **Determine** the limiting reagent. (2 marks)
- **b** **Calculate** the theoretical yield. (2 marks)

Knowledge utilisation

8 **Research** reasons why chemists would be interested in a percentage yield. (2 marks)

MODULE 13

Lesson 13.7

Review: Chemical synthesis

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.
- Chemical synthesis involves designing reaction pathways and selecting reagents and conditions to form a product with desirable properties.
- Ideal reagents and reaction conditions need to be selected to achieve optimal outcomes.

13.2
- Practical: Simulating the Haber process

13.3
- Practical: Simulating the contact process

13.4
- There are many alternatives to fossil fuels. Some of the important ones are biofuels, which include biodiesel, ethanol and hydrogen.
- The production of ethanol can be achieved by fermentation or by hydration of ethane.

13.5
- Hydrogen fuel cells can be used to power engines and generate electricity for other purposes.
- There are two types of fuel cells – one runs under acidic conditions and the other one runs under alkaline conditions.
- Hydrogen fuel cells operate by continually supplying the hydrogen fuel at the anode and oxygen (usually air) at the cathode.
- Diagrams and half-equations can be used to describe the processes occurring in a fuel cell.

13.6
- 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, and it is typically lower than the theoretical yield because of factors such as spills or incomplete reactions; for example, those limited by equilibrium.
- Yield calculations involve comparing stoichiometric quantities with actual quantities.
- The yield of chemical synthesis reactions is calculated by finding the fraction of the actual yield over theoretical yield and converting to a percentage.
- To calculate theoretical yield, the limiting reagent must be determined first.

Key formulas

Percentage yield	$\text{Percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$

Review questions 13.7A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

1 Which of the following is primarily made from natural biological materials and not through chemical synthesis of non-organic material?

A Car doors
B Sausages
C Drink bottles
D Phone screens

2 What is the molecular formula of ethanol?

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 bio-ethanol?

A Yeast
B Reduction
C Fermentation
D Saccharification

4 In a hydrogen fuel cell, electric current is generated by

A fusion.
B fission.
C combustion.
D redox reactions.

5 Identify which factor reduces the product yield of a chemical reaction.

A Catalysts
B Side reactions
C Impurities in reagents
D Removing product in reversible reactions

6 The limiting reagent can be identified by finding the reagent

A with the biggest number of moles.
B with the smallest number of moles.
C that is involved in the rate-determining step.
D that has fewer moles than the stoichiometric ratio required by other reagents.

7 A gas produced during fermentation is

A methane.
B hydrogen.
C water vapour.
D carbon dioxide.

8 In the production of sulfuric acid, which step is a reversible reaction?

A First step: $S(s) + O_2 \rightarrow SO_2$
B Second step: $SO_2 + O_2 \rightarrow SO_3$
C Third step: $SO_3 + H_2O \rightarrow H_2S_2O_7$
D Final step: $H_2S_2O_7 + H_2O \rightarrow H_2SO_4$

9 Which catalyst is required for the synthesis of ammonia in the Haber process?

A V_2O_5
B Fe_2O_3
C NaOH
D An enzyme

10 If 50 g of calcium carbonate is decomposed to form 23 g of calcium oxide and carbon dioxide, what is the percentage yield of calcium oxide?

A 25%
B 82%
C 50%
D 76%

11 Which of the following is true about hydrogen fuel cells?

A They are unsuitable for use in cars and other moving devices.
B Under acid conditions, the cell voltage is larger than under basic conditions.
C They can use hydrogen made from electrolysis using electricity from solar power.
D The anode half-equation involves hydrogen for acidic fuel cells but oxygen for basic fuel cells.

Review questions 13.7B Short response

Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

12 **Define** "chemical synthesis". (1 mark)

13 **Explain** the production of ethanol by the hydration of ethene. Include appropriate chemical equations. (2 marks)

14 **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. (3 marks)

15 **Identify** why the second step of the contact process is often referred to as the rate-limiting step in the production of sulfuric acid. (2 marks)

16 **Construct** the equation for percentage yield. (1 mark)

17 Ammonia, oxygen and methane are used for the synthesis of hydrogen cyanide, which is used in industry, according to the following balanced equation:

$$2CH_4 + 2NH_3 + 3O_2 \rightarrow 2HCN + 6H_2O$$

If 1,500 kg of each reactant is used in the reaction, **calculate** the mass of hydrogen cyanide that will be made, assuming ideal conditions are used to give 100% yield. (2 marks)

18 **Calculate** the mass of calcium oxide required to produce 150 g of calcium hydroxide if the reaction has a 75% yield, given the reaction equation:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \text{(2 marks)}$$

Analytical processes

19 Oxygen gas can be produced by two processes as given by the following skeleton equations:
Water electrolysis: $H_2O(l) \rightarrow H_2(g) + O_2(g)$
Decomposition of hydrogen peroxide:

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

- **a** **Determine** the role of the catalyst in both water electrolysis and the decomposition of peroxide in influencing the rate of oxygen production. (2 marks)
- **b** **Determine** which of the two methods would be considered most appropriate for large-scale oxygen production, making reference to energy requirements and reagent stability based on the data below:

Process	Theoretical yield (g)	Actual yield per 100 g of reactant (g)	Temperature (°C)	Catalyst used
Water electrolysis	89	80	50	None
Hydrogen peroxide decomposition	47	44	25	Manganese dioxide (MnO_2)

20 Two methods can be used to produce ethanol, either the fermentation of sugars such as glucose or the hydration of ethene.

Describe the production of ethanol by fermentation of glucose, including a balanced chemical equation. (3 marks)

21 **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. (2 marks)
- **b** **Calculate** the theoretical yield. (2 marks)
- **c** If there is an excess reagent, **determine** what it would be and its amount (in grams). (2 marks)

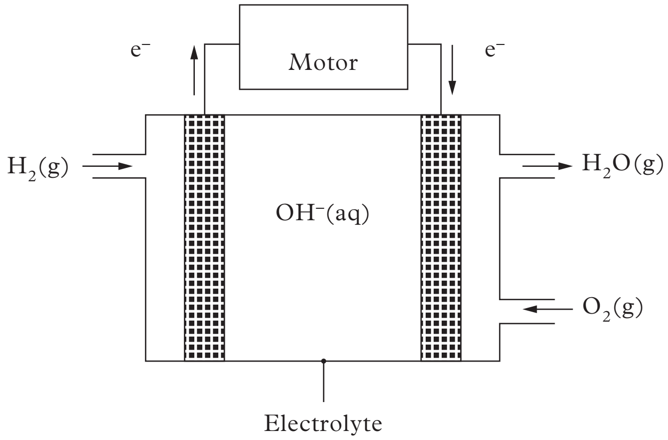
22 A study compared the production of ethanol by the fermentation of glucose and by ethene hydration using equal initial masses of reactants. The data below shows the percentage yield and reaction conditions for each process:

	Fermentation of glucose	Hydration of ethene
Initial reactant mass (g)	100	100
Actual yield of ethanol (g)	51	92
Theoretical yield of ethanol (g)	26	86
Temp. (°C)	30	300
Pressure (kPa)	100	6,000

- **a** Using balanced chemical equations for both processes, **calculate** the percentage yield of ethanol for both processes. (3 marks)
- **b** **Analyse** the data to compare the efficiency of ethanol production by both methods. (3 marks)
- **c** **Interpret** how reaction conditions (temperature, pressure and type of catalysts used) will influence the rate and yield of ethanol production. (6 marks)
- **d** Being an exothermic process, the hydration of ethene to ethanol requires the reaction conditions of temperature 300°C, pressure 6,000–7,000 kPa, catalyst phosphoric(V) acid. **Deduce** why temperature is often considered a compromising condition. (1 mark)
- **e** Considering the cost of reagents and reaction conditions, **determine** which method is likely to be more economical for large-scale ethanol production. (2 marks)

23 Car manufacturers use hydrogen gas as the main fuel in car fuel cells.

This fuel cell has two sections: hydrogen gas is pumped through one half and oxygen gas through the other. The two halves are joined, and an alkaline electrolyte passes through the middle. The electrodes consist of a porous nickel alloy mesh.



a **Construct** the balanced half-equations for the reactions occurring at the anode and the cathode, including the states. (2 marks)

b **Deduce** two roles of the nickel alloy electrodes. (2 marks)

c Research and **identify** any advantages or disadvantage of using acidic over basic electrolytes for the manufacturing of hydrogen fuel cells. (2 marks)

Knowledge utilisation

24 **Predict** the change to the position of equilibrium and the percentage yield of product when the temperature is increased in the synthesis of ammonia using the Haber process. (2 marks)

25 **Investigate** the different chemical synthesis reactions involved in producing ibuprofen commercially. (3 marks)

Data drill

Ammonia production

Ammonia is a precursor to the manufacture of fertilisers, explosives and cleaning agents and is produced in the Haber process. Its production depends on the careful selection of reaction conditions to optimise the amount produced while making it affordable to manufacture. Maximum rate of production occurs far from equilibrium and falls as equilibrium conditions are approached. Maximum yield is the estimated yield once equilibrium is reached.

The expression for the equilibrium constant based on pressure is:

$$\frac{P_{NH_3}{}^{2}}{P_{N_2} \times P_{H_2}{}^{3}}$$

In practice, manufacturing facilities cool the reaction mixture to condense and remove ammonia after a time, before reaching equilibrium, and recycle unused reactants. High pressures and temperatures are a cost in this industrial process

TABLE 1 The equilibrium constant for the production of ammonia at a range of temperatures

Temperature (°C)	Equilibrium constant calculated using pressures rather than concentrations (K_p)
300	not provided
350	1.6×10^{-3}
400	1.64×10^{-4}
450	4.51×10^{-5}
500	1.45×10^{-5}

TABLE 2 Maximum rate of ammonia production at different temperatures

Temperature (°C)	Maximum rate of ammonia production (mol s^{-1}) per m^3 of reactor
200	0.1
300	1.0
400	3.0
500	6.0
600	20.0

TABLE 3 Estimated percentage yield at equilibrium of ammonia at different temperatures when the reactor pressure is 30,000 kPa

Temperature (°C)	Estimated percentage yield at equilibrium of ammonia (%)
200	33.5
300	24.5
350	19.0
400	Not provided
450	11.2
500	7.5
600	1.0

Apply understanding

1 **Identify** the estimated percentage yield at equilibrium of ammonia at a temperature of 200°C. (1 mark)

2 A particular reactor has a volume of 50 m^3. **Calculate** the maximum rate of ammonia production at a temperature of 500°C. (1 mark)

Analyse data

3 **Identify** the trend in the percentage yield as temperature increases. Provide evidence. (2 marks)

4 **Classify** the reaction as exothermic or endothermic. Provide evidence. (2 marks)

Interpret evidence

5 **Determine** the value of the yield of ammonia at 400°C. **Justify** your reasoning. (2 marks)

6 **Determine** a possible value of the equilibrium constant at 300°C. **Justify** your reasoning. (2 marks)

Module 13 checklist: Chemical synthesis

MODULE 14

Macromolecules

Introduction

Macromolecules are large complex molecules often associated with biological processes such as energy storage, cellular structure, cellular function and biochemical reactions involved in growth and metabolism. Biochemical macromolecules are present in all living things and can be further categorised as proteins, carbohydrates, lipids or nucleic acids. Macromolecules have many shapes and forms. DNA is made up of repeating monomer units, as are proteins and carbohydrates. Proteins are long chains of amino acid monomers that can fold to form strong structures such as hair, fingernails and muscle tissue. Carbohydrates can be obtained from food and are the main energy source for our bodies.

Macromolecules can also be synthesised; for example, textile fibres, plastics and adhesives. Macromolecules are often referred to as “polymers”. Synthetic polymers include plastics, and natural biopolymers include silk and wool, which are part of many fabrics that are made up of repeating smaller molecules called monomers. Monomers are chosen for their specific characteristics such as malleability, biodegradability, tensile strength and transparency.

Prior knowledge

Prior knowledge quiz

Check your understanding of concepts related to macromolecules before you start.

Subject matter

Science understanding

→ Describe, using equations, how
  - addition polymers including polyethene (LDPE and HDPE), polypropene and polytetrafluoroethene can be produced from their monomers
  - condensation polymers, including polysaccharides (carbohydrates), polylactic acid (PLA), polyamide (proteins and nylon) and polyester, can be produced from their monomers.

- → Apply amino acid symbols to construct and name tripeptides.
- → Identify that tripeptides are formed when amino acid monomers are joined by peptide bonds.
- → Identify that disaccharides are formed when monosaccharides monomers are joined by glycosidic bonds.

Science inquiry

- → Investigate the properties of polymers.

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Practicals

This lesson is available on Oxford Digital.

Lesson 14.3 Investigating the properties of polymers

Lesson 14.1

Addition polymers

Key ideas

→ 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).

How are addition polymers formed?

Learning intentions and success criteria

free radical an uncharged species with an unpaired electron; highly reactive

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 and do not produce any by-products. Addition polymerisation occurs in three steps.

1 **Initiation**: a **free radical** (an uncharged species with an unpaired electron) such as a hydroxyl radical ($HO^{\bullet}$) attaches to the carbon–carbon double bond in monomers so that a new radical is formed in the process.
2 **Propagation**: the new free radical compound continues to react with another monomer, repeating until chains of many carbon atoms long are formed.
3 **Termination**: two free radicals combine to form a covalent bond that links the two chains together (Figure 1).

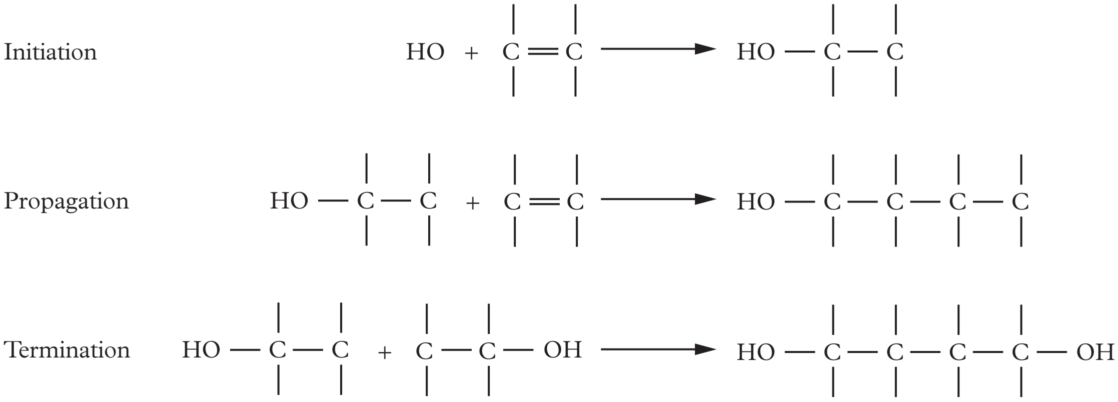


FIGURE 1 Stages of addition polymerisation

In this lesson, you will learn how three common addition polymers – polyethene, polypropene and polytetrafluoroethene – are formed from their monomers.

How is polyethene (LDPE and HDPE) formed?

Polyethene (also known as polyethylene) is the most common thermoplastic and often 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. Consequently, the type of plastic bag or bottle produced can be modified by the conditions of manufacturing. The average polymer molecule contains 4,000–40,000 carbon atoms. The two types of polyethene plastics are **low-density polyethene (LDPE)** and **high-density polyethene (HDPE)**.

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)

LDPE

LDPE is used for products such as trays and containers. Recall that LDPE is 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 recycling code 4, as shown in Figure 2.

FIGURE 2 LDPEs have the recycling code 4.

LDPEs are produced under very high pressure (100–300 MPa) at temperatures of about 300°C by passing ethene molecules onto a reactor with an initiator such as a small amount of oxygen or an organic peroxide (Figure 3).

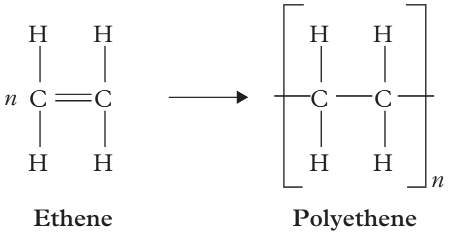
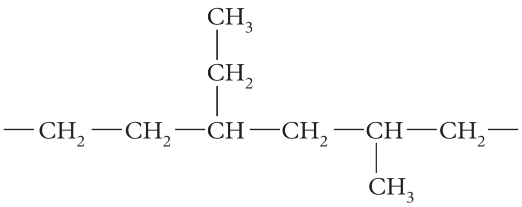


FIGURE 3 The production of polyethene from ethene monomers

The product, polyethene, is removed and cut into granules for further processing. The structure of the molecule has many branches, as shown in Figure 4.

The branches determine the degree of crystallinity of the polymer, which in turn determines its density. The branches prevent the molecules from coming close to each other and so LDPEs usually have low densities. LDPEs are typically amorphous and transparent.



$$-CH_2-CH_2-\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{\overset{CH_2}{\overset{|}{CH}}}}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-$$

FIGURE 4 Part of a multi-branched molecule of LDPE

HDPE

HDPE is used to construct products such as outdoor furniture, bottles for household cleaners (Figure 5) and household appliances. HDPE is a thermoplastic and has the recycling code 2 (Figure 6).

FIGURE 5 Bottles for household cleaners are often made of HDPE.

FIGURE 6 HDPEs have the recycling code 2.

HDPE is produced at low pressures and temperatures (a few hundred kilopascals and about 60°C). Catalysts such as the Ziegler–Natta and metallocene catalysts or activated chromium/silica enable the formation of free radicals at the ends of the growing polyethene chains. There are minimal or no branches, so the polymer chains pack closely together, resulting in a very strong, dense, highly crystalline material. HDPE melts at temperatures above 120°C, which is higher than that of LDPE (which is in the range of 105–115°C) and makes HDPE durable enough to be sterilised.

How is polypropene (PP) formed?

Polypropene (PP) (also known as polypropylene) is another thermoplastic that is used in a variety of applications where it is important that the structure can resist fatigue. It is formed from the addition polymerisation of propene monomers (Figure 7).

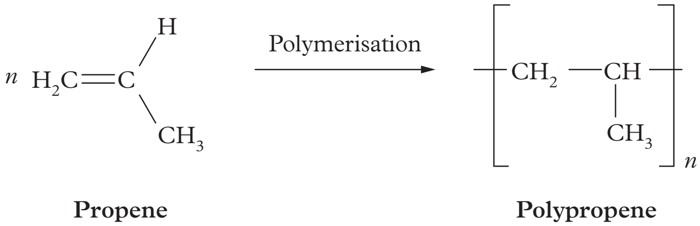


FIGURE 7 The production of polypropene from propene monomers

Polypropene is used for plastic parts in products such as toys, automobile products and fibres used in athletic clothing. This reflects how modifying the type of substituents affects the behaviour of the overall polymer. In PP, the CH_3 groups can vary in arrangement and in doing so the resulting PP plastic can consequently vary in strength and flexibility. When the CH_3 groups of PP are arranged on the same side of the chain an isotactic chain of PP is formed (Figure 8).

Study tip

Although "ethylene" might be more commonly used, the IUPAC name is "ethene". The common names for the polymer from ethene are "polythene" or "polyethylene", but the IUPAC name is "polyethene".

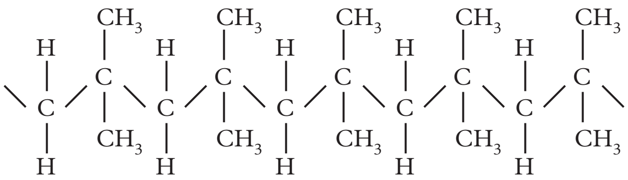


FIGURE 8 Isotactic polypropene

When the CH_3 groups are arranged on alternate sides of the chain, a syntactic chain form of PP is formed. When the CH_3 groups are randomly distributed along the PP chain, an atactic form of PP chain is formed (Figure 9).

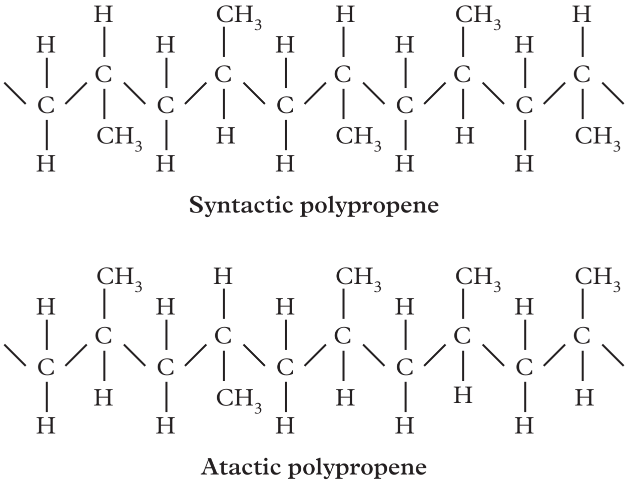


FIGURE 9 Syntactic (also known as syndiotactic) polypropene and atactic polypropene

Study tip

Syntactic polypropene is referred to as syndiotactic polypropene in some references. They mean the same thing. Use "syntactic" because that is the name the QCAA syllabus uses.

The most common form of PP is the isotactic form produced through the use of the Ziegler–Natta catalyst, $TiCl_4 + Al(C_2H_5)_3$. As a result of the high level of symmetry, isotactic PP chains tend to pack closer together to produce a more crystalline structure that makes it stronger and harder than the other two types of polypropene. It is used to produce pipes, fibres and moulded parts. Because isotactic polypropene can withstand heat, it is also used to produce medical and laboratory plastic products.

FIGURE 10 Polypropene has the recycling code 5.

How is polytetrafluoroethene (PTFE) formed?

Polytetrafluoroethene (PTFE) (also known as polytetrafluoroethylene) is another thermoplastic that has many applications due to its anticorrosive and non-reactive properties. For example, PTFE is used in non-stick frying pans (where it is known as Teflon Figure 11), medical implants, clothing, insulation for cables, chemical containers and pipes. PTFE does not have its own recycling code symbol. PTFE is a fluoropolymer or fluorocarbon that contains only carbon and fluorine. It is produced by free-radical polymerisation of tetrafluoroethene (Figure 12).

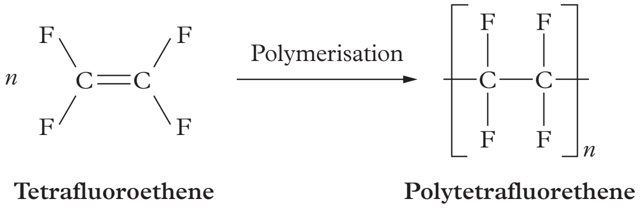


FIGURE 12 The production of polytetrafluoroethene from tetrafluoroethene

FIGURE 11 The surface of a non-stick frying pan is made of PTFE

Check your learning 14.1

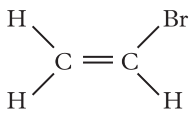
Check your learning 14.1: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain** the steps in an addition polymerisation reaction. (3 marks)

2 **Identify** which forms of polyethene requires:
  - **a** high temperatures and pressures for its formation (1 mark)
  - **b** Ziegler–Natta and metallocene catalysts. (1 mark)

3 **Construct** a section of the polymer made from an addition reaction of the monomer shown below. (2 marks)



4 The molecule chloroethene is commonly called vinyl chloride. It reacts to form the polymer, polyvinylchloride commonly known as PVC or vinyl. **Describe**, using an equation, how PVC is formed from *n* molecules of its monomer. (2 marks)

Analytical processes

5 **Distinguish** between LDPE and HDPE. (1 mark)

6 **Determine** the molecular formula of a molecule made from an addition polymerisation reaction of
  - **a** three ethene monomers (2 marks)
  - **b** four tetrafluoroethene monomers (2 marks)
  - **c** three propene monomers. (2 marks)

Knowledge utilisation

7 **Determine** whether LDPE or HDPE would be best for the following uses. **Justify** your answers.
  - **a** Wrapping material for food (2 marks)
  - **b** Drink bottles (2 marks)
  - **c** Flexible plastic lids (2 marks)

Lesson 14.2

Condensation polymers

Key ideas

→ 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 including polyamides (proteins), polysaccharides (carbohydrates) and polyesters are condensation polymers. Polylactic acid (PLA) is a biodegradable type of polyester formed from renewable sources.

Learning intentions and success criteria

How are condensation polymers formed?

Another type of polymerisation reaction is condensation polymerisation, in which a small molecule such as water or methanol is formed for each extension of the polymer chain. Condensation polymerisation is a form of step-growth polymerisation and produces linear polymers from **bifunctional monomers** (monomer with two functional groups). The functional group on one monomer reacts with the functional group of another monomer to produce a small by-product. The formation of this product then allows the monomers to bond together.

bifunctional monomer
a monomer that contains two functional groups, which can be the same or different

Naturally occurring condensation polymers include polypeptides (proteins) and polysaccharides (carbohydrates). Synthetic condensation polymers include polylactic acid (PLA), polyamides (proteins and nylons) and polyester. These synthetic polymers are often developed to produce textiles and industrial fabrics such as ropes, plastics and carpeting.

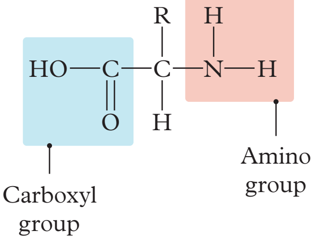
For polyesters, a single monomer containing both a carboxyl (acid) group and a hydroxyl (alcohol) group can be used; alternatively, two different monomers, a diacid with two carboxyl groups and a diol with two hydroxyl groups can be used. Similarly, polyamides can be produced from a single monomer that contains an acid and an amine, or two different monomers, a diacid and a diamine.

FIGURE 1 Nylon used in nylon rope is created through a synthetic condensation polymerisation reaction.

How are polypeptides (proteins) formed?

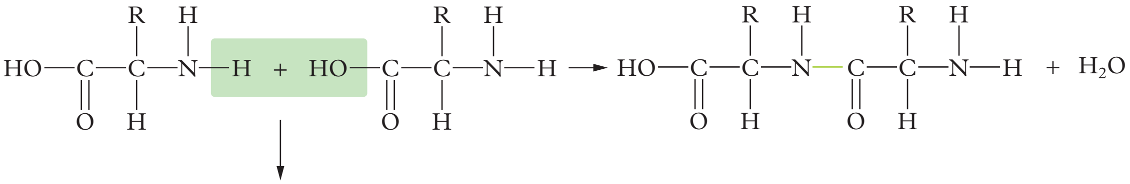
Polypeptides are chains of amino acids. Amino acids contain an amino (NH_2) group and a carboxyl (COOH) group, so they are bifunctional monomers in which the functional groups are different. Typically, there are 20 different amino acids in proteins and usually at least 300 amino acids per protein molecule. Amino acids differ in their R groups and have different properties (Figure 2).

Polypeptides are formed when the NH_2 of one amino acid reacts with the COOH group of another amino acid. A covalent bond forms between carbon and nitrogen atoms and water is produced as a by-product. This type of bond is a peptide bond and links together the monomers in the polypeptide (Figure 3). The sequence and number of amino acids in the polypeptide chain makes up the primary structure, which consequently folds into its final configuration as a functional protein molecule.



$\mathrm{HO{-}C({=}O){-}C(R)(H){-}N(H){-}H}$

FIGURE 2 Amino acids have a carboxyl (COOH) and amine (NH_2) functional groups.



$\mathrm{HO{-}C({=}O){-}C(R)(H){-}N(H){-}H + HO{-}C({=}O){-}C(R)(H){-}N(H){-}H \rightarrow HO{-}C({=}O){-}C(R)(H){-}N(H){-}C({=}O){-}C(R)(H){-}N(H){-}H} + H_2O$

FIGURE 3 Polypeptides are formed in a condensation reaction between two amino acids.

How are polysaccharides (carbohydrates) formed?

Polysaccharides (polymer carbohydrates) are long chains of smaller carbohydrates called monosaccharides. Polysaccharides, which include both starches and cellulose, are found in foods such as fruit, vegetables and grains. Starches are digested to form monosaccharides, which provide us with energy when they are oxidised. Cellulose is not digested by humans but plays an important role as dietary fibre. In humans, polysaccharides form part of the structures of some cells and tissues. They can be linear or branched and are typically 200–2,500 monosaccharides long. Glycogen is a branched carbohydrate found in the liver and is used as a storage for saccharides for energy. It can break down and release glucose into the blood for the cells. Glucose and fructose are two common monosaccharides.

Each monosaccharide monomer has multiple hydroxyl (OH) groups. When the OH of one monosaccharide reacts with the OH of another monosaccharide, a glycosidic bond (–O–) forms linking together the two monomers and water is produced as a by-product. Figure 4 shows two glucose molecules undergoing a condensation reaction to form maltose (a disaccharide).

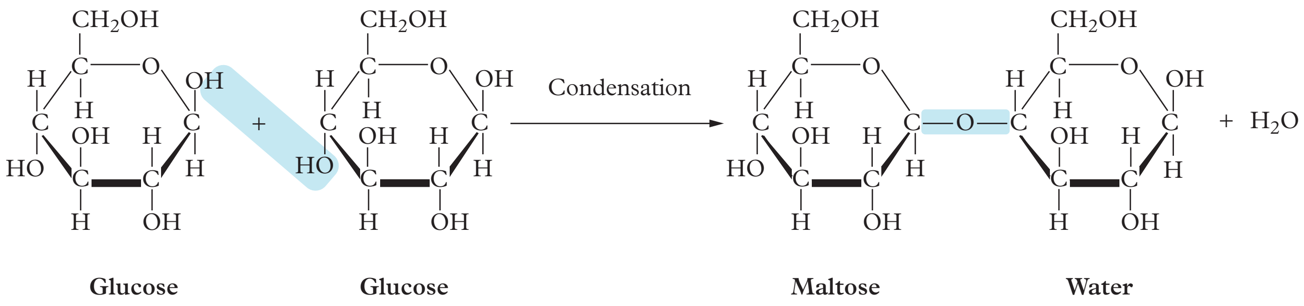


FIGURE 4 The condensation reaction of two glucose molecules to form maltose. Water is lost when a glycosidic bond is formed.

The formation of a polysaccharide from monosaccharides can be represented in the equation:

$$n(C_6H_{12}O_6) \rightarrow [C_6H_5O_5]_n + nH_2O$$

How are polyesters formed?

polyester
a type of polymer that contains an ester functional group in its main chain

Polyesters are extremely important polymers that contain an ester functional group in their main chain. Polyesters include thermoplastics and are extensively used for clothing and food packaging, and to make skydiving suits and parachutes (Figure 5).

FIGURE 5 Polyesters are typically used to make the suits and parachutes for skydivers.

For polyesters, a single monomer containing both a carboxyl (acid) group and a hydroxyl (alcohol) group can be used; alternatively, two different monomers, a diacid with two carboxyl groups and a diol with two hydroxyl groups can be used. 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 a diacid (benzene-1,4-dicarboxylic acid) and a diol (ethane-1,2-diol) (Figure 6).

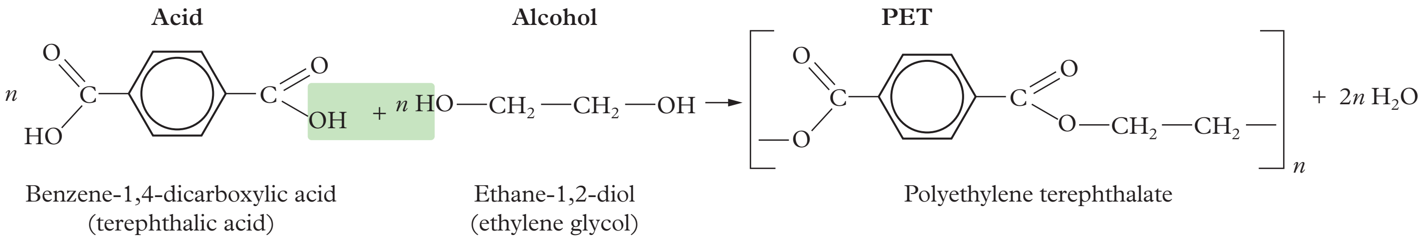


FIGURE 6 Formation of polyesters

How is polylactic acid formed?

Polylactic acid (PLA) is a type of polyester and can be synthesised from lactic acid monomers in the condensation reaction shown in Figure 7. The hydroxyl group from one lactic acid molecule reacts with the carboxyl group from another lactic acid molecule. A covalent bond is formed between an oxygen and a carbon atom and water is produced as a by-product.

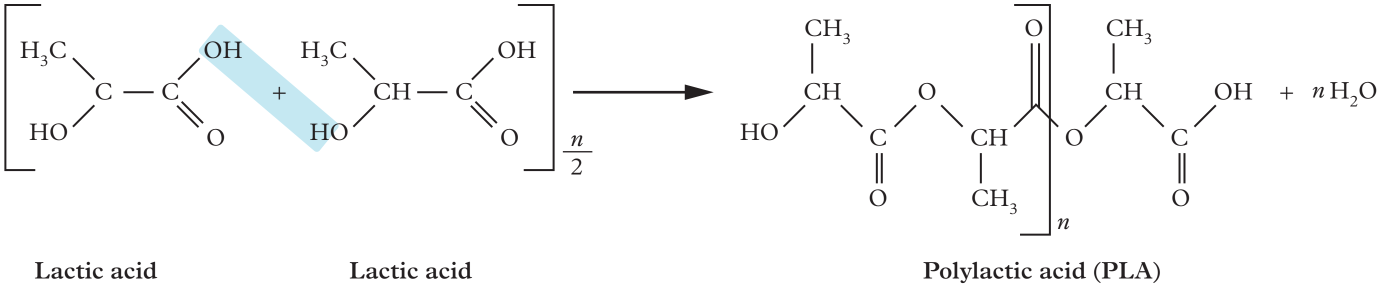


FIGURE 7 The formation of polylactic acid from lactic acid monomers

Because an equilibrium occurs between the reactants and products, water needs to be continually removed in order to generate polymers with a high molecular weight. The reaction in Figure 7 can be summarised as:

$$n\mathrm{C(CH_3)(OH)HCOOH} \rightarrow [\mathrm{-C(CH_3)HC(=O)O-}]n + n\mathrm{H_2O}$$

An alternative method uses the lactide, which is a dimer made from two molecules of lactic acid but with the H_2O already removed, and has the formula $[\mathrm{-C(CH_3)HC(=O)O-}]_2$.

PLA is produced from renewable sources; for example, fermented plant starch from plants such as corn, cassava, sugar cane or sugar beet pulp. It is considered a more environmentally friendly polymer than the many polymers that are synthesised from fossil fuels, including PET.

How are synthetic polyamides formed?

Natural polyamides include the proteins wool, silk and collagen; synthetic polyamides can be further categorised based on the composition of their main chain and include aliphatic polyamides, aromatic and semi-aromatic polyamides. Polyamides can be produced from a single monomer that contains an acid and an amine, or two different monomers, which are a diacid and a diamine. An example of an aliphatic polyamide is nylon (nylon 66).

Nylon is a well-known synthetic polyamide. There are several forms of nylon; some forms are made from a single monomer, which has an acid group at one end and an amine group at the other end. Other forms of nylon are copolymers, meaning they consist of two different precursor monomers that are joined together.

An example of nylon is one made from two monomers hexane-1,6-diamine (which has two amine functional groups) and hexanedioic acid (which has two carboxyl functional groups). An amine group of the hexane-1,6-diamine and a carboxyl group of the hexanedioic acid react to form a water molecule and an amide bond (C–N), which links the two monomers together. The name, nylon 66 refers to the six carbons in the diamine and the six carbons in the diacid (Figure 8).

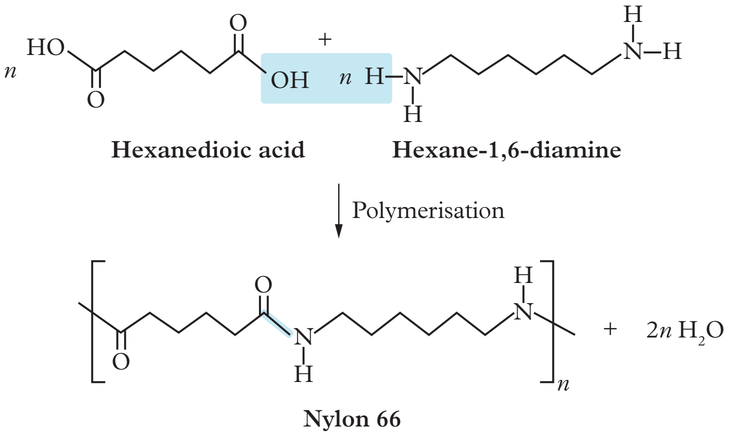


FIGURE 8 The condensation polymerisation reaction to produce nylon 66

The nylon dimer can undergo further condensation reactions because it has an amino group at one end and a carboxyl group at the other. Both ends of the dimer are free to react with other monomers to extend the polymer chain and give the basic structure of nylon.

Nylon's physical properties of strength and temperature resistance depend on the number of carbon atoms in the chain of the diacid or diamine monomers. Other common forms of nylon manufacturing include using glycols and dinitriles as monomers, or as in the case of nylon 16 formation adiponitrile, formaldehyde and water are used (Figure 9).

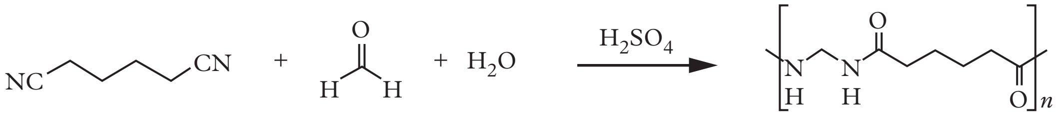


FIGURE 9 Formation of nylon 16 from adiponitrile, formaldehyde and water catalysed by sulfuric acid

Nylon 6 forms from a molecule with a 6-carbon chain and an acid and an amine group.

Real-world chemistry

Kevlar

In 1965, while working for DuPont at the polymer research unit, Stephanie Kwolek came across polyamide intermediates that line up in parallel to form cloudy liquid crystalline solutions. Kwolek specialised in synthesising aromatic polyamides by preparing viscous and clear intermediate compounds that could be dissolved in solvents and spun into fibres. At the time, Kwolek was tasked with developing a heat-resistant fibre as an alternative to steel wires in car tyres. Most researchers would have discarded the solution because of its cloudy state, and the likelihood of it clogging the spinneret. But Kwolek took the chance and spun the solution, only to realise that the resulting fibres were stronger and stiffer than anything she had seen before. This unexpected discovery led to the creation of Kevlar – a petroleum-based synthetic fibre that is lighter than fibreglass but five times stronger than steel.

Today, Kevlar's functionality and ability to resist tears, bullets, extreme temperatures and other conditions makes it versatile for use in bulletproof vests (Figure 10), protective gloves to spacecraft manufacturing, helmets and tyres. Kwolek continued to develop novel synthetic polyamide fibres until her retirement in 1986. She received various awards, including the Perkin Medal and the National Medal of Technology in 1999 and was inducted into the National Inventors Hall of Fame in 1994.

Apply your understanding

1 **Identify** the chemical property of the polyamide intermediates discovered by Stephanie Kwolek that contributed to the ultimate production of Kevlar. (1 mark)
2 **Explain** how Kwolek's decision to spin the cloudy liquid crystalline solution led to the development of Kevlar and its subsequent applications. (1 mark)
3 **Determine** two key characteristics of Kevlar fibres that help categorise them as either condensation polymers or addition polymers. (2 marks)

FIGURE 10 Kevlar is used in bulletproof vests.

Challenge

Synthetic and natural polymers

Spider silk has long been recognised for its remarkable strength and elasticity, making it an ideal model for developing high-performance synthetic polymers. Scientists have recently synthesised new polymers inspired by spider silk's molecular structure, which combine extreme strength with biodegradability. These polymers offer the toughness of traditional materials such as Kevlar while breaking down more readily in the environment, reducing long-term waste. Commercially, these synthetic polymers are now produced by advanced bioengineering and chemical synthesis methods, rather than relying on natural spider silk extraction. This shift towards synthetic production enables greater scalability, consistency and environmental control.

Discuss and suggest reasons for why synthetic production is preferred over natural extraction in modern polymer development. (3 marks)

Skill drill

Manufacturing polyproteins

Science inquiry skill: Evaluating evidence (Lesson 1.8)

Scientists have recently succeeded in isolating, sequencing and identifying the 10 integral amino acid monomer units responsible for the formation of the hormone insulin. Patients suffering from diabetes mellitus type I have low insulin levels. An environmentally induced insulin deficiency has also been identified in type II patients. The process of genetically manufacturing insulin naturally in patients is extensive, expensive and associated with risks and unknown potential side effects due to incorrect isomer forms of the polyprotein manufactured, through the stem cell research in which it is conducted.

Practise your skills

1 **Propose** a reason why random sequencing of the identified amino acid monomers may not always result in a functional polypeptide chain/protein. (1 mark)
2 **Evaluate** the claim "Stem cell genetic manipulation offers unparallelled potential to treat previously incurable diseases through the sequencing and development of super-polypeptides, polyesters and polymers in general". (3 marks)

Check your learning 14.2

Check your learning 14.2: Complete these questions online or in your workbook.

Retrieval and comprehension

1 **Explain** what a condensation reaction is. (2 marks)

2 **Describe** what components are needed to produce

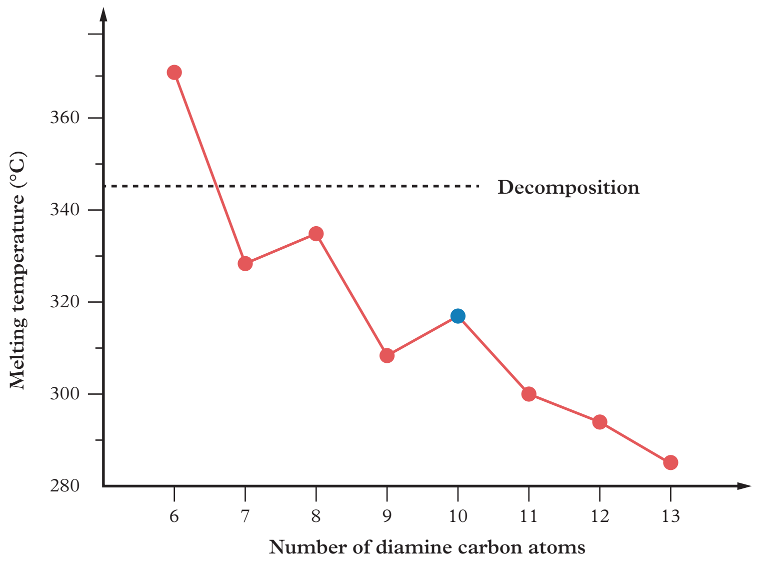
- a a polypeptide (1 mark)
- b a polysaccharide (1 mark)
- c polylactic acid (PLA). (1 mark)

3 **Explain** what a glycosidic bond is. (1 mark)

Analytical processes

4 **Contrast** polysaccharides, proteins and polyamides. Ensure that you refer to types of monomers and bonding that form the overall structures. (6 marks)

5 **Determine** the relationship between the carbon chain length of diamine monomers and the melting point of the nylon polymer derived from them as depicted in the graph. (2 marks)



Knowledge utilisation

6 **Predict** which polymers – polyesters, polyamides, proteins or polysaccharides – would degrade the fastest under natural environmental conditions. **Justify** your prediction by discussing the chemical structure and bond stability of each polymer. (4 marks)

Practical

Lesson 14.3

Investigating the properties of polymers

Learning intentions and success criteria

oxforddigital

This practical lesson is available on Oxford Digital. It is also provided as part of a printable resource that can be used in class.

Lesson 14.4

Amino acids and polypeptides

Key ideas

- → Amino acids contain an acid group and an amine group, and can be distinguished and named by their R group (side chain or residue).
- → Tripeptides are formed from three amino acids joined by peptide bonds.
- → Tripeptides are named in sequence using the three-letter symbols for each amino acid.

Learning intentions and success criteria

What are 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 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).

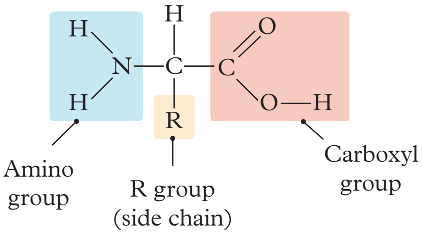


FIGURE 1 The general structure of an amino acid

Plants can produce all 20 amino acids, but animals cannot so they must obtain some through their diet. Humans can only synthesise 11 of the 20 amino acids (classified as non-essential). The remaining 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.

Study tip

The QCAA *Formula and data book* includes the 20 amino acids, with their common names, three-letter symbols, structural formulas and pH values at their isoelectric point.

FIGURE 2 Fish, chicken, eggs and soy all provide the nine essential amino acids.

How are tripeptides formed?

Amino acids contain two main functional groups, an amine group (–NH_2) and a carboxylic acid group (–COOH). These two groups can react together to produce an amide product known as a dipeptide. A dipeptide is produced when the carboxyl group of one amino acid reacts with the amine group of another amino acid producing water and a polypeptide bond between carbon and nitrogen (Figure 3).

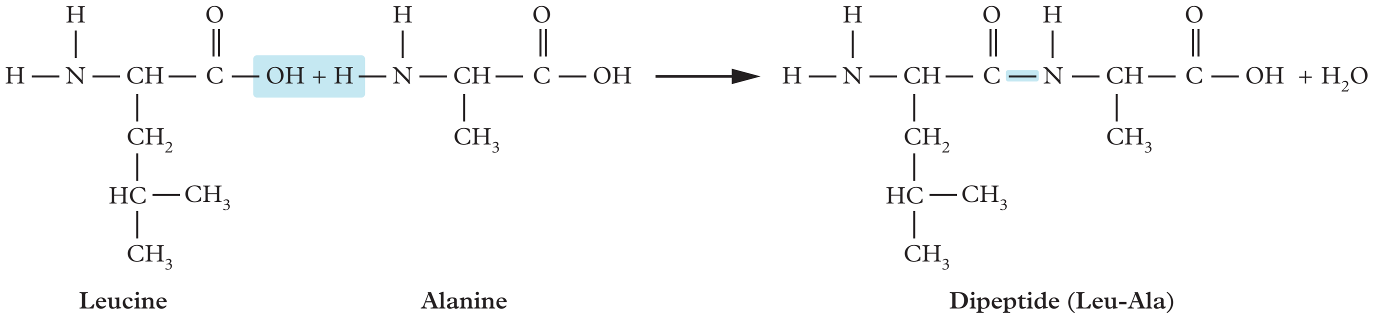


FIGURE 3 The formation of the dipeptide Leu-Ala from a condensation reaction between leucine and alanine

tripeptide
a molecule that contains three amino acids linked by peptide bonds

Since the resulting dipeptide still has a functional amine group and a carboxylic acid group at each end of the molecule, another condensation reaction can occur with a third amino acid to form a **tripeptide**. The formation of a tripeptide occurs when the amine group of the third amino acid reacts with the carboxylic acid group of the dipeptide or vice versa (Figure 4).

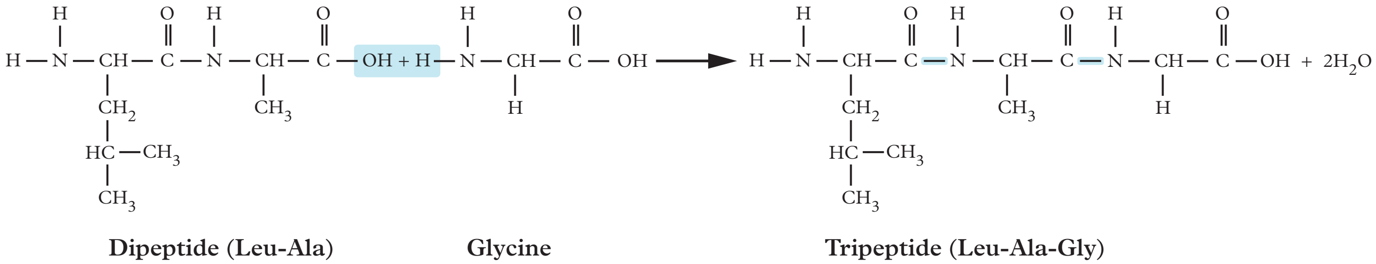


FIGURE 4 The formation of the tripeptide Leu-Ala-Gly from a condensation reaction between the dipeptide Leu-Ala and glycine

Because the third amino acid has two possible locations where a peptide link can be formed to produce a tripeptide, variations in the exact order of the amino acids in sequence exists. Additional condensation reactions lengthen the amino acid chain to eventually produce a polypeptide, which is the basis for a functional protein molecule.

The order of amino acids in peptides is indicated by a three-letter code for each amino acid (see the QCAA *Formula and data book*) separated by hyphens. By convention, the terminal amine group of the first amino acid is on the left-hand side of the peptide chain. The terminal carboxyl group of the last amino acid is on the right-hand side of the peptide chain. For example, one possible sequence containing the three amino acids glutamine, methionine and cysteine (Gln-Met-Cys) is shown in Figure 5.

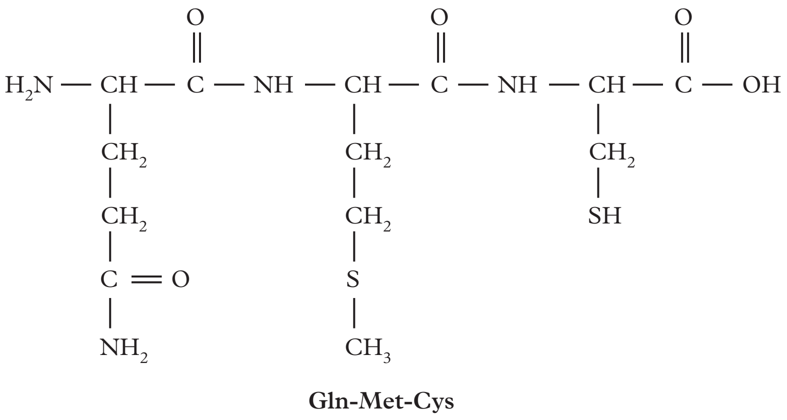


FIGURE 5 The tripeptide Gln-Met-Cys

It is worth noting that five other alternatives of tripeptides could have been formed from the same three amino acids: Gln-Cys-Met, Cys-Gln-Met, Cys-Met-Gln, Met-Gln-Cys or Met-Cys-Gln. Because of this, tripeptide sequences are identified with the amine end stated first and the carboxylic acid end stated last. Names can also have the three-letter symbol for the first two amino acids, and end with the prefix of the name of the third, with a suffix of "-ic acid".

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 because it produces a molecule of water. Since a total of six different tripeptides can be formed from three amino acids, a polypeptide with 20 acids can form a much larger variety of combinations to construct proteins. This flexibility allows an organism to tailor the specific proteins manufactured for a variety of functions

Worked example 14.4A

Applying amino acid symbols to name a tripeptide

Identify the three amino acids that form the tripeptide shown and **determine** the name of the tripeptide in Figure 6. (2 marks)

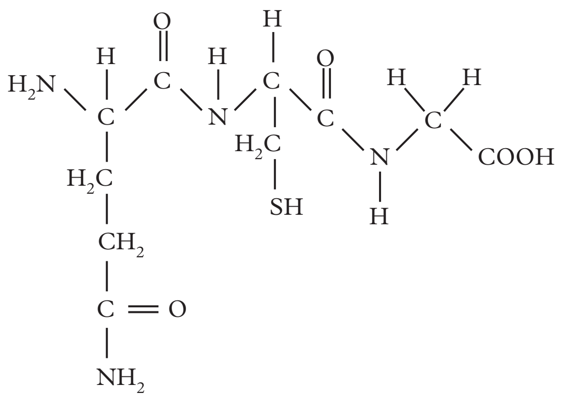
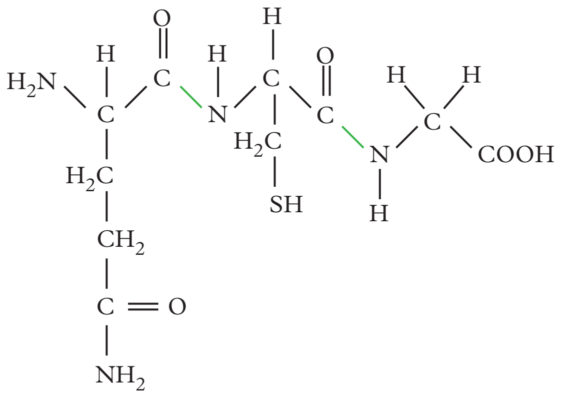
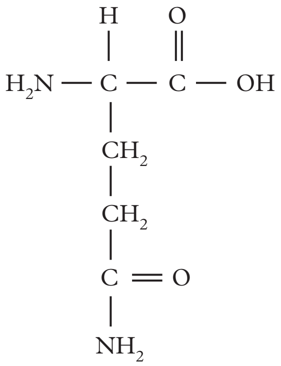
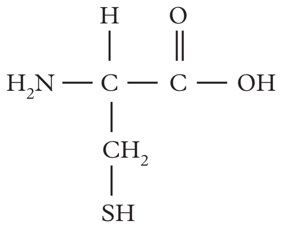
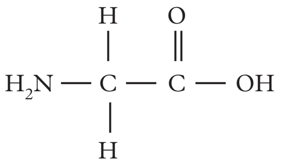


FIGURE 6 A tripeptide

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the question requires you to do.	"Identify" means to recognise and name something. "Determine" means to establish after consideration. The question is worth 2 marks, 1 mark for identifying the three amino acids that make up the tripeptide and 1 mark for determining the correct name of the tripeptide.
Step 2: Locate the two peptide bonds in the molecule (C–N). These bonds indicate where one amino acid ends and another begins.	
Step 3: Break up the tripeptide to identify the three amino acids. Remember that each amino acid should have a carboxyl group and an amine group, so remember to add the OH and H back to each amino acid where applicable.	 Amino acid 1  Amino acid 2  Amino acid 3
Step 4: Use the common amino acids table in the QCAA *Formula and data book* to determine the names of the three amino acids.	Amino acid 1 is glutamine because it is composed of a 5-carbon chain molecule with one amine and one amide functional group. Amino acid 2 is cysteine because it is composed of a 3-carbon chain molecule with an SH bond. Amino acid 3 is glycine because it is composed of only a 2-carbon chain. (1 mark)
Step 5: Name the tripeptide in sequence using three-letter codes separated by hyphens.	From the amine end, in sequence, to the acid end, the amino acids are glutamine (Gln), cysteine (Cys) and glycine (Gly), linked by peptide bonds. Therefore, the tripeptide is Glu-Cys-Gly. (1 mark)

Your turn

Identify the three amino acids that form the tripeptide shown and **determine** the name of the tripeptide in Figure 7. (2 marks)

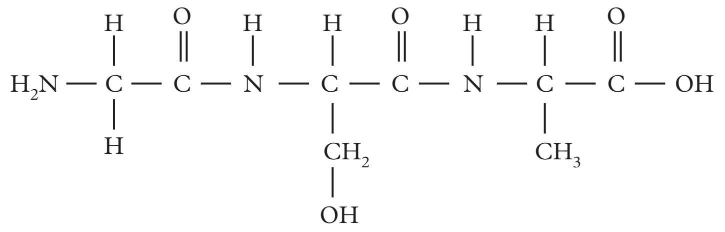
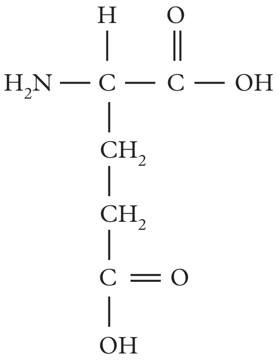
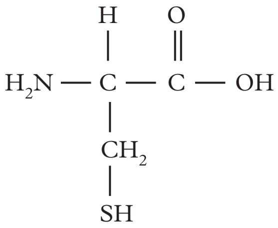
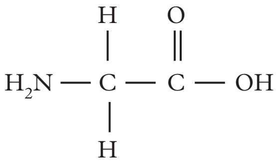
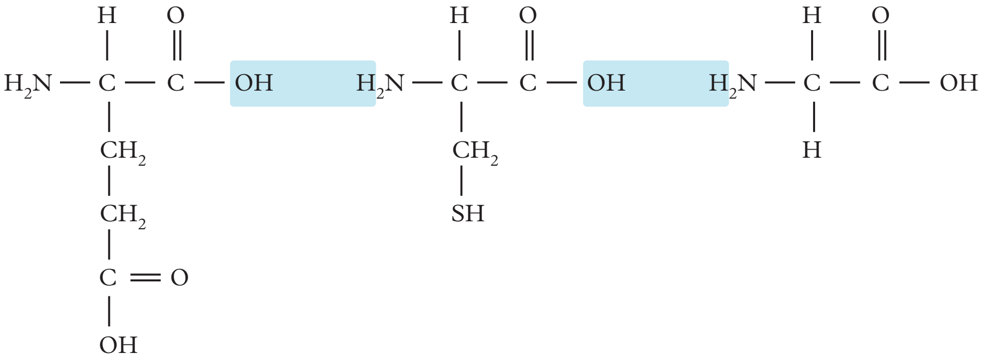


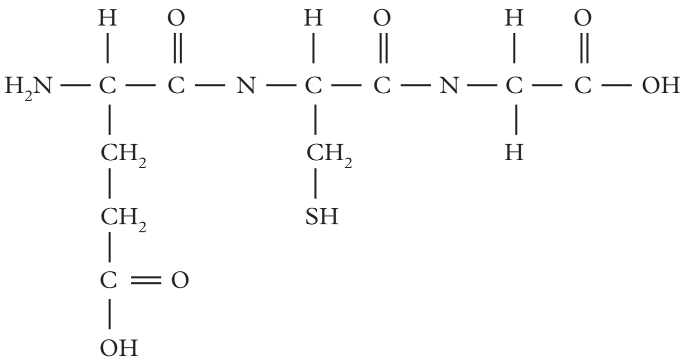
FIGURE 7 A tripeptide

Worked example 14.4B

Identifying amino acid symbols to draw a tripeptide

Sketch the structure of the tripeptide represented by the sequence Leu-Cys-Gly. (1 mark)

Think	Do
Step 1: Look at the cognitive verbs and mark allocation to determine what the question requires you to do.	"Sketch" means to represent using a diagram or a graph. The essential features will be the peptide bonds and the residues as well as the amino acids being in the correct order. There is no need to attempt to draw in 3D. The question is worth 1 mark.
Step 2: Locate the three amino acids represented by the three-letter codes in the sequence from the QCAA *Formula and data book*.	Leu = leucine Cys = cysteine Gly = glycine
Step 3: Draw the structures of the three amino acids in sequence from left to right as given by the name.	 **Leucine**  **Cysteine**  **Glycine**
Step 4: Form a peptide bond between amino acids 1 and 2 and amino acids 2 and 3. Peptide links are bonds produced because of a condensation reaction that produces a water molecule each time a link is formed.	

Think	Do
Step 5: Sketch the final tripeptide.	 (1 mark)

Your turn

Sketch the structure of tripeptide represented by the amino acid sequence Asn-Glu-Asp. (1 mark)

Check your learning 14.4

Check your learning 14.4: Complete these questions online or in your workbook.

Retrieval and comprehension

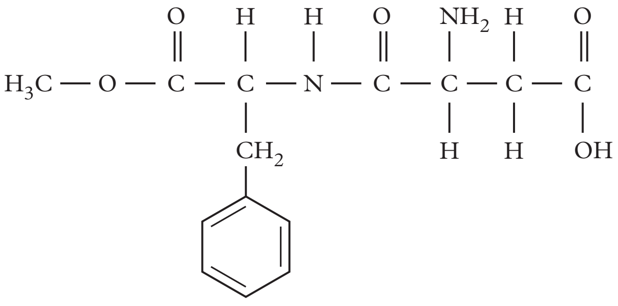
1 **Describe** the structure of an amino acid. (1 mark)

2 **Sketch** the structure of the tripeptide Gly-Ala-Ser, identifying the peptide link within the sequence. (1 mark)

4 **Explain** how the tripeptide drawn in question **2** differs from the tripeptide Ser-Ala-Gly. (2 marks)

5 **Identify** the sequences of all possible tripeptides composed of the amino acids tyrosine, histidine and glycine. (6 marks)

6 Aspartame is an artificial sweetener that is a methyl ester of a dipeptide.



Aspartame

a **Identify** the two amino acids that are used to prepare aspartame. (1 mark)

b **Construct** an equation for the reaction of methanol being produced from the decomposition of aspartame when hydrolysed with water. (1 mark)

c **Identify** the portion of the molecule that methanol can be produced from. (1 mark)

Lesson 14.5

Monosaccharides and disaccharides

Key ideas

→ Carbohydrates are an important part of our diet and are found in dairy products, fruit, grains and legumes.

→ Sugars are simple carbohydrates and can be classified as monosaccharides and disaccharides.

What are the monomers of carbohydrates?

Learning intentions and success criteria

The term "carbohydrate" is based on its two components – carbon ("carbo") and water ("hydrate"). Carbohydrates can be classified as monosaccharides, disaccharides and polysaccharides. Monosaccharides are simple sugars with typically three to seven carbons and are the monomers of carbohydrates. Hexoses are common, with six carbon atoms and will be the main focus of this lesson. Table 1 lists the general 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′).

TABLE 1 Naming monosaccharides according to the number of carbons

Number of carbons	Name
3	Triose
4	Tetrose
5	Pentose
6	Hexose
7	Heptose

Monosaccharides with five or more carbon atoms can be linear chains or ring-shaped molecules; the monosaccharides classed as hexoses 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.

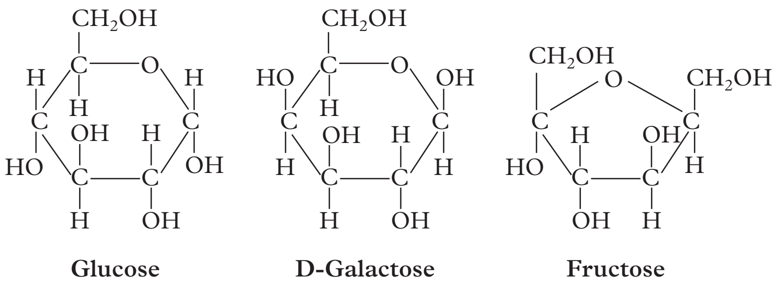


FIGURE 1 Glucose, D-galactose and fructose molecules

FIGURE 2 Fructose is in every fruit and is a monosaccharide.

How are disaccharides formed?

Disaccharides are soluble sugars formed with two monosaccharides joined by a 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). The formation of a disaccharide, like the formation of a tripeptide, is considered a condensation reaction – since water molecules are eliminated with each new glycosidic bond formed. Sucrose derived from sugar cane is widely used and is the type commonly available in packets of sugar. Lactose is the sugar in milk, and fructose is the sugar in fruit (Figure 2).

Lactose

Lactose consists of the two monosaccharides glucose and galactose and is formed in a condensation reaction. Lactose 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 between carbon 1 of the beta-D-galactose monomer and carbon 4 of the alpha-D-glucose monomer.

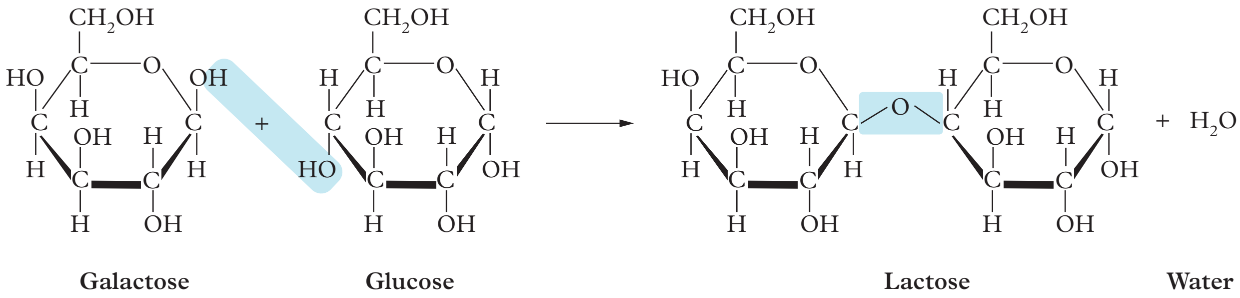


FIGURE 3 Lactose formation from glucose and galactose

Maltose

Maltose, also known as malt sugar, found in fruits and vegetables such as peaches, pears and sweet potatoes, 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).

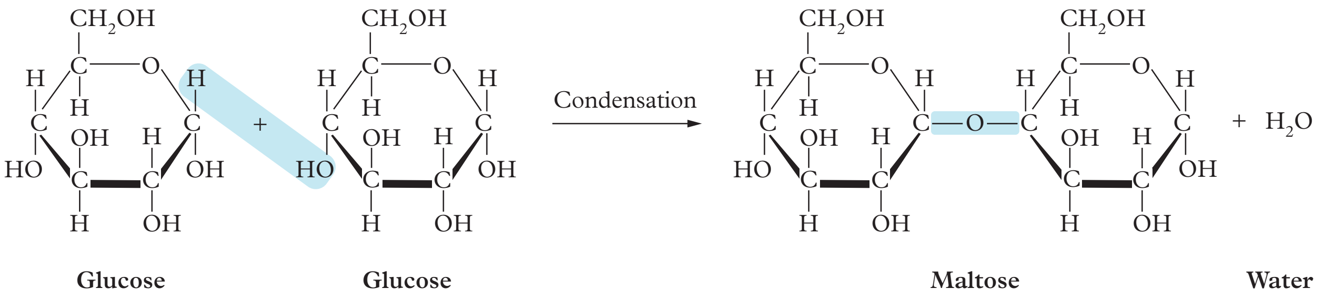


FIGURE 4 Maltose formation from two molecules of glucose

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).

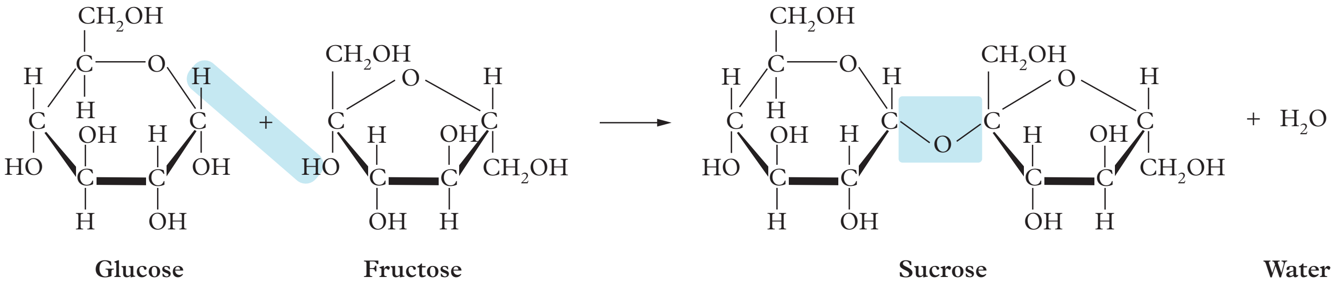


FIGURE 5 Sucrose formation from glucose and fructose

Check your learning 14.5

Check your learning 14.5: Complete these questions online or in your workbook.

Retrieval and comprehension

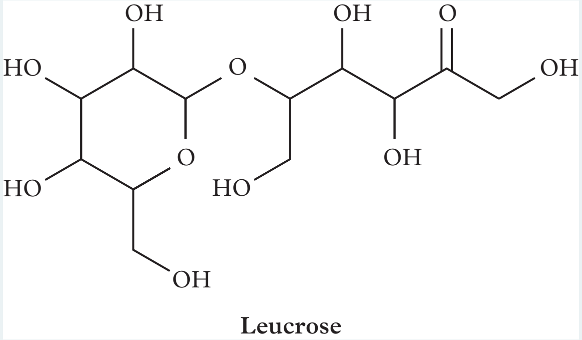
1 **Identify** the chemical formula of
  a fructose (1 mark)
  b maltose. (1 mark)

2 **Describe** maltose and its structure. (2 marks)

3 **Identify** the families of monosaccharides that have three to seven carbons. (2 marks)

4 **Identify** three different disaccharides. (3 marks)

5 **Identify** the location of the glycosidic link in leucrose, a disaccharide in honey.



Analytical processes

6 **Compare** the structures of glucose and fructose. (2 marks)

Knowledge utilisation

7 **Infer** why aldose monomers are often referred to as reducing sugars, by referring to your knowledge of organic reactions. (2 marks)

MODULE 14

Lesson 14.6

Review: Macromolecules

Summary

14.1
- 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).

14.2
- 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 including polyamides (proteins), polysaccharides (carbohydrates) and polyesters are condensation polymers. Polylactic acid (PLA) is a biodegradable type of polyester formed from renewable sources.

14.3
- Practical: Investigating the properties of polymers.

14.4
- Amino acids contain an acid group and an amine group, and can be distinguished and named by their R group (side chain or residue).
- Tripeptides are formed from three amino acids joined by peptide bonds.
- Tripeptides are named in sequence using the three-letter symbols for each amino acid.

14.5
- Carbohydrates are an important part of our diet and are found in dairy products, fruit, grains and legumes.
- Sugars are simple carbohydrates and can be classified as monosaccharides and disaccharides.

Review questions 14.6A Multiple choice

Review questions: Complete these questions online or in your workbook.

(1 mark each)

1 An addition reaction occurs when

A two or more molecules combine to form a larger one.

B the products of different reactions are added together.

C an additional substance is added after an initial reaction.

D two substances are added together; therefore, all reactions are addition reactions.

2 Starch is a

A polyester.

B disaccharide.

C polysaccharide.

D monosaccharide.

3 A monosaccharide is

A a building block of proteins.

B a simple sugar with three to seven carbons.

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 The main disadvantage presented by plastics in causing harm to the environment is that they

A are a source of renewable energy.

B are readily accessible or they have high theoretical yields of energy on combustion.

C break up into microplastics and serve as biomagnified toxins in the aquatic food chain.

D are not degradable, taking up to thousands of years to break down, and can wrap around animals and trap them.

5 Kevlar is a type of
- **A** protein.
- **B** polyester.
- **C** polyamide.
- **D** polytetrafluoroethene.

6 Which type of reaction is responsible for the production of polyesters and proteins?
- **A** Hydrolysis
- **B** Esterification
- **C** Addition polymerisation
- **D** Condensation polymerisation

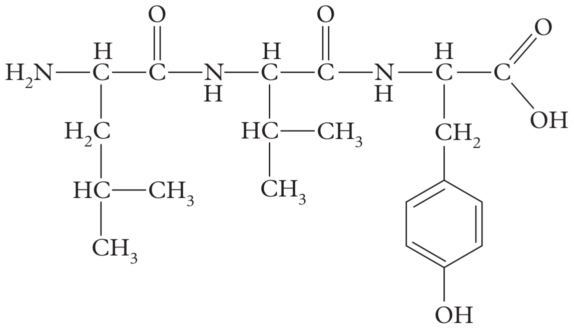
7 Identify the bond responsible for the production of disaccharides from monosaccharide monomers.
- **A** Amide link
- **B** Ester bond
- **C** Peptide bond
- **D** Glycosidic bond

8 Identify the common characteristic of polyethene and ethene.
- **A** Same empirical formula
- **B** Same molecular formula
- **C** Same physical properties
- **D** Same chemical properties

9 Identify which of the following statements correctly differentiates high-density polyethene (HDPE) from low-density polyethene (LDPE).
- **A** HDPE is less crystalline than LDPE, resulting in lower density.
- **B** HDPE has a branched structure, whereas LDPE has a linear structure.
- **C** HDPE has stronger intermolecular forces and higher melting point than LDPE.
- **D** LDPE is used for rigid containers, whereas HDPE is used for flexible packaging.

10 Identify which statement correctly describes the process of forming a tripeptide from three amino acids: glycine (Gly), alanine (Ala) and serine (Ser).
- **A** Peptide bonds form by addition reactions.
- **B** Peptide bonds form by hydrolysis reactions.
- **C** Peptide bonds form by hydrolysis reactions.
- **D** Peptide bonds form by condensation reactions.

11 If the amino acids valine (Val), leucine (Leu) and tyrosine (Tyr) form the tripeptide, which of the following is a correct naming convention?



- **A** Leu-Val-Tyr
- **B** Tyr-Val-Leu
- **C** Tyr-Leu-Val
- **D** Val-Leu-Tyr

12 Which statement correctly distinguishes between the different forms of polypropene?
- **A** Atactic polypropene is highly crystalline and suitable for rigid plastic applications.
- **B** Atactic polypropene has all the methyl groups on the same side, making it highly crystalline.
- **C** Syntactic polypropene has alternating methyl group arrangements, contributing to crystallinity.
- **D** Isotactic polypropene has random methyl group arrangements, resulting in an amorphous structure.

Review questions 14.6B Short response

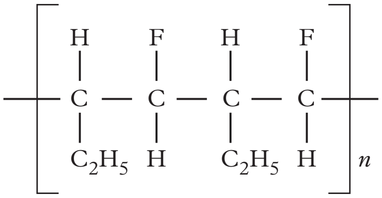
Review questions: Complete these questions online or in your workbook.

Retrieval and comprehension

13 A polyethene molecule has the chemical formula $CH_3(CH_2)_nCH_3$, where on average $n = 200$. **Calculate** its average molecular mass. (2 marks)

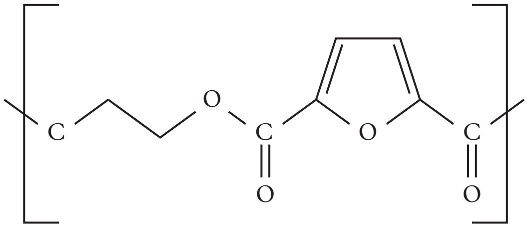
14 **Sketch** the structures of two dipeptides that can be formed from serine and alanine. (2 marks)

15 **Identify** the structure of the monomer used to produce a polymer with the repeating unit formula shown below and determine the type of reaction used in its formation. (2 marks)



$$-\!\left[\underset{C_2H_5}{\overset{H}{C}}-\underset{H}{\overset{F}{C}}-\underset{C_2H_5}{\overset{H}{C}}-\underset{H}{\overset{F}{C}}\right]_n\!-$$

16 PEF, or polyethylene furanoate is a biobased polyester.



PEF

Identify the structure of the two monomers from which it is made, and comment on the advantage that biopolymers may present over fossil fuel-based plastics. (3 marks)

Analytical processes

17 **Compare** addition polymerisation and condensation polymerisation. (2 marks)

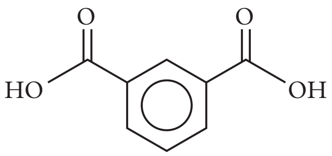
18 **Distinguish** between a monosaccharide and disaccharide and give an example of each. (3 marks)

19 **Distinguish** between Teflon and HDPE. (1 mark)

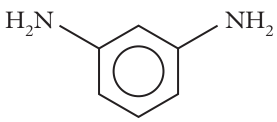
20 **Determine** the sequence of all possible tripeptides composed of two glycine molecules and one phenylalanine. (3 marks)

21 **Distinguish** between the physical properties of atactic and syntactic polypropene based on the extent and arrangement of methyl functional groups within the plastic. (3 marks)

22 Nomex is used in fire-resistant clothing and is a polymer produced from the monomers shown below.



Monomer 1



Monomer 2

- **a** **Determine** the balanced structural chemical equation for the formation of Nomex polymer. (2 marks)
- **b** **Compare** the structure of Nomex to the structure of Kevlar, another aromatic polyamide. Ensure that you refer to the strength and flexibility of the two materials based on the level of crystallinity of the polymers. (2 marks)
- **c** **Determine** the type of polymerisation reaction used to produce Nomex. (1 mark)

Knowledge utilisation

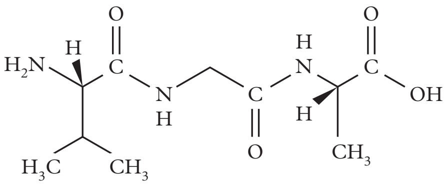
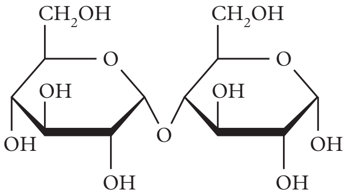
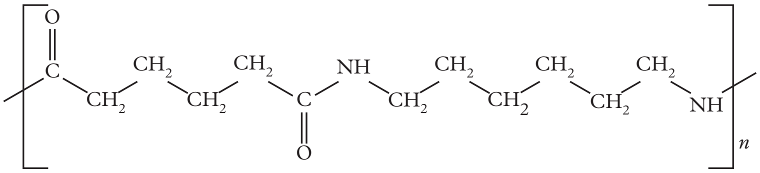
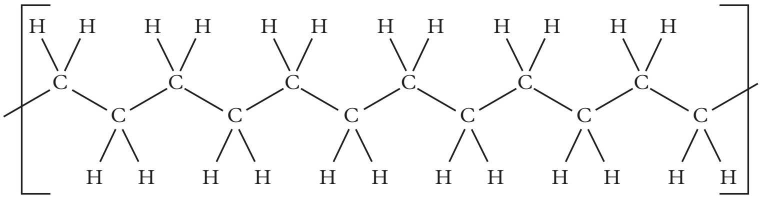
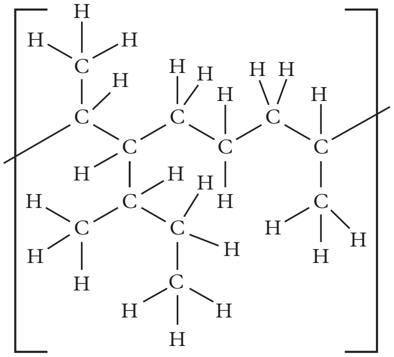
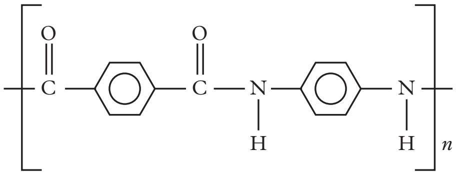
23 **Investigate** alternative materials for single-use plastics. **Create** a poster describing how to combat the over-production of these materials. (3 marks)

Data drill

Identifying unknown polymers

A materials scientist was tasked with identifying an unknown polymer and determining its most suitable application, based on a comparison of polymers and their experimentally derived physical properties. Unfortunately, three of the labels of the known polymers were mistakenly disposed of and only the molecular structures along with the corresponding properties remained. Table 1 lists the polymers, their physical properties and applications.

TABLE 1 Some unknown and known polymers

Polymer	Polymer structure	Melting point (°C)	Tensile strength (MPa)	Common applications
Tripeptide		Denatures at 600	0.1	Food, medicine and forensic science
Maltose		NA	NA	Food, specifically fermentation, baking and medicine
C (known)		260	53	Clothing, industrial products and medical devices
D (known)		135	25	Plastic manufacturing, specifically bottles and storage containers
E (known)		105	10	Plastic manufacturing, specifically plastic bags
F (unknown)			10	

Apply understanding

1 **Identify** the type of plastic polymers labelled D and E. (2 marks)

Analyse data

2 **Categorise** the synthetic polymer C and identify the type of monomer units used in its production. (2 marks)

3 **Identify** each of the amino acids used in the formation of the tripeptide illustrated in Table 1. Refer to the QCAA *Formula and data book*. (3 marks)

Interpret evidence

4 **Predict** whether polymer C or polymer F would be more suitable for use in bulletproof vests and justify your response. (3 marks)

5 **Infer** the type of intermolecular forces present in the unknown polymer and explain how these forces affect the choice of common use applications and melting point. (3 marks)

Module 14 checklist: Macromolecules

UNIT 4 Topic 2 review

Multiple choice

(1 mark each)

1 Energy released in chemical reactions is directly and efficiently converted to electrical energy in

A solar cells.
B electrolytic cells.
C fossil-fuel power stations.
D hydrogen–oxygen fuel cells.

2 A key reaction in the contact process is the conversion of sulfur dioxide to sulfur trioxide:

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

What is the maximum amount of sulfur trioxide (in litres) that can be prepared from 100 L of SO_2 and 100 L of O_2, if all gases are at the same temperature and pressure?

A 50
B 100
C 150
D 200

3 Which of the following is true for a polyester?

A Bifunctional monomers must be used.
B An addition polymerisation reaction is used in manufacturing polyesters.
C The monomers always contain both a carboxyl and a hydroxyl functional group.
D Polyesters are thermosetting polymers due to the presence of a C=O double bond.

4 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?

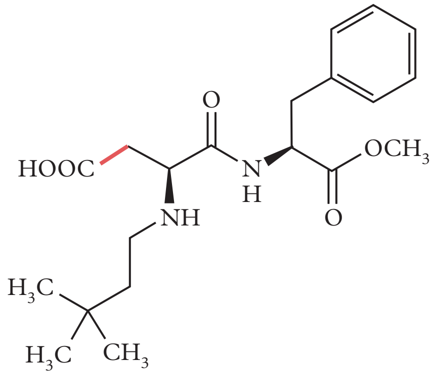
A A low temperature (20°C) and a low pressure (200 kPa)
B A low temperature (20°C) and a high pressure (400 kPa)
C A high temperature (400°C) and a low pressure (200 kPa)
D A high temperature (400°C) and a high pressure (400 kPa)

5 Select the condensation polymer from the following polymers.

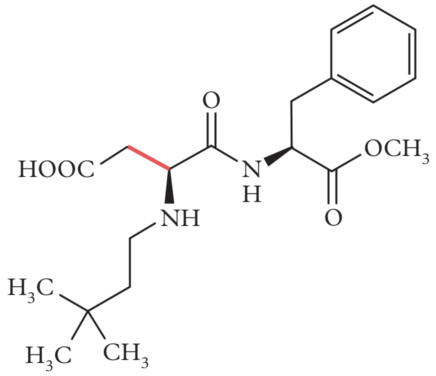
A Polystyrene
B Polypropene
C Polylactic acid
D Polyvinyl chloride

6 Identify the ester linkage in Neotame – an artificial sweetener used in food and beverage products.

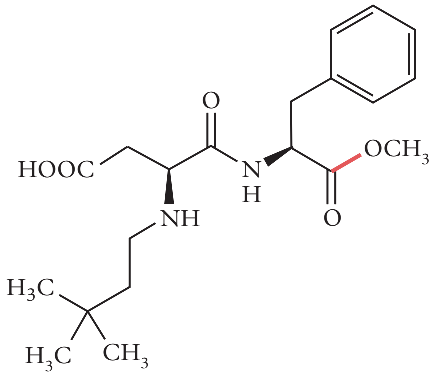
A



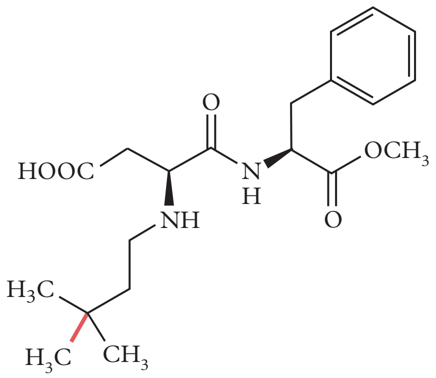
B



C



D



7 Which of the following options is true for the effect that catalysts have in the Haber process for ammonia production?

	Rate of formation of $NH_3(g)$	Amount of $NH_3(g)$ formed
A	No change	Increases
B	Increases	No change
C	Increases	Decreases
D	Increases	Increases

8 Identify which molecule is a saccharide.

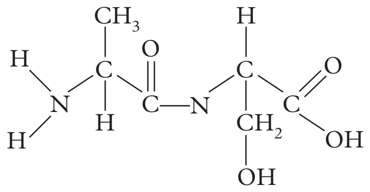
A CH_4

B $C_{18}H_{34}O_2$

C $C_3H_7NO_2$

D $C_{12}H_{22}O_{11}$

9 The molecule shown is best described as



A a dipeptide.

B a tripeptide.

C an amino acid.

D a nitrogenous carboxylic acid.

10 Identify the maximum number of tripeptides that can be produced containing three different amino acids if each amino acid only appears once.

A 4

B 6

C 7

D 3

11 Glycosidic bonds are formed between

B lipid monomer units.

B protein monomer units.

C vitamin monomer units.

D carbohydrate monomer units.

12 HDPE is different from LDPE because it is more

A crystalline and has a lower melting point.

B crystalline and has a higher melting point.

C amorphous and has a lower melting point.

D amorphous and has a higher melting point.

13 What is the ratio of hydrogen gas to oxygen gas placed into a hydrogen fuel cell, regardless of the type of electrolyte?

A 2:1

B 1:2

C 1:3

D 3:1

14 Determine why a fairly high temperature is used for the Haber process even though lower temperatures favour the products at equilibrium?

A Lower temperatures require lower pressures, which is unfeasible for industry.

B The temperatures are chosen to ensure that the product ammonia does not evaporate.

C The temperature for the Haber process is chosen to allow for a reasonable rate of production.

D The temperatures are preferred to lower temperatures since the Haber process is exothermic.

Short response

15 Ethanol is produced industrially by either hydration of ethene or fermentation. If sufficient raw material (reactants) is used to theoretically produce 1,000 kg of ethanol by both methods, it is found that hydration of ethene produces 940 kg of ethanol and fermentation produces 920 kg of ethanol. Due to fermentation being carried out by a biological organism, yeast, the rate is slower than the rate of hydration of ethene.

a Use balanced equations to **describe** these two methods. Include conditions. (2 marks)

b **Calculate** the percentage yield for both methods. (2 marks)

c **Compare** the rate, conditions and yield of hydration of ethene with those of fermentation. **Identify** which, if any, of these factors favour the choice to increase production of ethanol by fermentation. (4 marks)

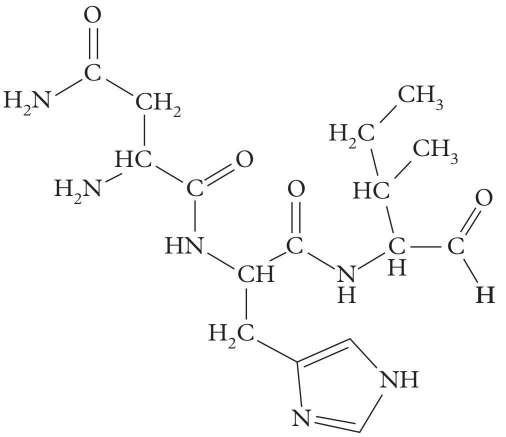
	Ammonia	Sulfuric acid
Process used	Haber process	Contact process
Main reaction(s)	Exothermic, releases 46.2 kJ mol^{-1}	Exothermic Sulfur combustion: exothermic, releases 297 kJ mol^{-1} Conversion of SO_2 to SO_3: exothermic, releases 98 kJ mol^{-1} Absorption of SO_3 by oleum: exothermic, heat released depends on conditions
Pressure (kPa)	15,000–25,000	100 for sulfur combustion 100–200 for conversion of SO_2 to SO_3 100 for absorption of SO_3 by oleum
Temperature (°C)	400–500	1,000–1,200 for sulfur combustion 400–450 for conversion of SO_2 to SO_3 50–80 for absorption of SO_3 by oleum
Catalyst	Fe with, for example, K_2O, Al_2O_3, CaO and MgO promoters	V_2O_5
Typical yield (%)	15–30	98–99

16 Two important industrial chemicals, ammonia and sulfuric acid, are produced in very large quantities annually. The table lists information about the production of these chemicals.

- **a** **Describe** the production of ammonia with a balanced thermochemical equation. Include conditions. (2 marks)
- **b** **Describe** the production of sulfuric acid with balanced equations. Include conditions and ΔH where known. (6 marks)
- **c** **Determine** whether higher temperatures or lower temperatures favour products at equilibrium for both the Haber process and the contact process. (2 marks)
- **d** **Determine** whether higher pressures or lower pressures favour products at equilibrium for both the Haber process and the contact process. (2 marks)
- **e** **Determine** whether the use of catalysts favours products at equilibrium for both the Haber process and the contact process. (2 marks)
- **f** The conditions used for the production of ammonia are not the conditions that favour products at equilibrium. **Explain** why it is more beneficial to operate under these conditions. (2 marks)

17 The following questions relate to the structure and identification of a tripeptide.

- **a** **Construct** a diagram of Cys-Ala-Gln. (3 marks)
- **b** **Apply** amino acid symbols to name the molecule shown. (1 mark)



18 A double displacement reaction between 1 g of sodium carbonate and 1 g of calcium chloride produces 0.75 g of insoluble calcium carbonate. Calcium carbonate has $K_{sp} = 2.8 \times 10^{-9}$.

- **a** **Calculate** the percentage yield. (5 marks)
- **b** Use the K_{sp} to **calculate** K_c for the double displacement reaction. (1 mark)
- **c** Use the answer from part **b** to **determine** the extent to which products are favoured in the double displacement reaction. (1 mark)
- **d** **Compare** your answers from parts **b** and **c** with the actual yield found in part **a**, and **identify** a reason why the yield may be smaller than predicted by equilibrium considerations for this type of reaction. (2 marks)

19 Aspirin can be produced in the laboratory according to the following reversible reaction:

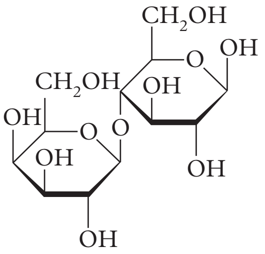
$$C_7H_6O_3 + CH_3COOH \rightleftharpoons C_9H_8O_4 + H_2O$$

Salicylic acid + ethanoic acid ⇌ aspirin + water

2.00 g of salicylic acid was mixed with an excess of ethanoic acid in the presence of concentrated H_2SO_4 catalyst and heated. At the end of the reaction, mass of the aspirin crystals produced was 1.85 g.

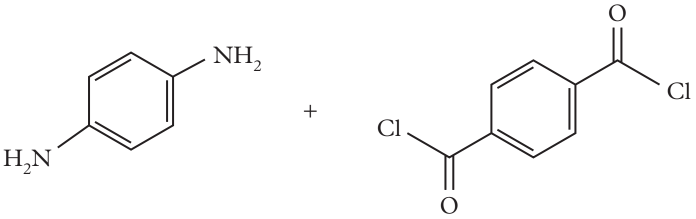
- **a** **Calculate** the theoretical yield for this reaction. (3 marks)
- **b** **Calculate** the percentage yield for this reaction. (1 mark)
- **c** This reaction is conducted using pure salicylic acid and pure ethanoic acid (known as glacial acetic acid). **Deduce** the effect on the yield of aspirin if aqueous solutions were used instead. **Justify** your answer. (4 marks)

20 Lactose is a sugar in milk with the formula $C_{12}H_{22}O_{11}$ and the structure shown. As a carbohydrate, it is responsible for some of the energy content of milk-based dairy foods. Lactose can be digested by many people. However, some people stop producing the enzyme lactase, which catalyses the hydrolysis of the compound and produces two smaller molecules; these people become lactose intolerant.



- **a** **Identify** the type of bonding between the two ring structures in lactose. (1 mark)
- **b** **Sketch** the two products of the hydrolysis reaction between water and lactose. (2 marks)
- **c** Lactase can be added to milk, to enable hydrolysis to occur before consumption. This is how lactose-free milk is produced. **Deduce** the effects, if any, of the hydrolysis of lactose on the sweetness and the energy content of the milk. **Justify** your reasoning. (4 marks)

21 The Kevlar chain used in the manufacturing of bulletproof vests is made by the condensation polymerisation of the following two monomers.

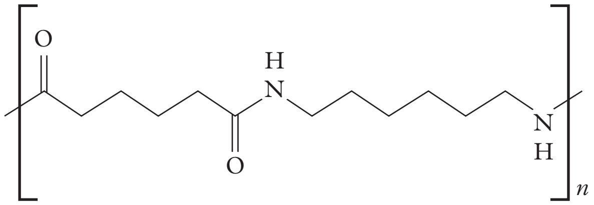


- **a** **Describe**, using a balanced equation, the formation of the polymer from *n* moles of each monomer. (2 marks)
- **b** **Identify** the type of bond involved in the linkage of the monomers to produce the polymer. (1 mark)
- **c** **Deduce** the expected physical properties of the polymer. **Justify** your response with reference to the intermolecular forces present. (2 marks)

22 Consider the amino acid monomers serine, alanine and glycine.

- **a** **Identify** the maximum number of tripeptides that can be formed from the three amino acids. (1 mark)
- **b** Using the three-letter codes, **identify** all the possible tripeptides that can be formed. (2 marks)

23 Nylon, a common polymer used in fibres, is known for its excellent properties of strength and elasticity. It is formed from monomers of a carboxylic acid and a diamine. A section of the nylon 66 polymer is shown.



- **a** **Describe**, using a balanced equation, the formation of the polymer from *n* moles of each monomer. (2 marks)
- **b** **Determine** the type of polymerisation used to form nylon 66. (1 mark)

c **Identify** the functional group formed by the reaction of the monomers in nylon 66. (1 mark)

d **Explain** how the position of the carbonyl carbons and amine functional groups affect the linearity of the polymer, resulting in strength and elasticity. (3 marks)

24 Similar to the contact process, nitric acid is produced commercially by the Ostwald process, which is also a multistep process shown below:

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

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

$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$

Calculate the mass of ammonia (NH_3) required to produce 1000 kg of nitric acid (HNO_3), assuming 80% yield. (4 marks)

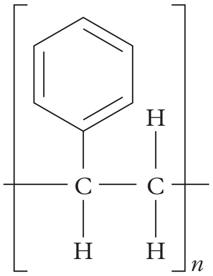
25 Polyethene is commonly manufactured as either high-density polyethene (HDPE) or low-density polyethene (LDPE), which have different physical properties. The following table shows the properties of samples of LDPE and HDPE with similar average molecular masses.

Polymer	Melting point (°C)	Tensile strength (MPa)	% crystallinity
HDPE	135	29	75
LDPE	80	15	50

a **Describe** the differences between the two types of polyethene in terms of structure and their polymer chains. (2 marks)

b **Explain** why HDPE has a higher melting point and tensile strength than LDPE. (4 marks)

26 The polymer polystyrene has the formula shown. Polystyrene is made into small beads and can then be expanded into a solid foam, trapping many tiny bubbles. This produces a material with excellent properties as a thermal insulator.



a **Determine** the type of polymerisation used to form polystyrene. (1 mark)

b **Describe**, using a balanced equation, the formation of polystyrene. (1 mark)

c By considering the structure of polystyrene, **explain** why it can be expanded into a solid foam. (2 marks)

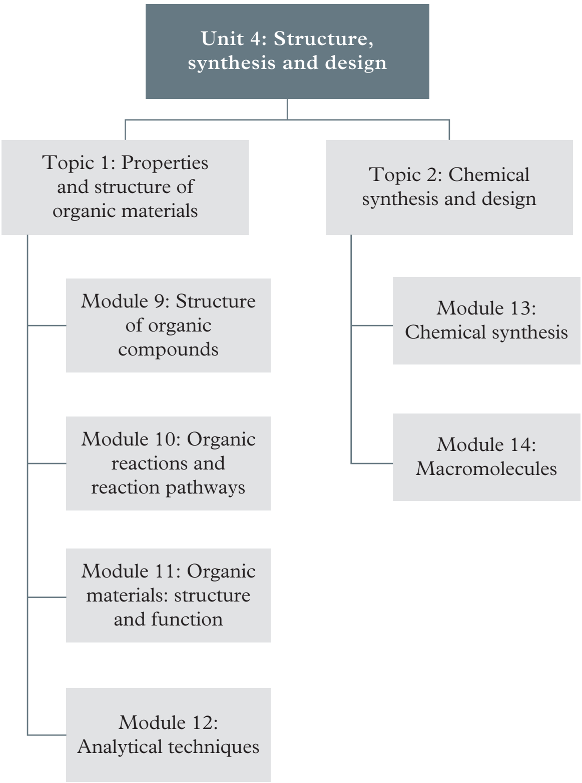
TOTAL MARKS

/95

UNIT 4 Review

PART A – Revisit and revise

Part A of the Unit review asks you to reflect on your learning and identify areas in which you need more work.



PART B – Exam essentials

Now that you've completed your revision for Unit 4, it's time to learn and practise some of the skills you'll need to answer exam questions like a pro! Our expert authors have created the following advice and tips to help you maximise your results on the end-of-year examination.

Exam tip 1: Consider the cognitive verbs

The cognitive verb(s) in the question indicate the nature of the response required. Know the meanings of the cognitive verbs in the syllabus and apply them correctly and fully when responding. Some verbs that students sometimes provide an incomplete response to are:

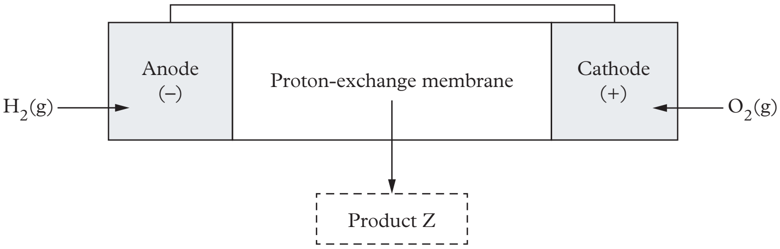
- Compare: display recognition of similarities and differences and recognise the significance of these similarities and differences. Students may fail to recognise differences or may not detail the significance of the similarities or differences.
- Explain: make an idea or situation plain or clear by describing it in more detail or revealing relevant facts; give an account; provide additional information. Students may fail to provide the necessary additional information and simply restate the question or the provided data.

See it in action

Read the real exam question below and see how the tip has made a difference between a response that has scored full marks and a response where marks have been lost.

QUESTION 23 (6 marks)

The diagram represents a hydrogen fuel cell with an acid electrolyte.



(a) Determine the redox half-equation occurring at the anode and cathode. [2 marks]

Anode half-equation:

Cathode half-equation:

(b) Identify product Z. [1 mark]

(c) Compare the movement of electrons and hydrogen ions in the fuel cell. [3 marks]

Similarity:

Difference:

Significance:

Source: *QCAA 2023 Chemistry External Examination Paper 1* © State of Queensland (QCAA)

Complete response

Identifies anode half-equation [1 mark]

(a) Anode half-equation: $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$

Cathode half-equation: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Identifies cathode half-equation [1 mark]

(b) Product Z is water — Identifies product Z as water [1 mark]

Identifies one similarity about the movement of hydrogen ions and electrons [1 mark]

(c) Similarity: Electrons and hydrogen ions move from the anode to the cathode.

Difference: Hydrogen ions move through the proton-exchange membrane while electrons move through the wire.

Identifies one difference about the movement of hydrogen ions and electrons [1 mark]

Significance: Flow of electrons (current) in the external circuit is due to the potential difference. Hydrogen ions must flow in the internal circuit from the anode where they are produced to the cathode where they are used up.

Discusses the significance of the similarity/difference [1 mark]

Incomplete response

Identifies both half-equations, but despite the response space for each, has them reversed [0 marks]

(a) Anode half-equation: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Cathode half-equation: $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$

(b) Product Z is water — Identifies product Z as water [1 mark]

Identifies one similarity about the movement of hydrogen ions and electrons [1 mark]

(c) Similarity: Electrons and hydrogen ions move from the anode to the cathode. Difference: Hydrogen ions move through the proton-exchange membrane while electrons move through the wire. Significance: These movements are to balance the fuel cell.

Identifies one difference about the movement of hydrogen ions and electrons [1 mark]

Fails to adequately discuss the significance of the similarity/difference [0 marks]

Think like an assessor

To maximise your marks on an exam, it can help to think like a QCAA assessor. Consider how many marks each question is worth and what information the assessor is looking for.

A student has given the following response in a practice exam. Imagine you are a QCAA assessor and use the marking guide below to mark the response.

QUESTION 21 (4 marks)

(a) Idenitfy whether 2-bromopropane is a saturated or unsaturated compound. Explain your reasoning. [2 marks]

2-Bromopropane is a saturated compound because you can tell from the name of it.

(b) Determine whether 2-bromopropane is a primary, secondary or tertiary halogenoalkane. Explain your reasoning. [2 marks]

2-Bromopropane is a secondary haloalkane because the halogen is not at the end of the molecule or it would have 1 at the start of its name.

Source: *QCAA 2022 Chemistry External Examination Paper 1* © State of Queensland (QCAA)

Marking guide

Question 21a	• Identifies that 2-bromopropane is saturated [1 mark] • Indicates that 2-bromopropane contains only single bonds [1 mark]
Question 21b	• Determines that 2-bromopropane is a secondary halogenalkane [1 mark] • Explains that the bromine (halogen) is bonded to a carbon that is attached to two other carbon atoms [1 mark]

Source: *QCAA 2022 Chemistry marking guide and response* © State of Queensland (QCAA)

Fix the response

Consider where you did and did not award marks in the above response. How could the response be improved? Write your own response to the same question to receive full marks from a QCAA assessor.

Exam tip 2: Multi-faceted questions

Some questions seek a breadth and depth of understanding.

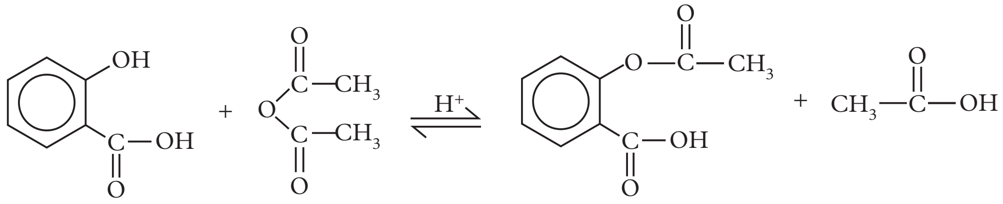
- Depth of understanding: Multi-step questions may require students to apply understanding and perform a sequence of steps that are logically connected to each other. Ensure that the logical connection between steps is shown clearly. Read over the question at the end, to ensure your answer is complete and has addressed what is asked.
- Breadth of understanding: Some questions require application of understanding from two or more areas of the subject matter and connect them in ways not typically encountered. Make the links between topics explicit and show that they connect the concepts and subject matter. Again, read over the question at the end, to make sure that you have fully addressed it.

See it in action

Read the real exam question below and see how the tip has made a difference between a response that has scored full marks and a response where marks have been lost.

QUESTION 2 (12 marks)

Salicylic acid reacts with ethanoic anhydride in an aqueous solution to produce acetylsalicylic acid, as shown in the equation. Acetylsalicylic acid is commonly known as aspirin.



Salicyclic acid ($C_7H_6O_3$) | Ethanoic anhydride ($C_4H_6O_3$) | Acetylsalicylic acid ($C_9H_8O_4$) | Ethanoic acid ($C_2H_4O_2$)

(a) Identify the type of chemical reaction used to produce aspirin. [1 mark]

(b) Write the equilibrium expression, K_c, for the reaction. [1 mark]

(c) At 20°C, the equilibrium constant (K_c) for the reaction is 2×10^{-3}. Determine whether the concentration of the reactants or products is greater at equilibrium at this temperature. [2 marks]

(d) Calculate the minimum mass of salicylic acid required to produce 500.0 mg of aspirin if the yield of aspirin is 45.0%. Show your working. [4 marks]

Mass = ____________ mg (to three significant figures)

(e) When the reaction is heated to 40°C and equilibrium is re-established, the concentration of acetylsalicylic acid and ethanoic acid increases. Apply Le Châtelier's principle to predict if the forward reaction is exothermic or endothermic. Explain your reasoning. [4 marks]

Source: *QCAA 2020 Chemistry External Examination Paper 2* © State of Queensland (QCAA)

Complete response

(a) Esterification ← Identifies the reaction as esterification [1 mark]

(b) $K_c = \dfrac{[C_9H_8O_4][C_2H_4O_2]}{[C_7H_6O_3][C_4H_6O_3]}$ ← Uses the general formula for K_c and these products and reactants to provide the correct expression [1 mark]

Uses the value of K_c to identify that the equilibrium lies towards the reactants [1 mark]

(c) K_c Is very small, much less than 1, so the equilibrium favours reactants. This means that the concentration of the reactants will be much greater than the concentration of the products.

Identifies that [reactants] > [products] [1 mark]

Determines molar mass of aspirin as 180 g [1 mark]

(d) M(aspirin) = (12.01 × 9)+(16.0 × 4) + 8.08

= 180.17 g

$n(\text{aspirin}) = \frac{m}{M} = \frac{0.5\text{ g}}{180.17\text{ g}} = 2.78 \times 10^{-3}\text{ mol}$

Determines n(aspirin) is 2.78×10^{-3} [1 mark]

Ratio 1:1

45% efficient

n(salicylic acid) =

$\frac{2.78 \times 10^{-3}}{0.45} = 6.17 \times 10^{-3}\text{ mol}$

Determines n(salicylic acid) [1 mark]

m(salicylic acid) =

$n \times M = 6.17 \times 10^{-3} \times 138.13 = 0.852\text{ g}$

Mass = 852 mg (to 3 sf)

Determines m(salicylic acid) [1 mark]

Identifies that the increased temperature has made more products [1 mark]

(e) An increase in the amount of products means that the equilibrium has shifted to the products at the higher temperature and K_c is larger. Increasing temperature shifts the equilibrium in the direction of the endothermic reaction. Le Chatelier's principle means that when a system at equilibrium experiences an increase in temperature, the equilibrium shifts in the endothermic direction to decrease the temperature. As the forward reaction has occurred, this means that the reaction as written must be endothermic.

Identifies that the equilibrium has shifted in the endothermic direction [1 mark]

Uses Le Châtelier's principle to explain a shift in equilibrium for an increase in temperature [1 mark]

Identifies the forward reaction as endothermic [1 mark]

Incomplete response

(a) Esterification ← Identifies the reaction as esterification [1 mark]

(b) $K_c = \frac{[C_9H_8O_4] + [C_2H_4O_2]}{[C_7H_6O_3] + [C_4H_6O_3]}$

Incorrectly applies the general formula for K_c [0 marks]

Uses the value of K_c to identify that the equilibrium lies towards the reactants [1 mark]

(c) K_c Is very small, much less than 1, so the equilibrium favours reactants.

Does not go on to identify that [reactants] > [products] [0 marks]

Determines molar mass of aspirin is 180 g [1 mark]

(d) M(aspirin) = $(12.01 \times 9)+(16.0 \times 4) + 8.08$

$= 180.17$ g

n(aspirin) $= \frac{m}{M} = \frac{0.5 \text{ g}}{180.17 \text{ g}} = 2.78 \times 10^{-3}$ mol

Determines n(aspirin) is 2.78×10^{-3} [1 mark]

Ratio 1:1

45% efficient

n(salicylic acid) =

$2.78 \times 10^{-3} \times 0.45 = 1.261 \times 10^{-4}$ mol

There should be more reactant than product.

Incorrectly applies the percentage and cannot determine n(salicylic acid). Recognises that this answer is too small [0 marks]

Does not attempt to complete the question [0 marks]

Identifies that the increased temperature has made more products [1 mark]

(e) The equilibrium has shifted to the products and made more at the higher temperature. Increasing temperature shifts the equilibrium in the direction of the endothermic reaction. This means that the forward reaction as written must be endothermic.

Identifies that the equilibrium has shifted in the endothermic direction [1 mark]

Does not use Le Châtelier's principle [0 marks]

Identifies the forward reaction as endothermic [1 mark]

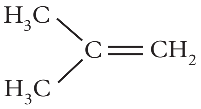
Think like an assessor

To maximise your marks on an exam, it can help to think like a QCAA assessor. Consider how many marks each question is worth and what information the assessor is looking for.

A student has given the following response in a practice exam. Imagine you are a QCAA assessor and use the marking guide below to mark the response.

QUESTION 4 (10 marks)

Consider the organic molecule shown.



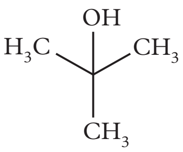
(a) Identify the molecule as saturated or unsaturated. [1 mark]

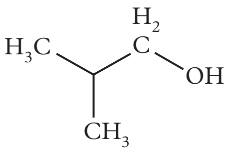
It has a double bond.

(b) Apply IUPAC rules to name this molecule. [1 mark]

2-methylprop-1-ene

(c) Write an equation to show the products formed by the hydration of this molecule. [2 marks]





(d) Predict which is the major product formed in c). [1 mark]

The major product is 2-methylpropan-2-ol.

(e) Identify a physical property and experimental technique that could be used to separate products formed by hydration in c). Explain your reasoning. [5 marks]

The two compounds in part c will have different physical properties, such as different boiling points. Different boiling points allow the two compounds to be separated by distillation because one will boil off at a lower temperature and it can be separated.

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Marking guide

Question 4a	• Provides unsaturated [1 mark]
Question 4b	• Provides 2-methylpropene [1 mark]
Question 4c	• Identifies $(CH_3)_3CHOH$ as a product [1 mark] • Identifies $(CH_3)_2CHCH_2OH$ as a product [1 mark] (Note: Accept condensed or expanded structural formula)
Question 4d	• Identifies tertiary alcohol as the major product [1 mark]
Question 4e	• Identifies the products as primary and tertiary alcohols [1 mark] • Identifies boiling point as a property that can be used to separate the alcohols [1 mark] • Identifies distillation as a suitable technique [1 mark] • Links the position of the hydroxyl group in the primary alcohol to increased hydrogen bonding [1 mark] • Indicates that stronger intermolecular forces result in a higher boiling point for the primary alcohol [1 mark]

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Fix the response

Consider where you did and did not award marks in the above response. How could the response be improved? Write your own response to the same question to receive full marks from a QCAA assessor.

Exam tip 3: Make sure to use all available information and data to analyse and evaluate when problem solving

Some questions require students to problem solve, which requires a depth of understanding to:

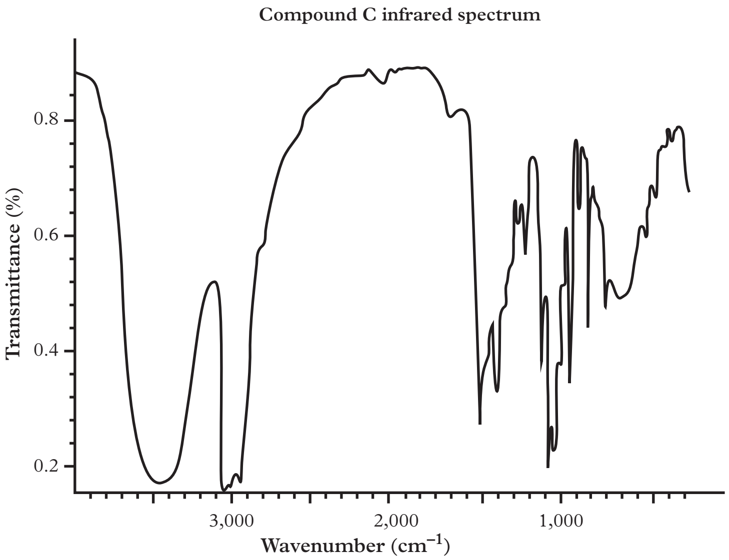
- use analytical processes; for example, to critically analyse and interpret evidence or to deduce outcomes
- demonstrate knowledge utilisation; for example, to hypothesise, evaluate and provide justified reasoning.

See it in action

Read the real exam question below and see how the tip has made a difference between a response that has scored full marks and a response where marks have been lost.

QUESTION 4 (8 marks)

Compound C has the molecular formula $C_4H_{10}O$ and is either an alcohol, an aldehyde or a carboxylic acid.



(a) Deduce the class of compound C. Explain your reasoning. [4 marks]

(b) Deduce the structural formula and IUPAC name of two isomers of compound C. [2 marks]

Isomer 1:

IUPAC name:

Isomer 2:

IUPAC name:

Note: if you make a mistake in the drawing, cancel it by ruling a single diagonal line through your work and use the additional response space at the back of this question and response book.

(c) Distinguish between structural and geometric isomers. [2 marks]

Source: *QCAA 2023 Chemistry External Examination Paper 2* © State of Queensland (QCAA)

Complete response

Determines that the compound is an alcohol [1 mark]

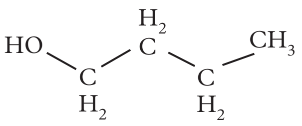
Explains that the peak at 3,200–3,600 cm^{-1} indicates OH functional group [1 mark]

(a) Compound C is an alcohol seen by the broad, strong peak at around 3,300 cm^{-1} on the IR spectrum which shows the presence of a hydroxyl group. Compound C cannot be an aldehyde as there is no peak at or near 1,700 cm^{-1} on IR spectrum therefore there is no carbonyl functional group. Compound C cannot be a carboxylic acid as the broad peak corresponding to the hydroxyl group would be around 3,000 cm^{-1} if it was a carboxylic acid, also there is only one oxygen atom.

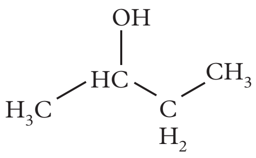
Explains that no peak at 1,700–1,759 cm^{-1} indicates that compound C cannot be an aldehyde [1 mark]

Explains that no peak at 2,500–3,000 cm^{-1} indicates that compound C is not a carboxylic acid [1 mark]

(b)



butan-1-ol



butan-2-ol

Deduces the structural formula and IUPAC name for another isomer [1 mark]

Deduces the structural formula and IUPAC name for one isomer [1 mark]

Explains that structural isomers have the same molecular formula but different structure [1 mark]

(c) Structural isomers have the same molecular formula but a different structure. Geometric isomers have the same order of atom bonding but the atoms are arranged differently in space.

Explains that geometric isomers have the same bonding of atoms, but the atoms are arranged differently in space [1 mark]

Incomplete response

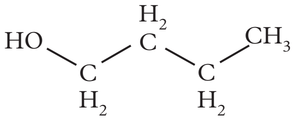
Determines that the compound is an alcohol [1 mark]

Explains that the peak at 3,200–3,600 cm^{-1} indicates OH functional group [1 mark]

(a) Compound C is an alcohol as evidenced by the broad, strong peak at around 3,300 cm^{-1} on the IR spectrum due to the presence of a hydroxyl group. The hydroxyl group peak is in the wrong place for an acid.

Does not explain that no peak at 1,700–1,759 cm^{-1} indicates that compound C cannot be an aldehyde [0 marks]

Does not explain that no peak at 2,500–3,000 cm^{-1} indicates that compound C is not a carboxylic acid. Reference is made to it not being an acid, but the statement of evidence from the spectrum lacks detail [0 marks]



(b) butan-1-ol

Does not deduce the structural formula and IUPAC name for another isomer [0 marks]

Deduces the structural formula and IUPAC name for another isomer [1 mark]

Does not provide detail when explaining that structural isomers have the same molecular formula but different structure [0 marks]

(c) Structural isomers have a different structure. Geometric isomers could be cis and trans, for example.

Does not explain that geometric isomers have the same bonding of atoms, but the atoms are arranged differently in space. Providing a possible example only is not sufficient for the cognitive verb “explain” [0 marks]

Think like an assessor

To maximise your marks on an exam, it can help to think like a QCAA assessor. Consider how many marks each question is worth and what information the assessor is looking for.

A student has given the following response in a practice exam. Imagine you are a QCAA assessor and use the marking guide below to mark the response.

QUESTION 26 (5 marks)

The table shows a series of reactions that were performed to produce organic compounds A, B and C.

Reaction	Reactant	Reagents/conditions	Products
1	propanol	conc. H_2SO_4(aq)/heat	compounds A and water
2	compound A	H_2O(g)/heat	compound B and propanol
3	compound B	H^+(aq)/$KMnO_4$(aq)/heat	compound C

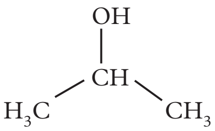
(a) Determine the IUPAC name for compound A. [1 mark]

IUPAC name: propene because H_2O has been removed from propanol.

(b) Explain one structural difference between compound B and propanol. [2 marks]

Compound B must be a structural isomer of propanol so they have different structures. The OH group will be attached to a different carbon atom.

(c) Deduce the structural formula of compound C. [1 mark]



propan-2-ol

(d) Describe on qualitative observation that would be expected for reaction 3. [1 mark]

Reaction 3 uses up the $KMnO_4$.

Source: *QCAA 2023 Chemistry External Examination Paper 1* © State of Queensland (QCAA)

Marking guide

Question 26a	• Determines compound A is propene [1 mark]
Question 26b	• Identifies compound B as a secondary alcohol and propanol as a primary alcohol [1 mark] • Explains that the OH group in propanol is attached to a terminal carbon while the OH group in compound B is attached to the second C in the parent chain [1 mark]
Question 26c	• Deduces the structural formula for propanone [1 mark]
Question 26d	• Describes a qualitative observation [1 mark]

Source: *QCAA 2023 Chemistry marking guide and response* © State of Queensland (QCAA)

Fix the response

Consider where you did and did not award marks in the above response. How could the response be improved? Write your own response to the same question to receive full marks from a QCAA assessor.

Part C – Practice exam questions

Now it's time to put the tips and advice you've learnt into practice while you complete these exam-style questions!

Multiple choice

(1 mark each)

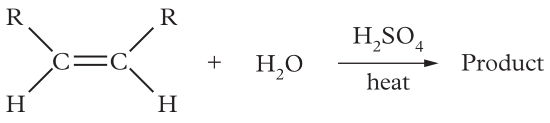
1 Identify which molecule will be least soluble in water.

A Butanal
B Hexanal
C Butan-1-ol
D Hexan-1-ol

2 Haloalkanes undergo a substitution reaction with ammonia to form

A amides.
B amines.
C alcohols.
D amino acids.

Use the following information to answer questions 3 and 4.



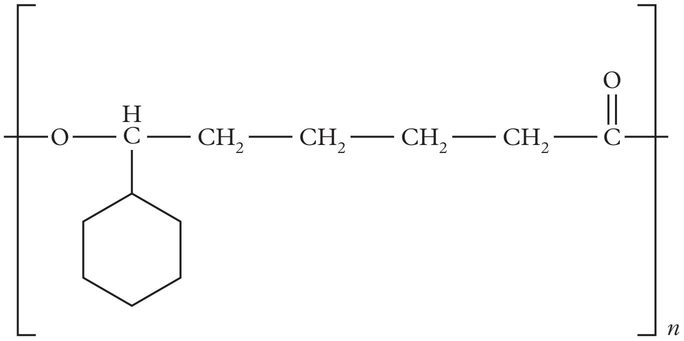
3 What type of compound is the product?

A Ketone
B Aldehyde
C Primary alcohol
D Secondary alcohol

4 Identify the type of reaction.

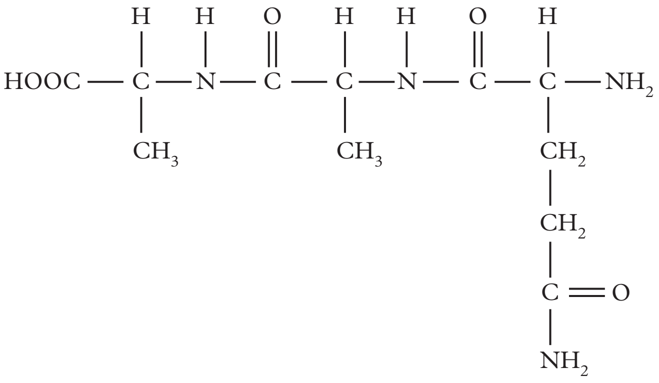
A Hydration
B Substitution
C Condensation
D Hydrogenation

5 Identify the type of polymer shown.



A Polyester
B Polyamide
C Polyethene
D Polylactic acid

6 The structural formula for a tripeptide is shown. The name of the tripeptide is:



A di–Ala–Gln
B Gln–di–Ala
C Ala–Ala–Gln
D Gln–Ala–Ala

7 Which of the following statements is correct?

A Monosaccharides are aldoses and disaccharides are ketoses.
B Disaccharides are formed from two or more monosaccharides.
C Disaccharides are formed from monosaccharides in a condensation reaction.
D Monosaccharides have the formula $C_6H_{12}O_6$ and disaccharides have the formula $C_{12}H_{24}O_{12}$.

8 Which of the following is correct for amino acids?

A Amino acids form zwitterions at a neutral pH of 7.0.
B Amino acids form positive ions at low pH values due to having donated a proton.
C Each amino acid has just one carboxylic acid group and one amine group.
D Amino acids are classified as basic, acidic or neutral depending on the R group.

9 Stereoisomers are compounds that have the same molecular formula but differ

A in the structural arrangement of atoms.
B only in the spatial arrangement of atoms.
C only in the arrangement of atoms around a chiral carbon atom.
D only in the arrangement of branches on either side of a double bond.

10 Which pair of reagents would react to form a peptide bond?

A Glycine and leucine
B Glucose and fructose
C Propan-1-ol and pentanoic acid
D Methanamine and butanoic acid

11 Ethanol can be produced by fermentation or by hydration of ethene. Which of the following is an advantage of ethanol production by fermentation?

A It requires a high temperature and pressure.
B The process is faster than the hydration of ethene.
C It uses renewable resources, making it more sustainable.
D The process is highly efficient and produces large amounts of ethanol.

12 In the following reaction pathways, what are the unknown compounds X, Y and Z?

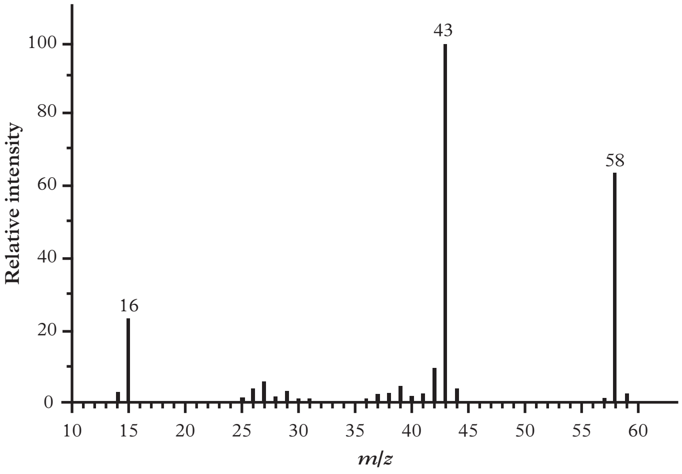
$$\text{Haloalkane} \longrightarrow \text{Compound X}$$

$$\text{Compound X} + \text{Compound Z} \longrightarrow \text{Ester}$$

$$\text{Compound Z} + \text{Compound Y} \longrightarrow \text{Amide}$$

A Alcohol, acid, amine
B Alcohol, amine, acid
C Amine, acid, alcohol
D Amine, alcohol, acid

13 A compound has the molecular formula C_3H_6O. The mass spectrum of the compound is shown. Identify the compound.



A CH_3COCH_3
B CH_3CH_2CHO
C $CH_3CHCHOH$
D CH_2CHCH_2OH

14 An unbranched non-cyclic hydrocarbon with the formula C_5H_{10} can exist as more than one isomer. Which types of isomers could exist for the given formula?

A Structural isomers only
B Geometric isomers only
C *cis* and *trans* isomers only
D Structural and geometric isomers

15 Ammonia is produced industrially at an optimal temperature range of 450–500°C. This temperature is selected because it

A accelerates the rate of the forward reaction, although the equilibrium position remains relatively unaffected.
B shifts the equilibrium to favour ammonia production, while the reaction rate is sufficiently high for industrial-scale efficiency.
C increases the rate of reaction significantly, while still maintaining a somewhat favourable equilibrium for ammonia production.
D favours the formation of ammonia by shifting the equilibrium to the right, while ensuring the temperature is safe on an industrial scale.

16 As the number of carbon atoms in linear alkanes increases, the boiling point increases because

A very long alkane molecules can be entangled with each other and so resist boiling.
B there are more hydrogen atoms and so stronger hydrogen bonds form between molecules.
C longer alkane molecules have more electrons and a larger surface area, increasing the dispersion forces between molecules.
D longer, larger alkane molecules will experience an increase in both dispersion forces and hydrogen bonding, raising the boiling point.

17 Methyl ethanoate, which is an ester, was made in a school laboratory. The yield was 71%. The yield was not higher because the

A students should have waited longer for the reaction to go to completion.
B limiting reactant was completely used up and no more products could form.
C reaction is reversible and reached equilibrium at this point so the amount of products could not increase.
D reaction is reversible and although the reaction went to completion, some of the products then turned back into reactants.

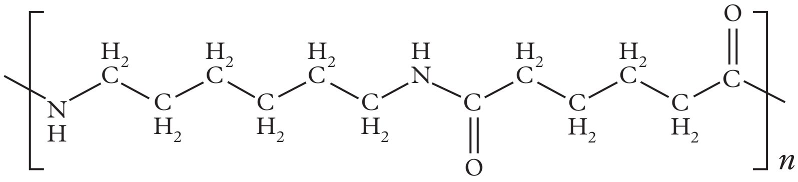
18 What is the main difference between low-density polyethene (LDPE) and high-density polyethene (HDPE)?

A The type of monomer used
B The polymerisation temperature
C The degree of branching in the polymer chains
D LDPE is formed by addition and HDPE is formed by condensation

19 Polylactic acid (PLA) is biodegradable and degrades into

A nitrogen and methane.
B sulfur dioxide and water.
C carbon dioxide and water.
D ammonia and carbon monoxide.

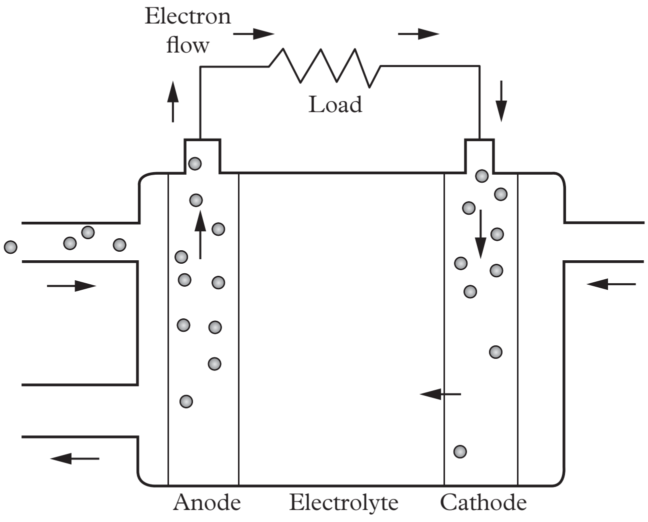
20 The polymer shown in the diagram is a



A polyester and is produced in an addition reaction.
B polyamide and is produced in an addition reaction.
C polyester and is produced in a condensation reaction.
D polyamide and is produced in a condensation reaction.

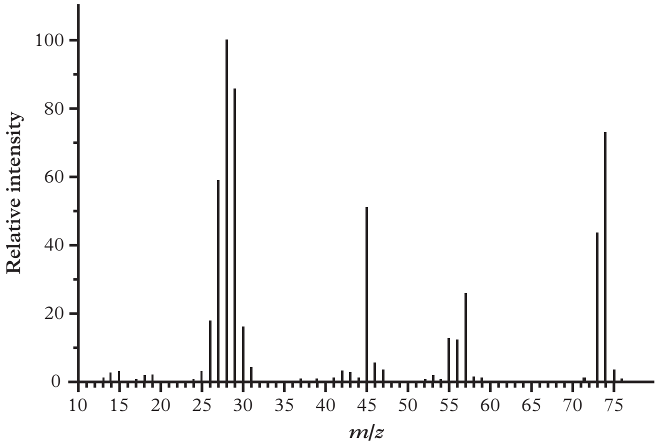
Short response

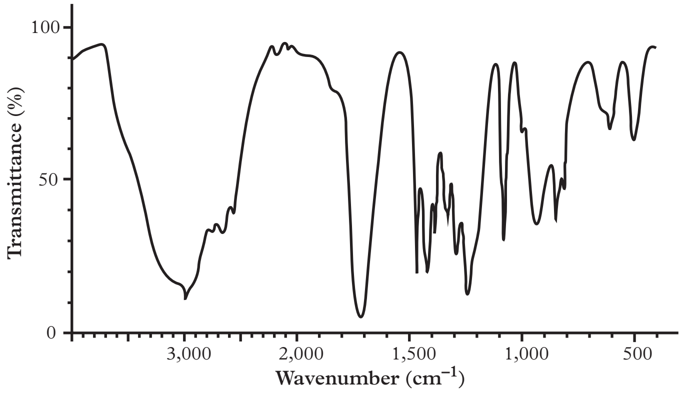
21 The diagram depicts a hydrogen fuel cell operating under alkaline conditions.



On the diagram, mark the inputs and outputs of water, hydrogen and oxygen. **Identify** the ion in the electrolyte and mark the direction it moves in. (4 marks)

22 The mass and infrared spectra of an organic compound are as follows.





Analyse the spectra to **deduce** the structural formula of the compound. **Explain** your reasoning. (5 marks)

23 Polypropene exists as three different stereoisomers with the following properties.

Stereoisomer	Properties
X	Rubbery and flexible
Y	Melting point 165°C, strong, tough and hardwearing
Z	Melting point 125°C, used for insulation

Identify the names and structures of X, Y and Z based on these properties. **Explain** your reasoning, based on structural differences. (6 marks)

24 The polymer nylon 6 is formed from the monomer $H_2N(CH_2)_5COOH$.

- **a** **Construct** the structural formula of nylon 6. (1 mark)
- **b** **Determine** whether nylon 6 is an addition or condensation polymer. **Explain** your reasoning. (2 marks)

25 Paper chromatography is carried out on three amino acids. The retention factors are 0.85, 0.46 and 0.31. **Explain** why these three amino acids have different retention factors. (3 marks)

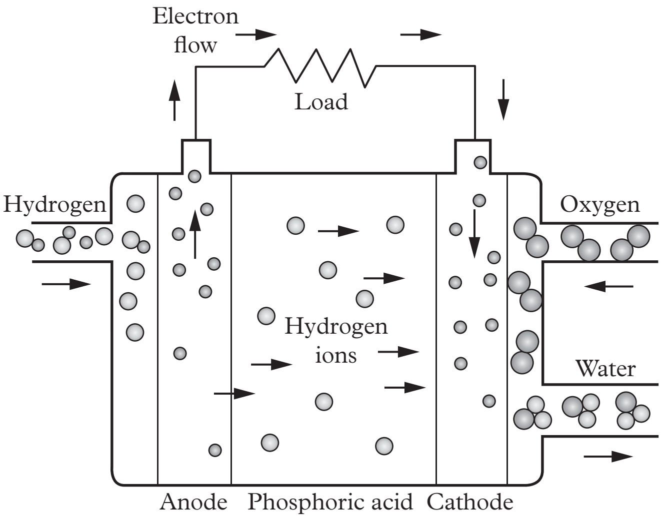
26 During electrophoresis of asparagine and arginine, the amino acids move in opposite directions. **Deduce** the pH range of the electrophoresis buffer, the ionic charge of each of the two amino acids and which electrode each is moving towards. **Explain** your reasoning. (6 marks)

27 **Sketch** and name the non-cyclic isomers of $C_3H_4Cl_2$. (2 marks)

28 **Compare** polyethene and polytetrafluoroethene in terms of their structures and properties. (5 marks)

29 **Construct** balanced equations to show how you would synthesise 1,2-dibromopropane from propyne. Show all conditions. (2 marks)

30 A hydrogen fuel cell operating under acid conditions is shown.



- **a** **Identify** the half-reactions and electrode potentials for this cell. (2 marks)
- **b** **Calculate** the cell potential (voltage) produced by this cell. (1 mark)
- **c** **Compare** the half-reactions, electrode potentials and cell potential of this cell with those of a hydrogen fuel cell operating under alkaline conditions. (5 marks)

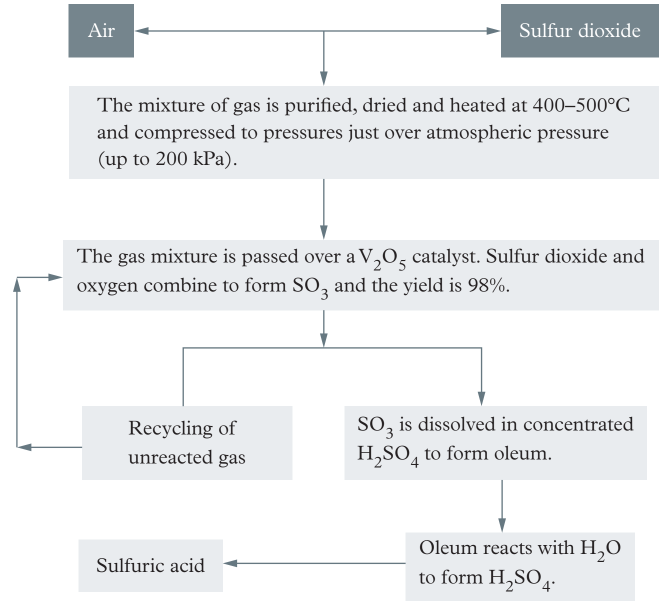
31 Compound X is known to contain carbon, hydrogen and oxygen. An aqueous solution of the compound reacts with $NaHCO_3$ to form a gas. 100 mg of compound X undergoes complete combustion and produces 227 mg of CO_2 and 93.0 mg of H_2O. **Deduce** the

- **a** empirical formula. Show all working (5 marks)
- **b** structural formula and name. **Explain** your reasoning. (3 marks)

32 2-Chlorobutane reacts with a large excess ammonia to form compound Z.

- **a** **Determine** the balanced equation for the reaction, including conditions. (1 mark)
- **b** **Sketch** the structure of compound Z, **identify** the class of compound and state whether it is primary, secondary or tertiary. (3 marks)
- **c** Compound Z has a K_b of 3.6×10^{-4}. **Determine** the pH of a 0.50 M aqueous solution of this compound. State any assumptions made. (6 marks)

33 The preparation of sulfuric acid by the contact process can be explained in a flow chart as shown.



The formation of sulfur trioxide from sulfur dioxide is exothermic. A 1:1 mixture of sulfur dioxide to oxygen is mixed in the reaction chamber.

a **Construct** a balanced equation for the formation of sulfur dioxide in this process. (1 mark)

b **Propose** a justified reason why a ratio of 1:1 sulfur dioxide to oxygen is used, even though this is not the stoichiometric ratio shown in your answer to part **a**. (2 marks)

c **Use** Le Châtelier's principle to **determine** the temperature and pressure conditions that would favour the highest yields at equilibrium. (4 marks)

d **Propose** a justified reason for using relatively high temperatures. (2 marks)

e **Propose** a justified reason for using relatively low pressures. (2 marks)

34 Compound A is an organic compound that has the molecular formula C_4H_8. It decolourises bromine water. It also reacts with H_2O at high temperature and pressure with a phosphoric acid catalyst to form two products, compound B and compound C. These are separated and about 3% of the product is compound B while the remainder is compound C.

Compound B is oxidised twice, forming compound D at the final stage. Compound C cannot be oxidised.

Compound B and compound D are reacted under reflux to form compound E, which has a distinctive smell.

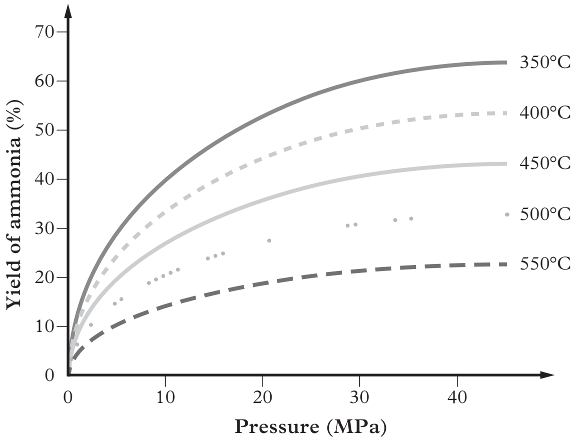
a **Determine** whether compound A is saturated or unsaturated. Provide evidence. (2 marks)

b **Deduce** the structures and names of compounds B and C. **Justify** your reasoning. (5 marks)

c **Deduce** the structure of compound D. Justify your reasoning. (2 marks)

c **Deduce** the structure of compound E. Justify your reasoning. (2 marks)

35 Ammonia is produced by the Haber process. The reaction is exothermic and releases 46 kJ for the formation of one mole of ammonia. The following graph depicts the equilibrium yield of ammonia at various temperatures and pressures.



a **Construct** a balanced thermochemical equation for the reaction. (1 mark)

b From the graph, **determine** which temperature and pressure produce the highest yield at equilibrium. (1 mark)

c **Use** Le Châtelier's principle to **explain** why the temperature and pressure from part **b** produce a higher yield when compared to other temperatures and pressures. (3 marks)

d In industry, a temperature of 450°C and a pressure of 20 MPa is typically used. **Propose** why these conditions are used in practice. (2 marks)

e The reaction is not allowed to go to completion; instead, the reaction mixture is periodically cooled under pressure and ammonia is allowed to condense and be removed before continuing. **Explain** why cooling under pressure allows the condensation and removal of pure ammonia. (3 marks)

f **Explain** how the step of ammonia removal affects the overall rate of reaction. (2 marks)

TOTAL MARKS

/116

MODULE 15

Practical manual

Introduction

This is a guide to all practicals included in the QCAA Senior Chemistry Syllabus. The practicals in this module have been trialled, and safety instructions are provided; however, teachers are legally obliged to perform their own risk assessments before undertaking any practical activity. The practicals are not prescriptive, and schools may adapt them to their own needs.

When undertaking practical experiments, you should always wear laboratory (lab) coats, safety glasses and enclosed footwear, and tie back long hair.

The following is a summary of general safety precautions to take in the laboratory.

→ Chemicals – handle all chemicals with care and consult your teacher and risk assessments for all hazards involved with each chemical.

→ Burns – hot water and hotplates can cause burns. These can be avoided by not moving boiling water and avoiding splashing, as well as leaving heated samples to cool before using them. It is also important to ensure that each member of your group is aware if a hotplate is on, and once you have finished with it, use a hazard sign to warn others that it may still be hot.

→ Electrical cords – always keep electrical cords away from water and hot metal surfaces.

→ Electric shock – electrical equipment can cause electric shocks and serious or fatal injury. When using electrical equipment, make sure there are no exposed wires.

→ Glass – glass can shatter and cut you. Be careful when using thermometers, conical flasks, beakers or other glassware. Handle each item with care. Place glassware away from the edge of the bench. Do not use your hands to pick up broken glass.

→ If an injury or accident happens, tell your teacher immediately.

Please familiarise yourself with your school's safety procedures, including the location of first aid kits, safety equipment, chemical waste disposal and the set-up and pack-down of practical stations. If you are unsure of any steps in any practical, check with your teacher for the best course of action.

Along with guidance for completing data collection and analysis for any practical you encounter in your QCE Chemistry course, Module 1 Chemistry toolkit is a good reference for how to keep safe in the laboratory.

oxforddigital

Full lessons for this module are available on Oxford Digital. They are also provided as part of a printable resource that can be used in class.

Unit 3 Practicals

Lesson 2.3	Investigating the effect of concentration on equilibrium
Lesson 2.4	Investigating the effect of volume and pressure on equilibrium
Lesson 2.5	Investigating the effect of temperature on equilibrium
Lesson 2.7	Determining the K_{sp} of calcium hydroxide
Lesson 2.9	Simulating equilibrium systems
Lesson 3.3	Investigating the properties of strong and weak, concentrated and dilute acids and bases
Lesson 4.3	Comparing the relative strengths of acids and bases
Lesson 5.3	Determining the concentration of ethanoic acid in white vinegar
Lesson 5.5	Conductometric titration
Lesson 6.4	Performing single displacement reactions
Lesson 7.3	Constructing a galvanic cell
Lesson 8.3	Investigating factors affecting electrolysis
Lesson 8.4	Electroplating using an electrolytic cell

Unit 4 Practicals

Lesson 9.6	Modelling isomers of organic molecules
Lesson 9.8	Investigating properties of homologous series
Lesson 10.2	Testing for saturation
Lesson 10.4	Testing alcohols
Lesson 12.2	Identifying amino acids using paper chromatography
Lesson 12.4	Identifying amino acids using electrophoresis
Lesson 12.6	Identifying organic compounds using mass spectrometry and infrared spectroscopy
Lesson 13.2	Simulating the Haber process
Lesson 13.3	Simulating the contact process
Lesson 14.3	Investigating the properties of polymers

Glossary

A

absolute uncertainty
the exact magnitude of difference between the mean and the range of measurements; an indicator of the precision of measurements

accuracy
a measure of how close the measured value is to the true or accepted value

acid dissociation constant (K_a)
the equilibrium constant for the dissociation of an acid in aqueous solution

activation energy (E_a)
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 made from alkene monomer units that bond together in an addition reaction

addition polymerisation
the successive addition reactions of alkene monomers to form a polymer

adsorb
the process of the component sticking onto the solid surface of the stationary phase (not the same as absorb)

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 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 carbon atoms

alkyl group
a group formed by removing a hydrogen from an alkane; can be present as a substituent in an organic compound

alkyne
a class of organic compound that contains one or more triple bonds between 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

amorphous
describes how polymer molecules are arranged randomly

amphiprotic
a molecule or an ion that can either donate or accept a proton and so therefore can act as an acid or base

anaerobic
the absence of air, which normally supplies oxygen

analyte
a solution of unknown concentration

anode
the electrode where oxidation occurs

aromatic
an organic compound containing at least one ring structure with delocalised electrons

B

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

best estimate
a value closest to the true value, usually found by taking repeated measurements and averaging

bibliography
a full list of all resources used in some research, provided at the end of a report or submitted along with another form of presentation

bifunctional monomer
a monomer that contains two functional groups, which can be the same or different

biodegradable
can be broken down by living organisms

biodegradation
the breakdown of a substance, such as plastic, by microorganisms

biofuel
a fuel made from biological raw materials

blank solution
a solution that does not contain the compound being measured, but contains all other compounds that would be present in the sample being tested; allows the response due to those other compounds to be subtracted from other measurements

boiling point
the temperature at which a liquid boils, forming bubbles of vapour below the surface of the liquid

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

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 with a stopcock (tap) that dispenses very precise volumes of a solution

by-product
a product of a chemical reaction that was not the main or intended product

C

calibration
the configuration of an instrument against standard values to ensure that it measures a true value

carbohydrate
a molecule consisting of carbon (C), hydrogen (H) and oxygen (O) having the general formula $C_x(H_2O)_y$ (although they do not have water molecules within their structure); carbohydrates include saccharides (sugars), starches and cellulose

carbonyl
a functional group consisting of an oxygen atom double bonded to a carbon atom in the main chain (–C=O)

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

cathode
the electrode where reduction occurs

causation
when a change in a single variable causes a change in a second variable

cell diagram
a diagram of a galvanic cell that has all key components, reaction mechanisms and electron/ion movements labelled

cell potential difference
the electrical potential difference (V) between two electrodes; the voltage that the galvanic cell can generate under standard conditions

central tendency
the tendency for repeated measurements of the same value to be grouped around the mean, mode or median

change in enthalpy
the amount of heat absorbed or released by a system during a process at constant pressure, usually during a chemical reaction

charge
a property of subatomic particles, e.g. each electron has a 1– charge; measured in coulombs (C) and represented by Q

chemical species
a general term that refers to any identifiable entity involved in a chemical reaction or present in a chemical system; can include atoms, ions, molecules and complexes; in a chemistry context, the word "species" may be used interchangeably with the term "chemical species"

chemical system
the reaction mixture, including reactants, products, catalysts and any solvents

chemistry
an experimental science concerned with the study of matter, and how substances can be combined or separated and how substances interact with energy

chiral centre
a carbon atom bonded to four different substituents

chromatography
an analytical technique that depends on the different rates at which molecules are carried along with a mobile phase (solvent) across a stationary phase (chromatography medium)

closed system
a chemical system that allows energy to move into and out of the system but does not allow the transfer of matter

cognitive verb
a task word that requires you to perform a specific cognitive task

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 a chemical species in a given volume in a solution

conclusion
a summary of the findings and results obtained from the research investigation

concordant titres
volumes of solution dispensed from a burette that differ by only 0.1 mL between the highest and the lowest

condensation polymer
a polymer formed when monomers undergo condensation and water is produced as a by-product

condensation reaction
a reaction in which two organic compounds combine to produce a main product and another small molecule, frequently water

conductivity
a measure of the ability of a solution to conduct an electrical current

confounding variable
an extraneous variable that changes systematically along with the variables being studied and offers an alternative explanation for the observations or measurements made

conjugate acid
an acid formed when a base accepts a proton (H^+)

conjugate acid–base pair
two chemical species differing only by the presence or absence of a proton

conjugate base
a base formed by removing a proton (H^+) from an acid

contact process
the production of very concentrated sulfuric acid

controlled variable
a condition that the experimenter tries to keep constant during an experiment, in order to minimise its effect on measurements or experiment outcomes

correlation
a link between a change in the independent variable and a change in the dependent variable; this does not mean that the changing independent variable caused the change in the dependent variable

corrosion
the degradation of a metal to form a more stable metal oxide when exposed to gases and liquids

coulomb
the unit used to measure charge, 1 coulomb (C) of charge is the amount of charge carried by a current of 1 amp (A) flowing for a time of 1 second

crystalline
describes regions in polymers where the polymer molecules are arranged in a regular way

current
the flow of electrons generated by a power source; the number of coulombs of charge per second, measured in amps (A); symbol for current is I

D

dependent variable (DV)
a variable that is measured or observed during an experiment, whose change is in response to changes made in the independent variable

desorb
the release of the compound being analysed from the solid surface of the stationary phase

dimer
a structure consisting of two identical molecules linked together; they may be linked by chemical bonds into a larger molecule, or simply held in place by intermolecular forces

disaccharide
two sugar monomers bonded together

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

E

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

electrochemical cell
a device that generates electrical energy from chemical reactions

electrochemical series
a table of 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

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

electrolytic cell
an electrochemical cell in which electricity is used to drive a non-spontaneous redox reaction

electromotive force (EMF)
the difference in potential across a cell that generates electricity

electronegativity
a measure of the tendency of an atom to attract a bonding pair of electrons when compared to an atom of another element

electrophoresis
a separation technique that involves the movement of charged particles, such as amino acids, along an electric field

elimination reaction
the removal of substituents to form a multiple bond

empirical formula
the simplest whole-number ratio of the elements in a compound

end point
the point in a titration when the indicator changes colour

equilibrium constant (K_c)

the ratio of products to reactants, raised to appropriate powers, 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 law that states that 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), which is a constant value for a particular reaction at a particular temperature.

equivalence point

the point in a titration when the reactants have reacted in the stoichiometric 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 to produce an ester

Eurocentrism

a world view that focuses on or favours Western or European histories and thinking

excess reagent

the reactant in a chemical reaction that is not completely used up

experimental yield

the actual amount of the product

extent of dissociation

the proportion of the total number of molecules of a substance that dissociate into its constituent ions or molecules

external circuit

the electric circuit (wires) that allow electrons to move from anode to cathode

extraneous variable

a variable not being intentionally studied during an experiment that could have an unplanned or unintended effect on the results

extrapolation

the prediction of values beyond the range of data points by extending the trendline

extrude

push through a small opening

F

Faraday's constant

$1\,F = 96{,}485\,\text{C mol}^{-1}$; states that the charge of 1 mole of electrons is $96{,}485\,\text{C}$

Faraday's first law

the mass of the metal plated at the cathode is proportional to the charge applied to the cell: $Q \propto m$

Faraday's second law

to produce 1 mole of a metal, 1, 2, 3 or another whole number of moles of electrons must be consumed

fermentation

the chemical breakdown of a substance by bacteria, yeasts or other microorganisms

First Nations peoples

past and current descendants of the original inhabitants and custodians of the Land we know today as Australia

forward reaction

the reaction between reactants to form products

free radical

an uncharged species with an unpaired electron; highly reactive

functional group

an atom or a group of atoms that has similar chemical properties whenever it appears in various compounds

G

galvanic cell

an electrochemical cell that converts chemical energy into electrical energy; the reduction and oxidation half-equations are separated and connected through a circuit to generate electricity

geometrical isomers

two organic compounds that have different arrangements of atoms around a rigid double bond

glycosidic linkage

a bond that connects sugar monomers together

gradient

the slope of a graph

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 half of the original analyte has reacted with the titrant; also called the midpoint

haloalkane

a class of organic compound that contains a halogen substituent

halogenation

the addition of a halogen across a carbon–carbon multiple bond

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 carbon–carbon multiple bond

hydrohalogenation

the addition of a hydrogen atom and a halogen atom across a double bond

hydroxyl

a functional group consisting of an –OH group, which is an oxygen atom and a hydrogen atom joined by a single bond

hypothesis

a proposed explanation used as a starting point for further investigation

I

implication

potential consequence or effect of scientific results or conclusions

in-text reference

an acknowledgement of the source immediately after the research or information is referred to

independent variable (IV)

a variable that is altered systematically in a controlled way by the experimenter to test the effect on a related dependent variable

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

interpolation

the prediction of values between data points using a trendline

ionic product constant of water (K_w)

the equilibrium constant for the self-ionisation of water

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

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

linearising
the process of transforming non-linear data by applying a mathematical function to one of the variables so that the relationship between the variables becomes closer to a straight line

locant
a number or letter that indicates the position of a substituent or functional group in an organic compound

low-density polyethylene (LDPE)
a polymer made from the monomer ethane, 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

maximum trendline
a line of best fit of maximum gradient within the bounds of the error bars

mean
the average of multiple values

median
the value that appears in the middle when the dataset is sorted from smallest to largest value

melting point
the temperature at which a material changes from a solid to a liquid, which is also the temperature at which a material freezes

meniscus
the curved upper surface of a liquid in a piece of measurement glassware

minimum trendline
a line of best fit of minimum gradient within the bounds of the error bars

miscible
completely soluble

mobile phase
the phase that moves across the stationary phase, i.e. the solvent

mode
the value that appears the most often in a dataset

mole ratio
the actual ratio of amounts in moles of reactants (or products) in a given reaction mixture or sample

molecular formula
the complete chemical formula of a compound that indicates the number of atoms of each element present

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

molten
melted or liquefied

monomer
a small molecule that is a subunit of 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

negative control
a test to make sure that an experiment is working as expected, which should not cause any change to the DV

nomenclature
a set of rules for naming organic compounds, e.g. the IUPAC rules of organic nomenclature

non-renewable
a source material or its product that exists in finite amounts that are not replenished

O

oleum
a solution of sulfur trioxide in sulfuric acid, also called fuming sulfuric acid

open system
a chemical system that allows both matter and energy to move into and out of the system

optical isomers
two organic compounds that have the same atoms and bonding but a different arrangement of four substituents around a chiral carbon atom

outlier
a value that is much smaller or larger than most of the other values in a set of data; it is greater than three standard deviations away from the mean

overall equation
a reaction that combines the two half-equations after electrons have been balanced and cancelled out

overall redox equation
an equation found by balancing electrons in both half-equations, cancelling the electrons, and adding the half-equations together

oxidation
a loss of electrons

oxidation number
the number of electrons gained or lost by an atom, relative to the element

oxidation reaction
an organic reaction involving the gain of oxygen atoms 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

paper chromatography
a chromatography technique that uses chromatography paper as the stationary phase and a solvent (e.g. water) as the mobile phase

peptide
a molecule made of amino acid monomers

peptide bond
the bond formed in a condensation reaction between the carboxyl group of one amino acid and the amine group of another amino acid; water has been eliminated

percentage error
the percentage difference between the accepted (true or theoretical) value and the measured (experimental) value

percentage uncertainty
an indicator of uncertainty in which the range of values for a measurement result (the absolute uncertainty) is expressed as a percentage of the measurement

pH
a measure of the 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 very precise 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

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

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

positive control
a test to make sure that an experiment is working as expected, which should give a positive result

precision
the consistency and reproducibility 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 area, by one substance on another substance

primary alcohol
an alcohol in which the carbon that is bonded to the OH group is bonded to one other carbon

primary data
first-hand data collected from an experiment designed to answer the specific research question

primary haloalkane
a haloalkane in which the carbon that is bonded to the halogen atom is bonded to one other carbon

primary standard
a substance that is readily available in a highly pure form that can be dissolved in a solvent to create a standard solution

proton acceptor
a substance that can accept H^+ (hydrogen ions)

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

Q

qualitative data
data about types or categories, which may be represented by names, symbols, codes etc.

quantitative data
numerical data about a substance, object or phenomenon

R

R group
the side chain of an amino acid

random error
an unpredictable error in measurement or experimental procedure that has no detectable pattern

raw data
primary data that is collected but not yet processed or analysed

reaction pathway
a series of chemical reactions in which one or more reactants produces a desired product

reaction quotient (Q_c)
the ratio of concentration of products to reactants, raised to the appropriate powers in a system when it is not at equilibrium

reagent
a substance or compound added to a system to cause a chemical reaction or test for the presence of another substance

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 or the gain of hydrogen atoms

reflux
a technique in chemistry where a reaction mixture is kept boiling, with the vapours being condensed and collected in the reaction mixture

refute
contradict or do not support (in relation to the claim or hypothesis)

reliability
the ability to be trusted to be accurate or correct, or to provide a correct result

renewable
replaceable at a rate equal to or greater than the rate of use, over an indefinite period

replicate
a repeated measurement, which gives an indication of the precision of measurements

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

rigid
unable to change shape

risk assessment
a systematic evaluation of the potential risks and the likelihood of them being involved in an experiment or activity

S

safety data sheet (SDS)
a document that lists information about hazardous and non-hazardous materials; also known as a product safety data sheet (PSDS)

salt bridge
an electrical connection between the two half-cells of an electrochemical cell; it allows the flow of charge by moving ions – cations to the cathode and anions to the anode

saturated hydrocarbon
a compound of carbon and hydrogen that contains the maximum possible number of hydrogen atoms for the number of carbon atoms present

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

secondary alcohol
an alcohol in which the carbon that is bonded to the hydroxyl group is bonded to two other carbons

secondary data
second-hand data obtained from other sources

secondary haloalkane
a haloalkane in which the carbon that is bonded to the halogen atom is bonded to two other carbons (the halogen atom is located in the middle of the chain)

secondary standard
a solution whose concentration has been accurately determined by titration with a primary standard, allowing it to be used in further titrations

self-ionisation of water
the reaction in which a water molecule transfers a hydrogen ion to another water molecule; the first molecule becomes a hydroxide ion (OH^-) and the second water molecule forms a hydronium (H_3O^+)

significant figures
the number of numerical figures that can be used to express a measured or calculated quantity

single displacement
a chemical reaction in which a more reactive metal ion replaces a less reactive metal ion in a compound

solubility
the degree to which a substance dissolves in a particular solvent to make a solution (frequently expressed as grams of solute per litre of solvent)

solubility titration
a titration performed to determine the ion concentrations, solubility and K_{sp} of an insoluble ionic compound

solute
the minor component of a solution; the substance dissolved in the solvent

solution
a homogeneous mixture of a solute dissolved in a solvent, where the concentration is the same throughout the solution

solvent
the major component of a solution; what the solute is dissolved in

spectator ion
any ion in a reaction mixture that does not take part in the reaction; they are omitted from the half-equations and overall equation, e.g. when $KMnO_4$ is used, K^+ is a spectator ion and MnO_4^- is the ion that reacts

standard conditions
the conditions under which all $E°$ values are measured: 25°C (298 K), 100 kPa and 1 M

standard deviation
a statistical value that expresses how spread out a group of values are or by how much they differ from the mean value for the group

standard electrode potential ($E°$)
the electrical potential that an electrode generates under standard conditions

standard operating procedure (SOP)
step-by-step guidance for operating a piece of equipment or an instrument correctly and safely

standard solution
a solution of accurately known concentration

standardise
the process of determining the exact concentration of a solution, typically by titration against a solution of known concentration

stationary phase
the phase that remains fixed in place while the solvent moves through it

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 the amount 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 a 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

supernatant solution
the saturated solution lying above the solid residue that did not dissolve

support
agree with (in relation to the claim or hypothesis)

systematic error
a consistent, repeatable error that occurs every time a piece of equipment is used

T

temperature
a measure of the average kinetic 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

tertiary haloalkane
a haloalkane in which the carbon that is bonded to the halogen atom is bonded to three other carbons

theoretical yield
the maximum amount of product expected by a chemical reaction

thermoplastic
a type of polymer that can be moulded into new shapes

thermosetting
a type of a polymer that, once set in its shape, cannot take on a new shape when subjected to heat and/or pressure; this is because it forms multiple cross-linking covalent bonds between parts of the polymer chain as it cures

thin-layer chromatography
a chromatography technique that uses a thin layer of aluminium oxide, cellulose or silica gel as the stationary phase and an organic solvent as the mobile phase

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 the reaction reaches neutralisation

titration curve
a graph of pH against volume of reactant added

titre
the volume of solution dispensed from a burette

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)

trendline (line of best fit)
a line drawn on a graph joining as many points as possible and showing the general direction of the data; should be drawn with an approximately equal number of points above and below the line

tripeptide
a molecule that contains three amino acids linked by peptide bonds

U

unsaturated hydrocarbon
a compound of carbon and hydrogen that contains double or triple bonds and therefore has fewer than the maximum number of hydrogen atoms for the particular number of carbon atoms

V

valence electron
an electron in the outermost shell of an atom, according to the Bohr model of electron configuration

validity
a measure of whether the investigation is sound and measures what it is intended to measure

variable
a condition or parameter that is changed or changes during an experiment

volatility
how easily a liquid substance evaporates (becomes a vapour)

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 centimetres)

weak acid
an acid that only partially ionises in water, with the equilibrium favouring the acid form

weak base
a base that does not completely ionise in water

Y

yield
the amount of product obtained from a chemical reaction

Z

zwitterion
a molecule that has separate positively and negatively charged parts

Index

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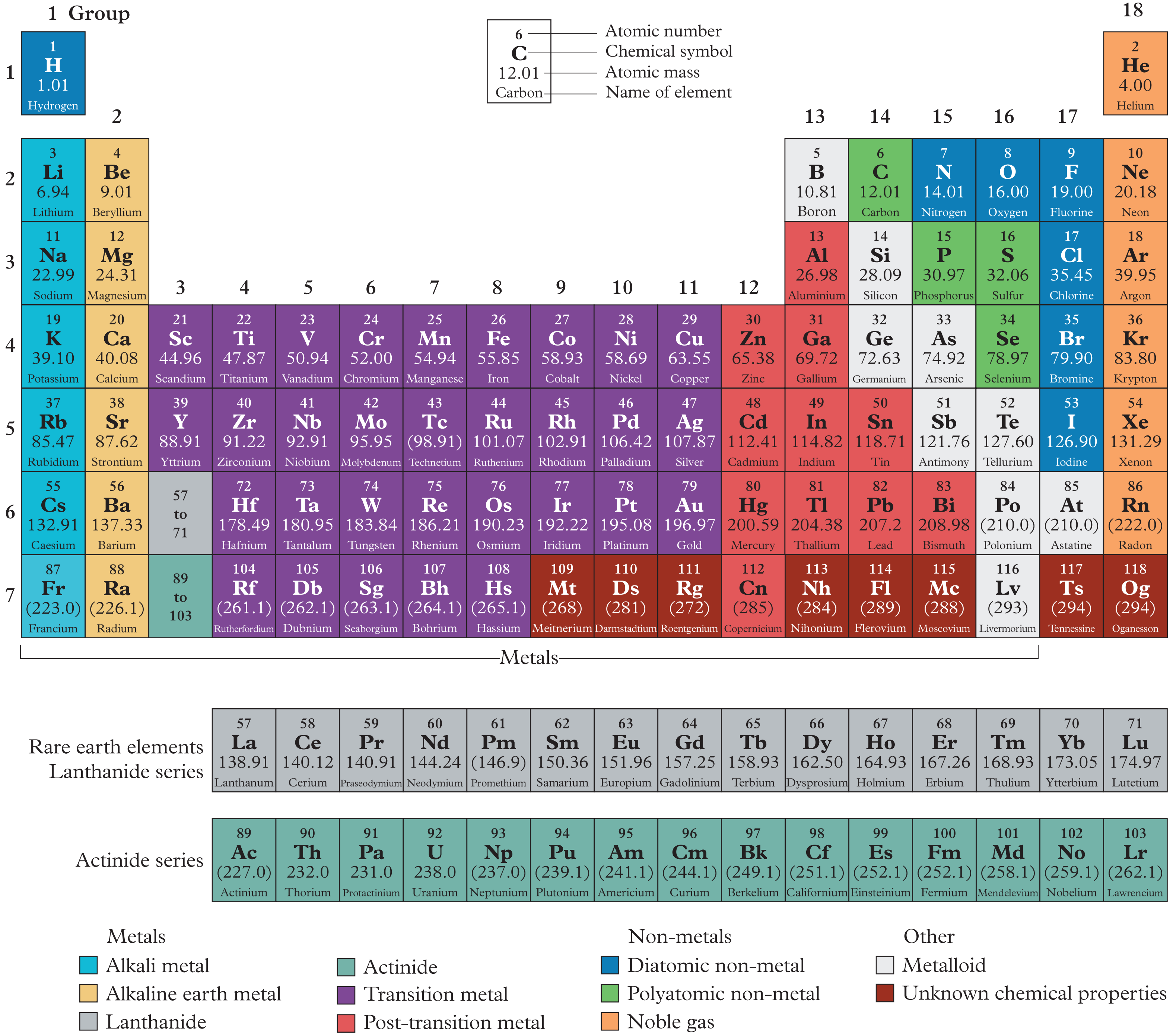
Appendix: Periodic table



	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** 32.06 Sulfur	17 **Cl** 35.45 Chlorine	18 **Ar** 39.95 Argon
4	19 **K** 39.10 Potassium	20 **Ca** 40.08 Calcium	21 **Sc** 44.96 Scandium	22 **Ti** 47.87 Titanium	23 **V** 50.94 Vanadium	24 **Cr** 52.00 Chromium	25 **Mn** 54.94 Manganese	26 **Fe** 55.85 Iron	27 **Co** 58.93 Cobalt	28 **Ni** 58.69 Nickel	29 **Cu** 63.55 Copper	30 **Zn** 65.38 Zinc	31 **Ga** 69.72 Gallium	32 **Ge** 72.63 Germanium	33 **As** 74.92 Arsenic	34 **Se** 78.97 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** 95.95 Molybdenum	43 **Tc** (98.91) Technetium	44 **Ru** 101.07 Ruthenium	45 **Rh** 102.91 Rhodium	46 **Pd** 106.42 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** 183.84 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 **Tl** 204.38 Thallium	82 **Pb** 207.2 Lead	83 **Bi** 208.98 Bismuth	84 **Po** (210.0) Polonium	85 **At** (210.0) Astatine	86 **Rn** (222.0) Radon
7	87 **Fr** (223.0) Francium	88 **Ra** (226.1) Radium	89 to 103	104 **Rf** (261.1) Rutherfordium	105 **Db** (262.1) Dubnium	106 **Sg** (263.1) Seaborgium	107 **Bh** (264.1) Bohrium	108 **Hs** (265.1) Hassium	109 **Mt** (268) Meitnerium	110 **Ds** (281) Darmstadtium	111 **Rg** (272) Roentgenium	112 **Cn** (285) Copernicium	113 **Nh** (284) Nihonium	114 **Fl** (289) Flerovium	115 **Mc** (288) Moscovium	116 **Lv** (293) Livermorium	117 **Ts** (294) Tennessine	118 **Og** (294) Oganesson

Metals

Rare earth elements Lanthanide series	57 **La** 138.91 Lanthanum	58 **Ce** 140.12 Cerium	59 **Pr** 140.91 Praseodymium	60 **Nd** 144.24 Neodymium	61 **Pm** (146.9) Promethium	62 **Sm** 150.36 Samarium	63 **Eu** 151.96 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** 173.05 Ytterbium	71 **Lu** 174.97 Lutetium
Actinide series	89 **Ac** (227.0) Actinium	90 **Th** 232.0 Thorium	91 **Pa** 231.0 Protactinium	92 **U** 238.0 Uranium	93 **Np** (237.0) Neptunium	94 **Pu** (239.1) Plutonium	95 **Am** (241.1) Americium	96 **Cm** (244.1) Curium	97 **Bk** (249.1) Berkelium	98 **Cf** (251.1) Californium	99 **Es** (252.1) Einsteinium	100 **Fm** (252.1) Fermium	101 **Md** (258.1) Mendelevium	102 **No** (259.1) Nobelium	103 **Lr** (262.1) Lawrencium

Metals
■ Alkali metal
■ Alkaline earth metal
■ Lanthanide
■ Actinide
■ Transition metal
■ Post-transition metal

Non-metals
■ Diatomic non-metal
■ Polyatomic non-metal
■ Noble gas

Other
□ Metalloid
■ Unknown chemical properties

Notes

Notes

Notes

Notes

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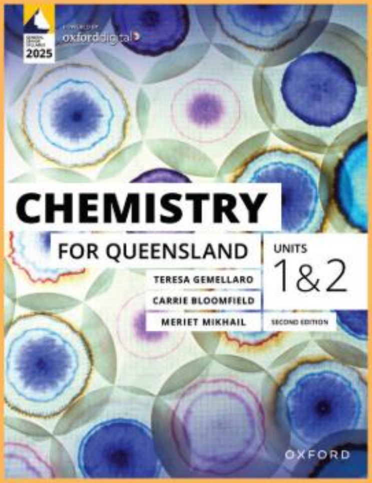

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