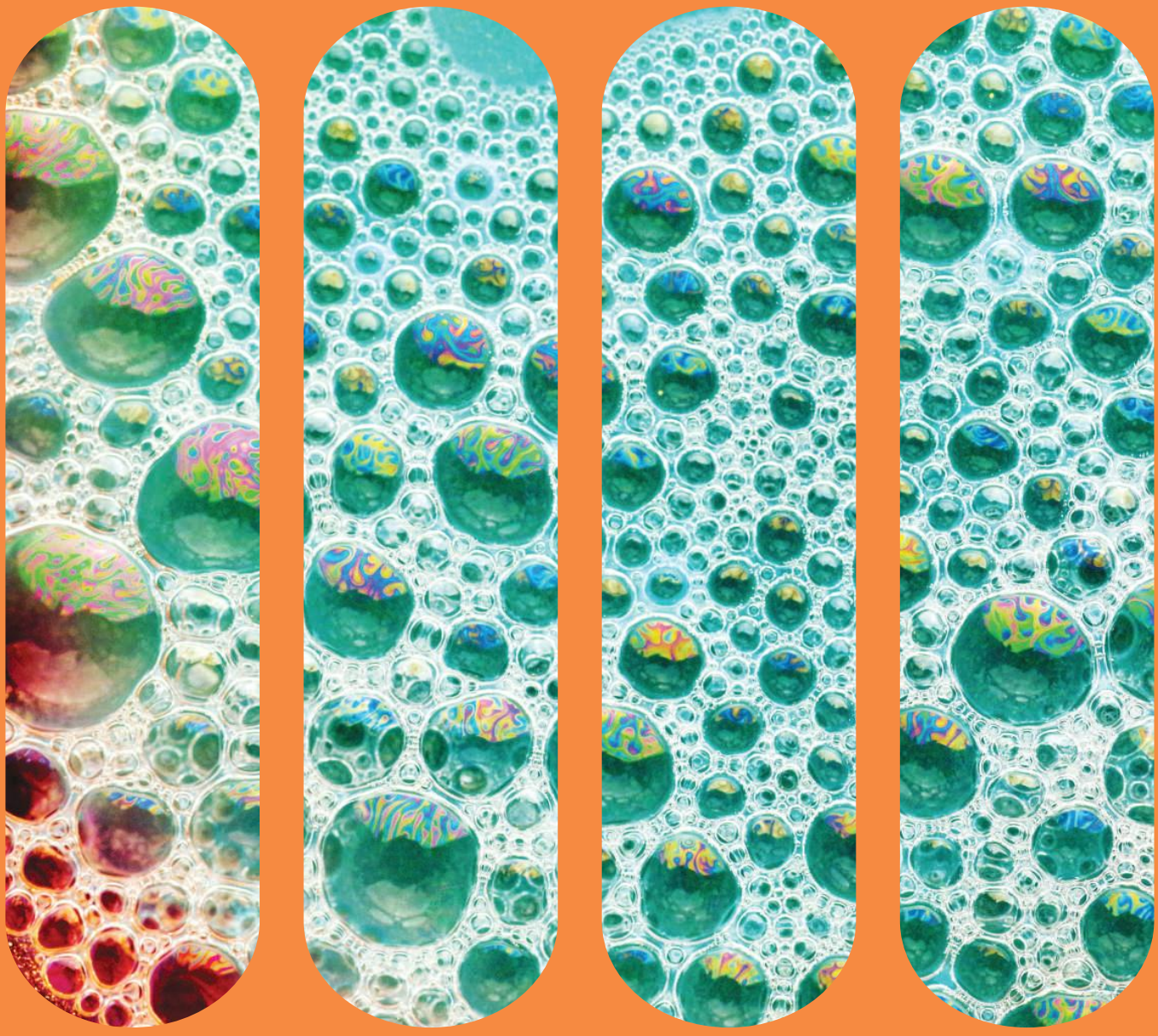
NELSON

QCE Chemistry

UNITS 3 4



Debra Smith
Michelle Brown
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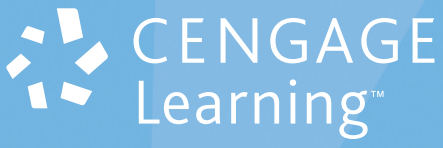

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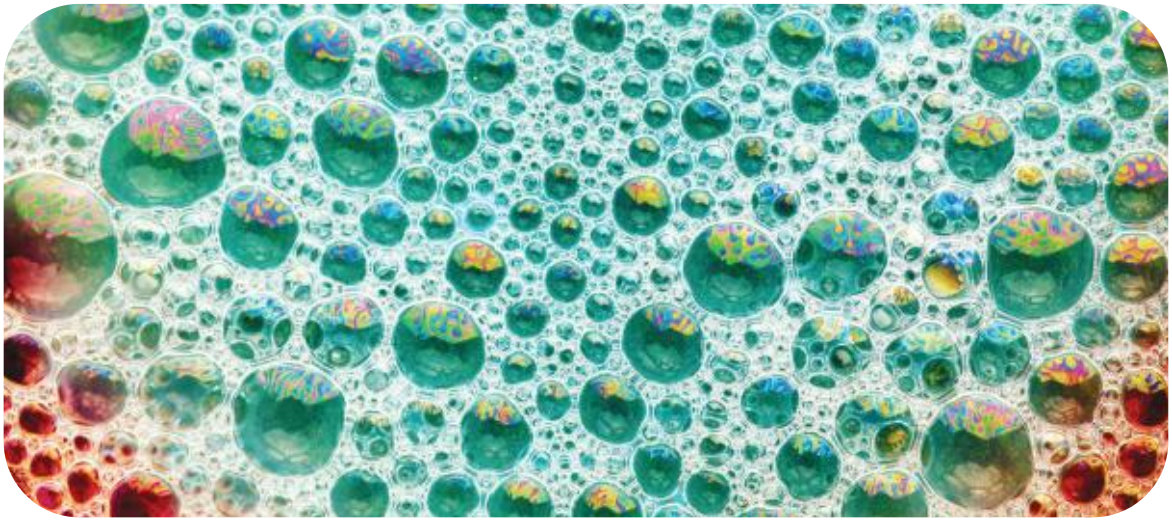
NELSON

QCE Chemistry

UNITS 3 4

LEARNING DISCOVERY

CHEMICAL EQUILIBRIUM SYSTEMS



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There are chemical reactions in this world that are able to go forwards and backwards; products can be made and then broken down to their original reactants at the same time. When the forward and reverse reactions occur at the same rate, the reaction reaches what we call equilibrium. Equilibrium reactions are all around us, like the process that allows us to transport oxygen around our body. Understanding how these reactions work and how we can influence them allows us to be more efficient.

Debra Smith
Michelle Brown
Rachel Bond

Nelson

Nelson QCE Chemistry Units 3 & 4
1st Edition
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Michelle Brown
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CONTENTS

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The following people have contributed to the review of the QCE Chemistry series: Colette Anderson, Bridie Smith and Selma Hassan.

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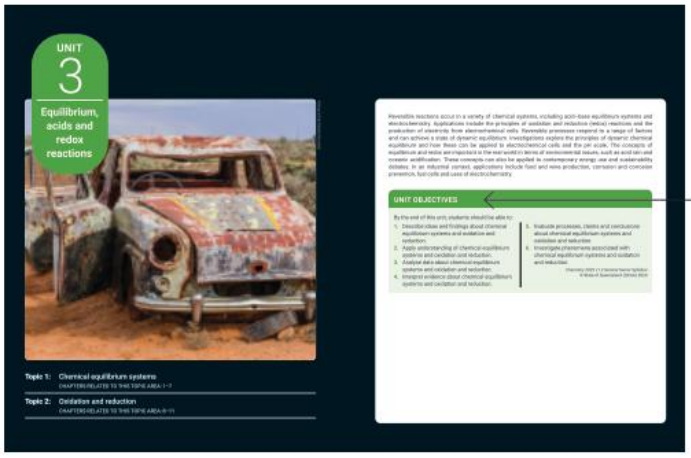
ABOUT THIS BOOK

Nelson QCE Chemistry Units 3 & 4 is a comprehensive textbook specifically tailored to align with the 2025 QCAA Senior Secondary Science Syllabus – Chemistry v1.2. It has been thoughtfully developed to empower students by providing a strong foundation in essential concepts and equipping them with the necessary skills to excel in their studies. Emphasising the importance of making connections between topics and practising exam techniques, this edition is designed to support students in unlocking their full potential and achieving success in their chemistry journey.

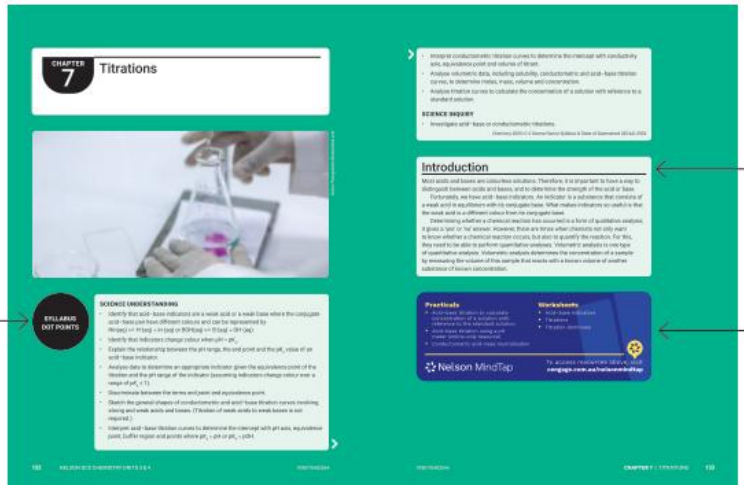
AT THE BEGINNING OF UNIT AND TOPIC

- Unit introductions are an overview of the key content in the unit.



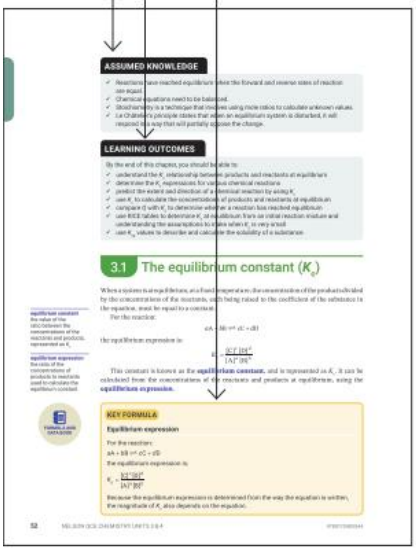
AT THE BEGINNING OF EACH CHAPTER

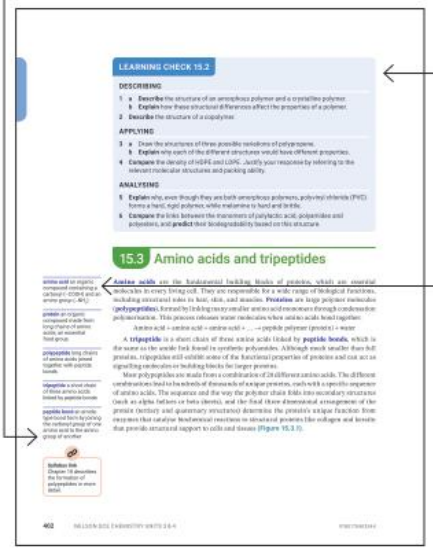
- Chapter introduction to set the context of the upcoming key content
- List of syllabus dot points being covered in the chapter
- List of resources available on Nelson MindTap



IN EACH CHAPTER

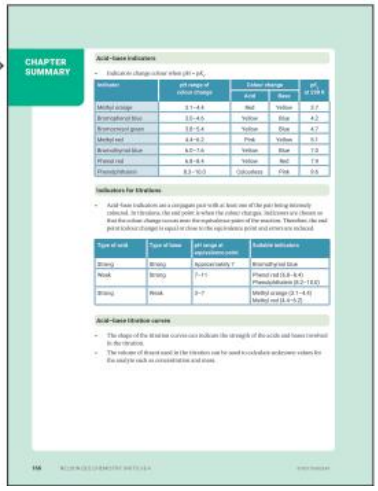
- **Assumed knowledge** – knowledge and skills students are expected to know coming into the chapter that relate to the chapter content
- **Learning outcomes** – highlights the key outcomes from the chapter
- **Key terms** – defined in situ to help students deconstruct scientific language
- **Learning check** – written to the developmental levels highlighted in the syllabus objectives
- **Syllabus links** – highlighting links to other areas in the syllabus to help students make connections
- **Key formulas** – important formulas to remember
- **Practicals** – syllabus-aligned practicals with guided instructions on the materials, procedure, collection and analysis of results, and discussion

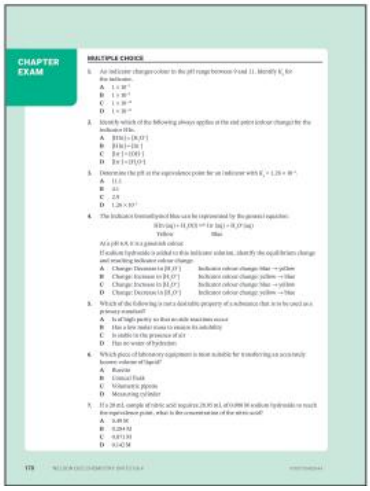




AT THE END OF EACH CHAPTER

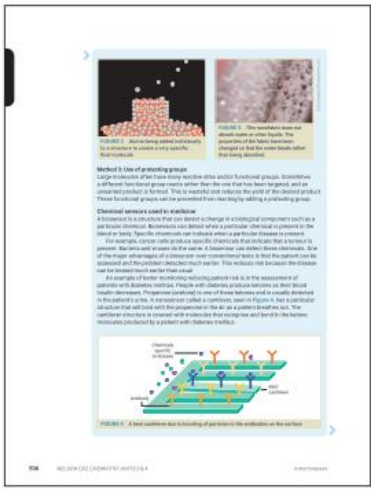
- **Chapter summary** – visual summaries to help summarise key concepts
- **Chapter exam** – exam-style questions to help students develop exam skills, including deliberate practice in data analysis and making connections across content





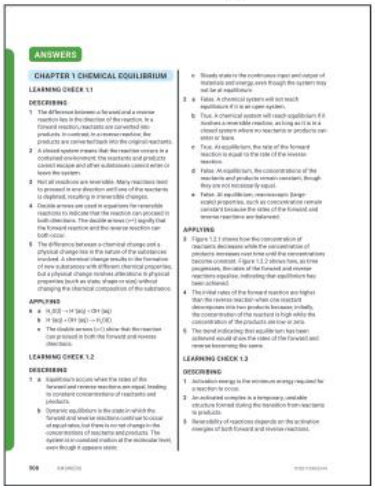
AT THE END OF EACH TOPIC

- **Science as a Human Endeavour** – a double-page deep dive on the evolution of science and how it has contributed to and influenced society



AT THE END OF THE BOOK

- **Glossary** provides explanations of all terms introduced in the text.
- **Answers** provide complete answers for student reference.



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- **Flexible formats:** choose how you navigate using either the online eText or offline PDFs.
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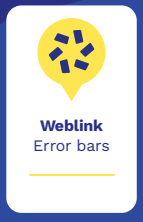

For students:

- **Engage** with the **online eText** by adding notes, highlights and bookmarks and using the **Search** and **Read Aloud** (in Australian voice) functions.
- **Check** your understanding with assumed knowledge reviews.*
- **Explore** key concepts with worksheets and additional online-only practicals.
- Access **supporting materials** such as the chapter summary pack and weblinks.
- **Revise** with chapter tests to practise your skills and build confidence.*
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*Available if assigned by your teacher in Cognero Assess.

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**Complimentary access to these resources is only available to teachers who use this book as part of a class set, book hire or booklist. Not available for single purchases. Alternatively, teacher access can be purchased as a separate subscription for schools. Contact your Cengage learning consultant for information about access and conditions.

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CHAPTER DC

Science research

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SYLLABUS DOT POINTS

SCIENCE INQUIRY SKILLS

Throughout the course of study, students will:

- identify, research and construct questions for investigation
- propose hypotheses and/or predict possible outcomes
- 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, sample size, 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
- 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
  - material safety data sheets
  - workplace health and safety guidelines

- appropriate disposal methods
- standard operating procedures
- acknowledgement of sources and referencing

- 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
- use scientific language and representations to systematically record information, observations, data and measurement error, e.g.
  - symbols, units and prefixes
  - tables, graphs and diagrams
  - 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.
  - logbooks
- translate information between graphical, numerical and/or algebraic forms, e.g.
  - units and measurement conversions
  - ratios and percentages
  - symbols and notation
- 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 $\left(\text{Formula: } \Delta\bar{x} = \frac{\pm(x_{max} - x_{min})}{2}\right)$ and percentage uncertainties $\left(\text{Formula: percentage uncertainty (\%)} = \frac{\text{absolute uncertainty}}{\text{measurement}} \times \frac{100}{1}\right)$
  - calculate the percentage error, when the experimental result can be compared with a theoretical or accepted result (value)

    $\left(\text{Formula: percentage error (\%)} = \left|\frac{\text{measured value} - \text{true value}}{\text{true value}}\right| \times \frac{100}{1}\right)$
  - 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
- discriminate between precision and accuracy
  - identify that all measurements have limits to their 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
- select, synthesise and use evidence to construct scientific arguments and draw conclusions
- extrapolate findings to determine unknown values, predict outcomes and evaluate claims
- 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 acceptance, bias, status, appropriateness and reasonableness
  - compare findings to theoretical models or expected values
  - discriminate between validity and reliability
- 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
- 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
- appreciate the role of peer review in scientific research.

Introduction

Conducting structured experiments is an important part of science because it allows for the gathering of information to help develop a greater appreciation and understanding of the world.

Performing research on scientific topics and the process of developing and implementing experimental methods form a large part of the scientific studies and formal internal assessment throughout this course. In fact, the Student Experiment (IA2) and Research Investigation (IA3) make up a significant portion of the internal assessments, incorporating both primary and secondary data. Furthermore, the scientific thinking acquired through these processes is regularly examined in the External Assessment. As such, it is important to develop these skills not just for this course, but also to improve critical thinking.

ASSUMED KNOWLEDGE

- ✓ The purpose of experiments is to collect information about a key idea or to answer a question.
- ✓ Controlled experiments have a general structure.
- ✓ Variables are factors or conditions that can be changed, controlled or measured and which can influence the result of an investigation.
- ✓ Variables include independent, dependent and controlled variables
- ✓ The data collected from an experiment needs to be related to the question being investigated.
- ✓ Data collected from an experiment can be presented in different ways depending on the nature of the data.
- ✓ Data can be classified as primary or secondary.

LEARNING OUTCOMES

- ✓ Develop research questions.
- ✓ Identify the importance of peer review in scientific research and compare different ideas and information from scientific texts.
- ✓ Plan and modify investigations, including the materials and methods needed to collect valid and reliable data (both primary and secondary data).
- ✓ Consider safety, ethics and the environment when conducting scientific investigations.
- ✓ Determine the best method to present data; for example, tables and graphs.
- ✓ Use scientific language and visual representations to organise and present information accurately.
- ✓ Identify and minimise errors in measurements.
- ✓ Calculate uncertainties and other measures of data accuracy and describe their impact on data.
- ✓ Select and construct the most appropriate data presentation technique.
- ✓ Make predictions based on trends observed in the data.
- ✓ Use mathematical techniques to analyse data to find patterns, trends and relationships, taking into account any limitations or sources of error or uncertainty.
- ✓ Draw conclusions based on evidence, comparing findings to expected results.
- ✓ Communicate scientific information in a clear and appropriate manner for different audiences, while acknowledging sources and using proper referencing techniques.
- ✓ Reflect on investigations and suggest ways to improve the quality and accuracy of data and findings.

DC .1 Student experiment

research question a question that directs the scientific inquiry activity; it focuses the research investigation or student experiment, informing the direction of the research, and guiding all stages of inquiry, analysis, interpretation and evaluation

Forming

The research question

For your Student Experiment (IA2), you will be required to design an experiment to answer a **research question** related to a topic in the syllabus. In science, the design of experiments is guided by the scientific method (Figure DC.1.1) – a systematic and structured approach that ensures that the results are objective, accurate and reliable.

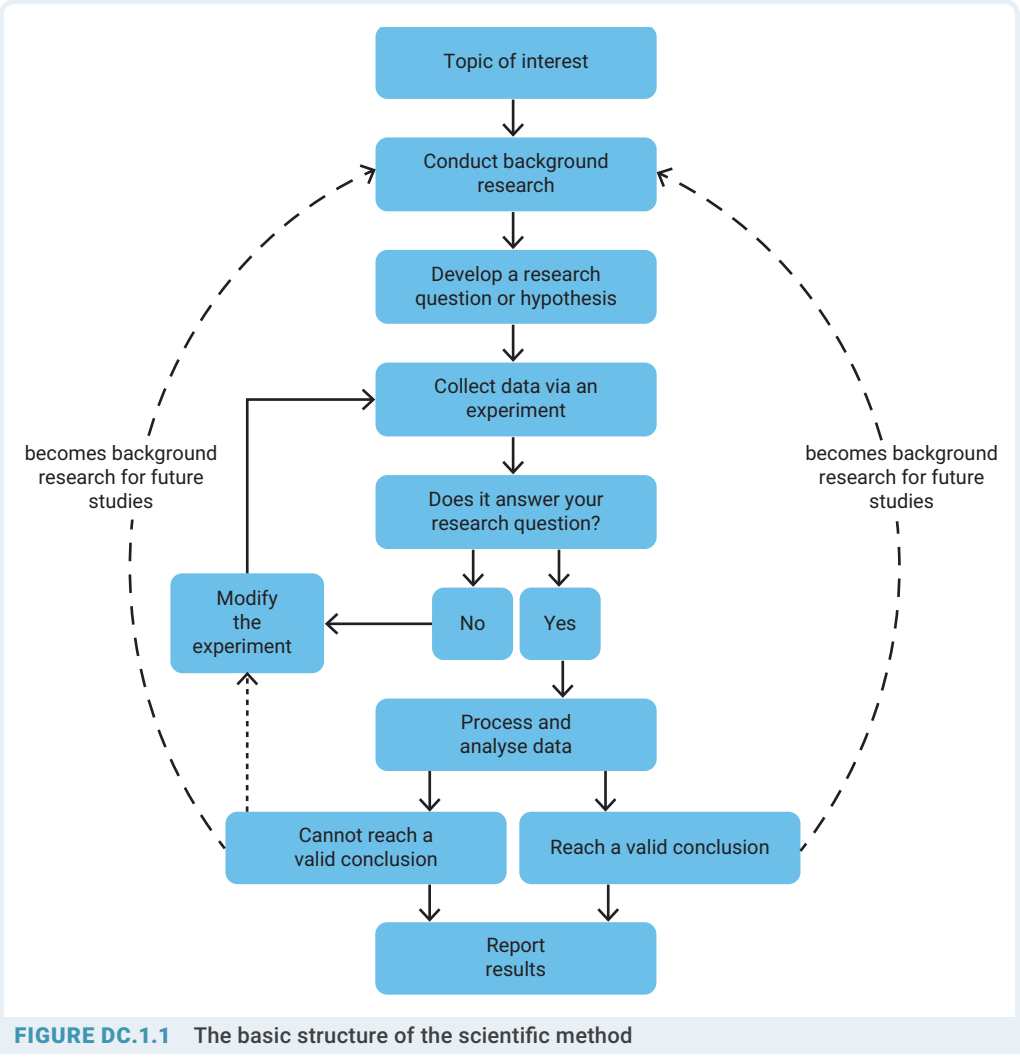


FIGURE DC.1.1 The basic structure of the scientific method

A research question is the question you are trying to answer with your research, and by doing so helps to guide and refine the research and experimental method. For example, a research question could be 'How does a fever of more than 38°C affect the function of enzymes in the body?'

Rationale

When developing a research question, it is important to demonstrate an understanding of the underlying theory related to the topic. This is described in the rationale of your experiment and is also implied through your research question. In the example above, the research question explores the relationship between enzymes and temperature. Given that it is known that the function of enzymes can be affected by changes in temperature, exploring the impact of an increase in temperature (because of a fever) expands our understanding of enzymes.

With an understanding of the topic, it is likely that you have developed a possible answer to the research question. As you know, this is the hypothesis. The hypothesis highlights the relationship between the **independent variable** and the **dependent variable**, showing the directional impact that one would have on the other. A possible hypothesis to the example above is 'As the temperature of the fever increases, enzyme function would be reduced'. In this case, the independent variable is the change in temperature and the dependent variable is the level of enzyme function, which can be measured by the amount of product produced over time.

independent variable the variable that is purposely changed or manipulated in an experiment

dependent variable the variable that changes due to changes to the independent variable

Methodology

For your experiment, you will need to modify an existing method from previous experiments. During your research, you may have encountered various studies conducted by scientists who were interested in investigating a similar topic. These studies can serve as a valuable foundation for you to build on and refine your own approach. How and what you modify in the experiment will depend on:

- the variables you are testing
- sources of error and bias in the previous method
- the type of data being collected (**quantitative** or **qualitative**)
- how many data points you will need to collect to ensure that there is sufficient data for analysis
- access to resources.

qualitative data
information that is not numerical in nature

quantitative data
numerical information

Once you have your base experiment (which could be one that you completed in class), you will be required to make some modifications to design your own student experiment. A modification may be one of three types (Table DC.1.1).

TABLE DC.1.1 Types of modifications that can be implemented for the Student Experiment (IA2)

Type of modification	Explanation	Instruction	Example
Refine	To improve by making subtle changes to the accuracy or precision of the data	• Make improvements without changing the independent or dependent variables.	• Use equipment with a higher level of precision. • Improve the methodology or way of measuring the independent variable. • Change the sample size.
Redirect	To gain further insight by changing the course or direction of the data	• Change the independent variable.	• Measure pH instead of temperature. • Use a different species. • Use different chemicals.
Extend	To change or extend the scope of the current data range	• Change the range of the independent variable. • Extend the range of independent variables.	• Use more concentrations of solution. • Use more sample categories or data ranges.

Although you will not need to write your entire methodology in your experiment, it is important that you can justify the modifications that you made. For example, if you decided to refine an experiment by using a digital thermometer instead of an analogue thermometer, you could justify this by saying that your refinement will improve the accuracy of your data collection because the digital thermometer has a smaller uncertainty and removes human error and/or that it has greater precision.

Having the right equipment is important; however, misreading the measuring instruments leads to inaccurate results. For example, when reading the volume of a liquid in a measuring cylinder, the measurement must be taken at eye level and measured from the bottom of the meniscus (Figure DC.1.2).

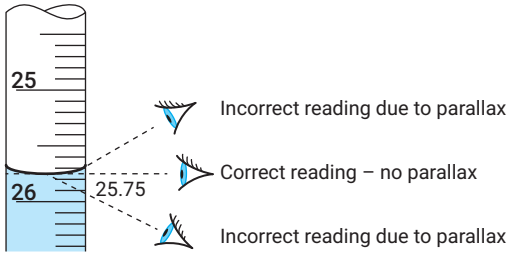


FIGURE DC.1.2 How to read measurements from a measuring cylinder

When collecting and recording data, ensure that it is measured in the appropriate units. For example, the concentration of solutions can be measured in different units such as $g\,L^{-1}$, $mol\,L^{-1}$ or ppm (parts per million). However, this will depend on the nature of the experiment. Since there are different units to express the same measurement, you will often need to convert between units, especially when analysing results. **Table DC.1.2** shows common unit conversions.

TABLE DC.1.2 Common unit conversions

Measurement	Common conversions
Distance	1 km = 1000 m = 100 000 cm = 1 000 000 mm
Mass	1 kg = 1000 g = 1 000 000 mg
Volume	1 L = 1000 mL = 1000 cm^3

Essentially, any modifications to the methodology are done to improve the reliability of data and validity of the experiment. Although you will not need to show your full methodology, you will need to explain and justify any modifications and refinements in your final presentation of your experiment.

If the proposed experiment involves exploring knowledges of First Nations peoples, it is extremely important to understand all the cultural guidelines and protocols involved in conducting such research. For example, the Australian Institute of Aboriginal and Torres Strait Islander Studies (AIATSIS) published the *Code of Ethics for Aboriginal and Torres Strait Islander Research* outlining the principles that underpin ethical Australian Indigenous research to help guide research that impacts on or is of significance to Aboriginal and Torres Strait Islander peoples.

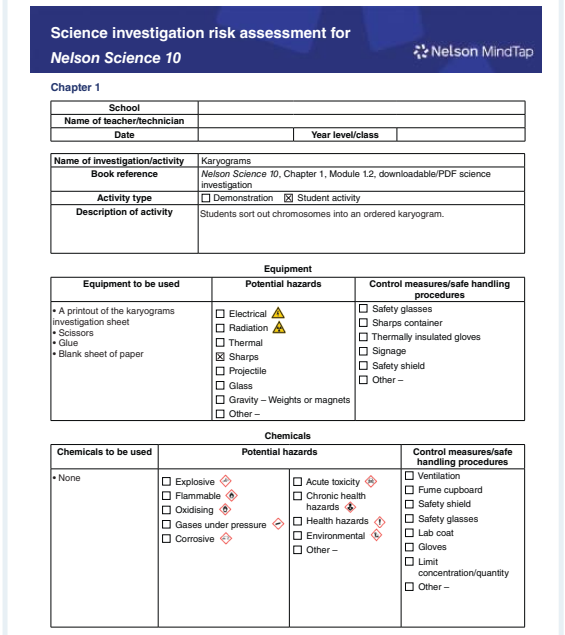
Weblink
Ethical research

Resource
Risk assessment

Finding

Health and safety

Health and safety are important considerations for practical exercises in all sciences. When undertaking your own practical research investigations, you must consider any relevant workplace health and safety guidelines. In Queensland, this includes the *Work Health and Safety Act 2011*. As the researcher, you must ensure safe laboratory practices when planning and conducting investigations by using risk assessments, supported by material safety data sheets (MSDSs), and accounting for risks. MSDSs are important when you are using chemicals as part of your investigation. This includes both the use and the disposal of any potentially harmful materials used and produced in your experiment. Even if your research does not use chemicals but requires participants to take some actions that may cause harm, you will still need to complete a risk assessment form **(Figure DC.1.3)**. Your school is likely to have one of these documents for you to complete when you conduct your experiment. If you are unsure of the ethical, environmental, or health and safety aspects of your experiment, check with your teacher. Not only are the risks inherent in the equipment to be identified, but the steps to reduce or manage the risk need to be stated.



Science investigation risk assessment for *Nelson Science 10*

Nelson MindTap

Chapter 1

School	
Name of teacher/technician	
Date	Year level/class

Name of investigation/activity	Karyograms
Book reference	*Nelson Science 10*, Chapter 1, Module 1.2, downloadable/PDF science investigation
Activity type	☐ Demonstration ☒ Student activity
Description of activity	Students sort out chromosomes into an ordered karyogram.

Equipment

Equipment to be used	Potential hazards	Control measures/safe handling procedures
• A printout of the karyograms investigation sheet • Scissors • Glue • Blank sheet of paper	☐ Electrical ☐ Radiation ☐ Thermal ☒ Sharps ☐ Projectile ☐ Glass ☐ Gravity – Weights or magnets ☐ Other –	☐ Safety glasses ☐ Sharps container ☐ Thermally insulated gloves ☐ Signage ☐ Safety shield ☐ Other –

Chemicals

Chemicals to be used	Potential hazards		Control measures/safe handling procedures
• None	☐ Explosive ☐ Flammable ☐ Oxidising ☐ Gases under pressure ☐ Corrosive	☐ Acute toxicity ☐ Chronic health hazards ☐ Health hazards ☐ Environmental ☐ Other –	☐ Ventilation ☐ Fume cupboard ☐ Safety shield ☐ Safety glasses ☐ Lab coat ☐ Gloves ☐ Limit concentration/quantity ☐ Other –

FIGURE DC.1.3 A section of a risk assessment form

Any risks that you identify need to be highlighted in your experiment, including the steps to mitigate these risks (Figure DC.1.4).

1.4 Management of risks

The overall experiment was given a low–medium risk due to several safety hazards. An over-heating power supply may cause melting to outer-plastic and can shut down – affecting connected outlets to the supply (Hill 2021). Consequently, the power supply was shut off every 2 minutes and was placed over a heat-resistant mat to eliminate heat-transfer and to allow a risk-free 8V supply. Furthermore, many power cables were connected to walls, computers and other equipment throughout the procedure, hence a safety hazard for potential "*trips and falls*" in the laboratory-safety-procedure section (Safety 2013). Thereby, chairs were placed over all wires – to caution to anyone in near premises.

FIGURE DC.1.4 An example of the inclusion of risks in an experiment

Apart from highlighting any potential dangers, another way to reduce the risk of injury and improve safety is to clearly outline the procedures in the experiment. This also includes the proper use and disposal of any materials involved in the experiment. This can be referred to as the standard operating procedures of an experiment.

Ethics

Ethics is a guiding framework that all research investigations must follow. Ethical concepts provide moral guidance for making decisions about the design and implementation of a research investigation. Examples of ethical concepts are shown in Table DC.1.3.

TABLE DC.1.3 Descriptions of different ethical concepts

Concept	Description
Beneficence	Having a commitment to do good for others (and minimise risk and harm)
Integrity	Acting with honesty and transparency
Justice	Ensuring fair distribution of benefits, risks, costs and resources
Non-maleficence	Avoiding harm or ensuring that potential harm is outweighed by benefits
Respect	Respecting individual differences and ensuring the right to autonomy and choice

You must apply your ethical understanding throughout your study of science, particularly for your own research.

Analysing data

primary data data collected directly by a person or group

logbook a complete, permanent record of how an experiment or research project was conducted; it shows what was done at every step along the way

The **primary data** collected in the experiment should be first organised into a raw data table. When constructing these tables, the independent variable is usually expressed in the first column and the dependent variables from the trials in the experiment are placed in the subsequent columns. For example, when measuring the time taken for a current to pass through a solution of different concentrations, the different concentrations (the independent variable) are presented in the first column, and the time measurements (dependent variable) are presented in subsequent columns (Table DC.1.4). It is often suggested that you record everything in your **logbook**; however, this is not a mandatory component of your investigation.

TABLE DC.1.4 An example of a table of raw data from an experiment

Concentration (mol L^{-1})	Time (±0.5 s)		
	Trial 1	Trial 2	Trial 3
0.2	359.5	368.5	364.5
0.4	360.0	345.5	327.5
0.6	325.5	339.5	333.5
0.8	343.5	307.0	327.5
1.0	307.0	339.5	326.5

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As shown in Table DC.1.4, the units for each measurement are included in the column headings.

Once the data has been collected, the next step is to analyse it. As part of this, we need to make a judgement on the quality of the data in terms of:

- accuracy
- precision
- reliability
- validity
- sources of error.

It is important to note that each senior subject has different and specific forms of mathematical analysis. What is appropriate for one type of data in one subject may not be appropriate for another. For example, calculated means and uncertainties might be appropriate for a Chemistry or Physics experiment, but mean and standard deviations might be more appropriate for Psychology or Biology experimental data. The following information is a general overview of the types of analysis you could undertake, but it is best to check that the type of analysis you choose is appropriate for your data.

accuracy the degree to which a measurement conforms to the correct value; depends on the measuring instrument being used

accepted value the value of a substance or quantity that is universally agreed as being a best estimate due to multiple and highly accurate measurements

percentage error the difference between a measurement result and an accepted value, expressed as a percentage of the accepted value

Accuracy and precision

In science, the **accuracy** of a measurement is how close it is to the true value of the quantity being measured. Even when the true value is unknown, scientists can rely on the best available **accepted value** to compare with the experimental measurement to determine its accuracy. Often the accepted value is the theoretical value calculated for the measurement.

A way to help indicate the accuracy of a measurement is to calculate **percentage error**. Percentage error shows us how close the measured value is to the true or accepted value:

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

A low percentage error indicates a high degree or accuracy, whereas a high percentage error indicates a low degree of accuracy.

KEY FORMULA

Percentage error

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

WORKED EXAMPLE DC.1.1

A student used a ruler to measure the height of a 100 mL beaker. These beakers are known to have a height of 7.2 cm. The measured value was 6.8 cm.
Calculate the percentage error of the measurement.

ANSWER

1 Determine the measured and true values.
Measured value: 6.8 cm
True value: 7.2 cm

2 Substitute and calculate the percentage error.

$$\text{Percentage error} = \left|\frac{6.8 - 7.2}{7.2}\right| \times 100$$

$$= 5.6\%$$

This suggests that the measurement is slightly lower than the true value.

precision a measure of how close a number of independent measurements of the same quantity are to each other

In contrast, **precision** describes how close a set of measured values are to each other. For single measurements, precision is about the level of detail given by the measurement. For example, 0.3 g is less precise than 0.312 g. As you can see, some measuring instruments are more precise than others. This can be due to the:

- technology used in the device
- quality of components
- resolution
- scale.

The ability to measure precise results is important because it can affect the reliability and uncertainty of data. Uncertainty will be discussed in further detail later in this chapter. It is important to note that measurements that are precise are not necessarily accurate (Figure DC.1.5).

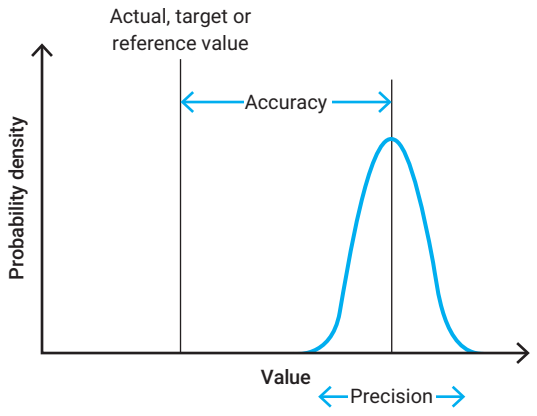

FIGURE DC.1.5 A graph showing the difference between accuracy and precision

Figure DC.1.6 helps further distinguish between accuracy and precision. In parts a and c, the individual indication values cluster closely around the mean, whereas parts b and d show imprecise measurement results because the individual measured values spread significantly around the mean.

For example, for an individual experiencing a fever, having precise measurements of body temperatures of 32.1°C, 33.2°C and 32.0°C does not mean that this is an accurate measure of their

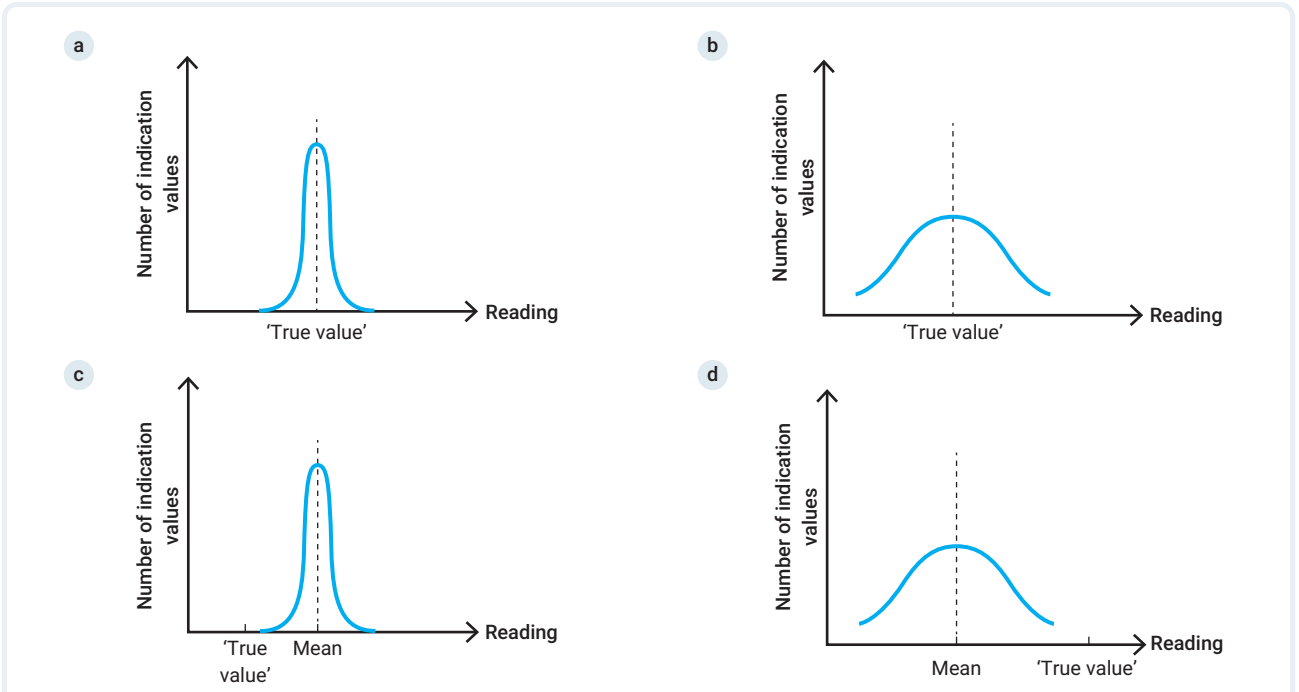

FIGURE DC.1.6 In a plot of measured values versus reading, results can be: (a) accurate and precise, (b) accurate and imprecise, (c) inaccurate and precise or (d) inaccurate and imprecise.

body temperature. We know this because humans have a core body temperature of approximately 37.0°C and fevers cause body temperature to increase, not decrease.

To improve the accuracy of measured values, you could:

- conduct multiple trials and average the results
- ensure that all variables except for the independent variable are controlled (also referred to as fair testing)
- ensure that the measuring tools used in the experiment are appropriate for what is being measured.

This helps to minimise the impact of any errors in the experiment that could affect the accuracy of the measured results. Errors will be discussed in more detail in a later section.

Reliability

If an experiment is repeated, you would expect to obtain very similar results. When this happens, we say that the experimental results are reliable. However, this is not always the case because errors can affect the data collected. **Reliability** can be measured with uncertainty and standard deviation, concepts that will be described in more detail in a later section. Reliability of results can be improved by carefully controlling all variables apart from the independent variable. We will discuss other factors affecting reliability later in this section.

reliability the extent to which the results of assessments are consistent, replicable and free from error

Validity

The quality of the data affects the **validity** of an experiment. We describe data as being valid if the result is due to the independent variable only and can answer the research question. In our example with measuring the effect of temperature on enzyme function, if variabilities in pH in the environment are not properly controlled, they can also affect enzyme function. As a result, we cannot confidently conclude that the results measured from the experiment are due to the changes in temperature only. This type of variable is known as an **extraneous variable** and can affect the relationship between the dependent and independent variables. In this example,

validity the extent to which the experiment measures what it is intended to measure

extraneous variable any variable that is not directly related to the experiment but could affect the results of the experiment

confounding variable a variable that is related to the independent and dependent variables

pH is a specific type of extraneous variable known as a **confounding variable** because it relates to both the independent and dependent variables. This is why it is important to ensure that all variables other than the independent variable are controlled.

error the difference between a measured value and true value

Apart from extraneous variables, **errors** can also affect the results of an experiment. The two main types of errors are random and systematic errors.

Errors

random error a variation that affects a measurement in a random way so that successive measured values may reflect small changes from each other

Random errors are unpredictable variations that can occur during measurement. When taking multiple readings of the same thing, random measurement errors cause small variations so that you end up recording a spread of readings. These errors affect the precision of a measurement and can be caused by limitations of measuring instruments. The effect of random errors can be reduced by making more or repeated measurements and calculating the **mean** (or average). To calculate the mean:

mean the average value of a set of values

$$\text{Mean} = \frac{\text{sum of measured values}}{\text{total number of measurements taken}}$$

KEY FORMULA

Mean

$$\text{Mean} = \frac{\text{sum of measured values}}{\text{total number of measurements taken}}$$

The mean value is then regarded as the most likely or best estimate of the true value; however, we cannot be certain that it is the true value.

While random errors affect the precision of data, **systematic errors** affect the accuracy of a measurement. These errors cause the readings to differ from the true value by a consistent amount in the same direction. This can occur when measuring instruments are not properly calibrated, so readings differ from the true value by the same amount. Systematic errors can also be caused by observational error if there is a consistent distortion in the way we view things that causes errors that are the same every time. For example, a tall person may read a thermometer from a higher viewpoint and record a lower measure than the true value every time. To minimise the impact of systematic errors, it is important to know how to use measuring tools properly and to calibrate them before use.

systematic error an error that acts to give a consistent offset in data; e.g. consistently above or consistently below

Figure DC.1.7 highlights the differences between random and systematic errors.

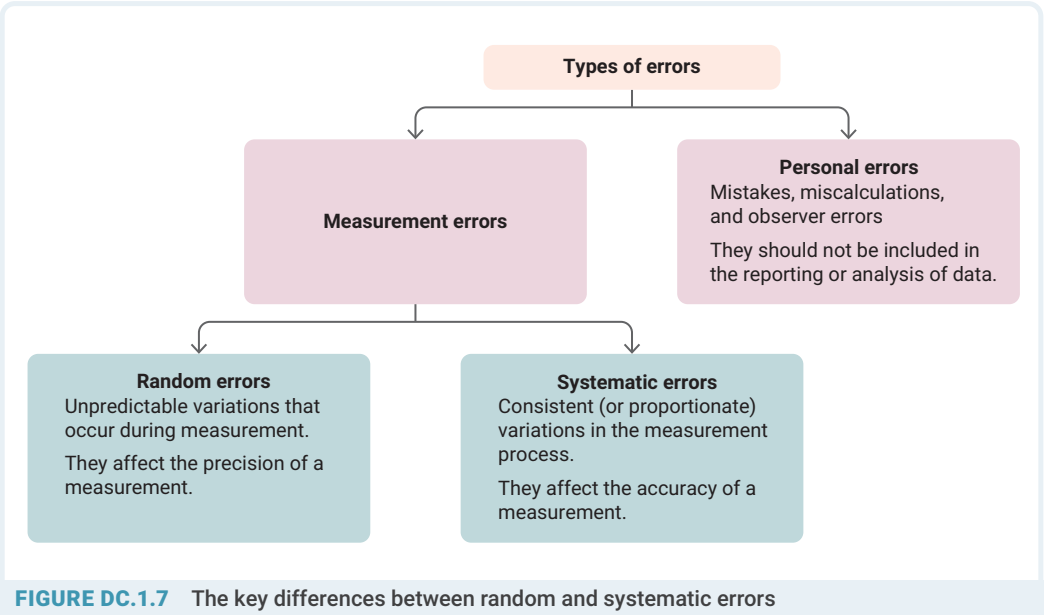

FIGURE DC.1.7 The key differences between random and systematic errors

Uncertainty

While systematic errors can be accounted for by subtracting or adding the value of the error, random errors contribute to the **uncertainty** of a measurement. This reflects the lack of exact knowledge of the true value of the measurement. All measurements are subject to uncertainty because there are many sources of variation. For example, **instrumental uncertainty** in measuring tools can result in variability and imprecision of results due to factors such as sensitivity, calibration and resolution. To minimise the effect of instrumental uncertainty, it is important to calibrate tools, ensure that the appropriate tools and techniques are used, and consider any limitations when designing the experiment. Uncertainty can also occur because of the way the person taking the reading interacts with the tool.

Errors and uncertainties can sometimes be quantified. We can estimate the uncertainty of a measurement, which is usually expressed as ± a certain value. This is known as **absolute uncertainty**.

uncertainty the range of values for a measurement result, taking account of the likely values that could be attributed to the measurement result given the measurement equipment, procedure and environment

instrumental uncertainty the inherent limitations and potential errors associated with the measuring instruments or tools used in scientific experiments or observations

absolute uncertainty the magnitude of the difference between the observed/measured value and the true value

range the difference between the maximum and minimum values of a measured confidence interval

Absolute uncertainty of repeated measurements

Most experiments require you to take multiple measurements. As mentioned above, doing so and averaging the results can help to reduce the effect of random errors. Imagine taking multiple measurements of your body temperature. The values are 35.6°C, 36.1°C, 35.9°C and 36.4°C. The difference between the maximum and minimum values is called the **range**. The absolute uncertainty is calculated as the halfway point between the maximum and minimum values, or half of the range:

$$\begin{aligned}\text{Absolute uncertainty} &= \pm\frac{\text{maximum} - \text{minimum}}{2}\\ &= \pm\frac{36.4 - 35.6}{2}\\ &= \pm 0.4°\text{C}\end{aligned}$$

The measurement result would be the mean of the values:

$$\begin{aligned}\text{Mean} &= \frac{35.6 + 36.1 + 35.9 + 36.4}{4}\\ &= 36.0°\text{C}\end{aligned}$$

The reported value includes both the mean and the absolute uncertainty. In this example, the reported value would be 36.0±0.4°C. In other words, the actual value could lie anywhere between 35.6°C and 36.4°C.

KEY FORMULA

Absolute uncertainty

$$\text{Absolute uncertainty} = \pm\frac{\text{maximum} - \text{minimum}}{2}$$

Absolute uncertainty of single measurements/device details

For analogue devices, the uncertainty is normally determined as half of the smallest division on the scale. For example, a glass thermometer with graduations of 1°C has an uncertainty of ±0.5°C.

With digital devices, the uncertainty is normally defined as the smallest division because we cannot see in between divisions as we can in an analogue device. For example, a digital thermometer that measures in 1°C has an uncertainty of ±1°C. One limitation of this calculation is that it does not indicate the direction of the error; we do not know if we overestimated or underestimated.

Percentage uncertainty

Absolute uncertainty can be used to calculate **percentage uncertainty**. Percentage uncertainty is calculated relative to the measured quantity, and is calculated by:

$$\text{Percentage uncertainty (\%)} = \frac{\text{absolute uncertainty}}{\text{measured value}} \times \frac{100}{1}$$

percentage uncertainty a measure of the uncertainty of a measurement compared with the size of the measurement, given as a percentage

KEY FORMULA

Percentage uncertainty

$$\text{Percentage uncertainty (\%)} = \frac{\text{absolute uncertainty}}{\text{measured value}} \times \frac{100}{1}$$

A lower percentage uncertainty indicates a more precise measurement, whereas a high percentage uncertainty indicates that the measurement is less precise because of greater variability.

Once data has been processed in this way, a table can be presented that also includes these measurements of uncertainty **(Table DC.1.5)**.

TABLE DC.1.5 An example of a summary table showing measurements of uncertainty

Voltaic cell	Cathode metal	Potential difference (±0.05 V)			Mean potential difference (V)	Absolute uncertainty of mean (±V)
		Trial 1	Trial 2	Trial 3		
1	B(s)	2.25	2.40	2.20	2.28	0.10
2	C(s)	1.30	1.28	1.37	1.32	0.45
3	D(s)	3.11	3.15	3.04	3.10	0.55

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Significant figures

Once uncertainty has been calculated, results need to be quoted with the appropriate significant figures.

The following steps can be used to determine the significant figures of a single value.

1. Reading a value from left to right, start counting significant figures at the first non-zero number. For example, for a measurement of 0.024 307 g, the first significant figure is 2. In this case, the first two zeros are not considered significant.
2. Every number after the first significant is deemed as significant, including any zeros. In 0.024 307 g, there are five significant figures.

These rules apply even when numbers are expressed in scientific notation. If the above example was expressed as 2.4307×10^{-2} g, then the first significant figure is still 2 and every number thereafter is considered significant.

WORKED EXAMPLE DC.1.2

A student measured the mass of a sample to be 0.0103 g. Determine the number of significant figures in this value.

ANSWER

1 **Identify the first non-zero digit.**
Reading from left to right, the first significant number is the first non-zero number. According to this rule, the first significant figure in this value is 1.

2 **Count the number of figures in the value that is considered significant.**
There are two significant figures 0 and 3 after the first significant figure. As such, there are three significant figures in this value.

When measurements are used to calculate a final value, the numbers and operations to arrive at the final answer contribute to the significant figures of the final answer.

1. For addition and subtraction, the final answer needs to be expressed to the least number of decimal places. For example, when adding the length of two pencils of 10.5 and 9.42 cm, the final answer should be expressed to 1 decimal place, 19.9 cm.

2. For multiplication and division, the final answer needs to be expressed to the least number of significant figures. For example, if we needed to calculate the percentage of sugar in a 50.0 g sample given that there is 2.4 g of sugar present:

$$\text{Percentage} = \frac{2.4}{50.0} \times 100$$
$$= 4.8\% \text{ sugar}$$

Because 2.4 has the least number of significant figures (two), the answer is expressed to two significant figures. For multistep questions, retain the appropriate number of significant figures at each step, where the final answer should be expressed based on the final step.

WORKED EXAMPLE DC.1.3

A student performed the following calculation using experimental data:

$$\frac{527.11 - 232.3}{5.4}$$

Determine the number of significant figures that the answer should be expressed in.

ANSWER

1 Identify the order of the steps involved in this calculation.
The calculation would be performed in the following order:
- **i** 527.11 – 232.4
- **ii** Answer from step **i** ÷ 5.4

2 Identify the number of significant figures in the each step.
- **i** 4. Since it is a subtraction calculation, we need to express the answer to the least number of decimal places.
- **ii** 2. Since it is a division calculation, we need to express the answer based on the number with the least significant figures (5.4)

3 Determine the number of significant figures for the final answer.
Two

Graphs

Although tables can be an effective way to collect and record data, it is difficult to visualise any trends or relationships between the independent and dependent variables. Presenting data in graphical form makes it easier to identify if any trends exist between the variables.

Many different types of graphs can be used to represent data; for example, column graphs, pie charts, scatterplots and line graphs. Choosing the right graph depends on the nature of the data collected and what you are trying to show. For graphs that involve an *x*-axis and a *y*-axis, the independent variable is represented by the *x*-axis and the dependent variable is represented by the *y*-axis (Figure DC.1.8).

It is also important to choose an appropriate scale when drawing graphs because it helps to ensure that the data is represented in a way that can be easily interpreted. It also avoids misleading representations that imply inaccurate relationships between data. All graphs need to have a title that outlines the information being presented.

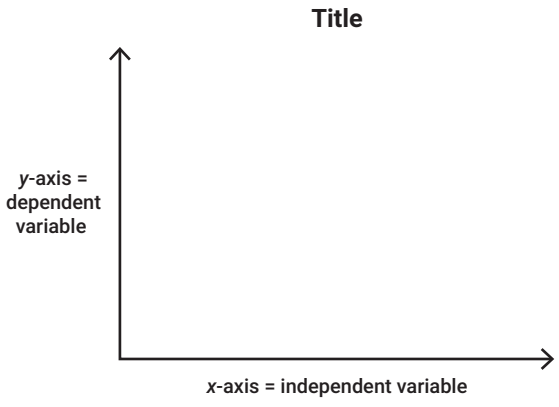


FIGURE DC.1.8 The positive quadrant of cartesian plane showing the variables represented on the *x*-axis and *y*-axis

Pie charts

Pie charts are best used to show parts of a whole and the percentage composition of each different category. For example, pie charts can be used to show the composition of a mixture of air – nitrogen, oxygen and other gases – and the percentage of each (Figure DC.1.9).

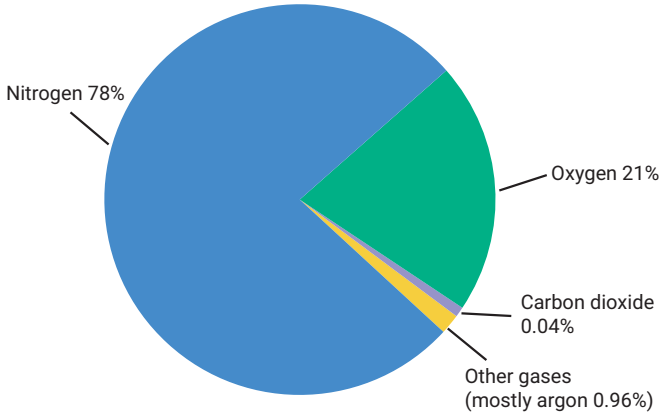


FIGURE DC.1.9 A pie graph representing the composition of air

A limitation with pie charts is that they become visually cluttered when there are many different categories.

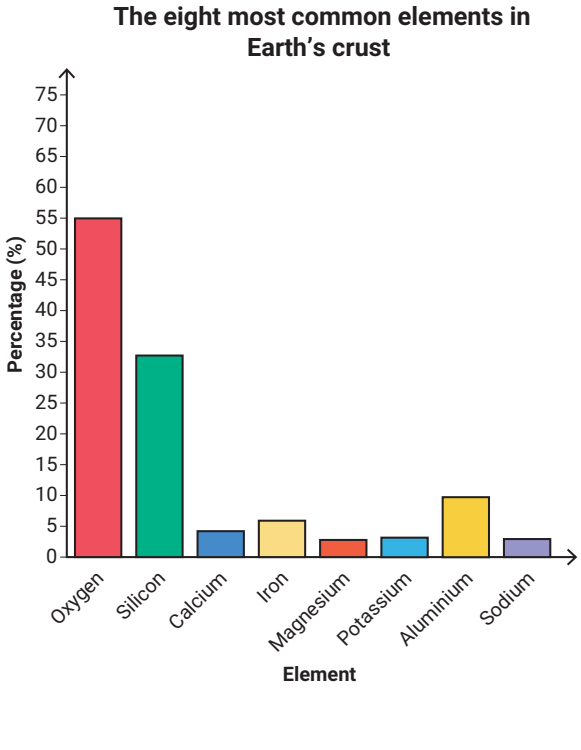


FIGURE DC.1.10 A column graph showing the differences in mineral composition of Earth's crust

Column graphs

Column graphs are useful when comparing quantities or different categories or groups (Figure DC.1.10).

These types of graphs are preferred for comparing categories or to show changes over time, or when comparing the differences between groups.

Line graphs

Line graphs are ideal when showing trends over time for continuous data, particularly when comparing multiple series over the same period. In line graphs, each data point is connected to the next and the relationship between the two variables can be represented as the equation:

$$y = mx + c$$

where: m = the gradient

c = the y intercept.

For example, the calibration curve measuring the absorbance of light based on concentration of a solution can be represented by a linear graph as shown in Figure DC.1.11. If using Excel to draw these graphs, it is sometimes useful to use the x,y scatter plot.

The gradient is a useful piece of information that helps to describe the relationship between the independent and dependent variables. For linear relationships, the gradient of the slope helps to identify the nature of the relationship

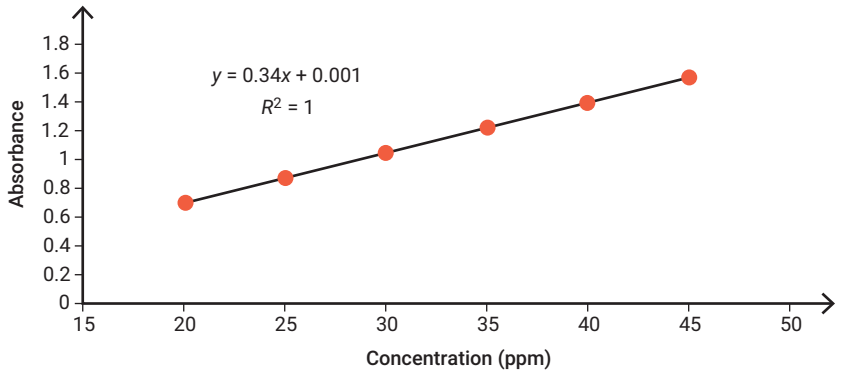


FIGURE DC.1.11 A line graph showing absorbance at different concentrations

between the independent and dependent variables. To calculate the gradient of a linear graph, m, where the equation is $y = mx + c$:

$$\text{Gradient } (m) = \frac{\Delta y}{\Delta x}$$

Determining the gradient in this way only requires two data points, where the difference in the y values is divided by the difference in the x values of the same two points. Depending on the value of the gradient, a:

- positive gradient **(Figure DC.1.12a)** indicates that as the x value (independent variable) increases, so does the y value (dependent variable)
- negative gradient **(Figure DC.1.12b)** indicates that as the x value (independent variable) increases, the y value (dependent variable) decreases
- gradient of zero **(Figure DC.1.12c)** indicates that as the x value (independent variable) increases, there is no change in the y value (dependent variable). As such, there is a constant relationship between the two variables.

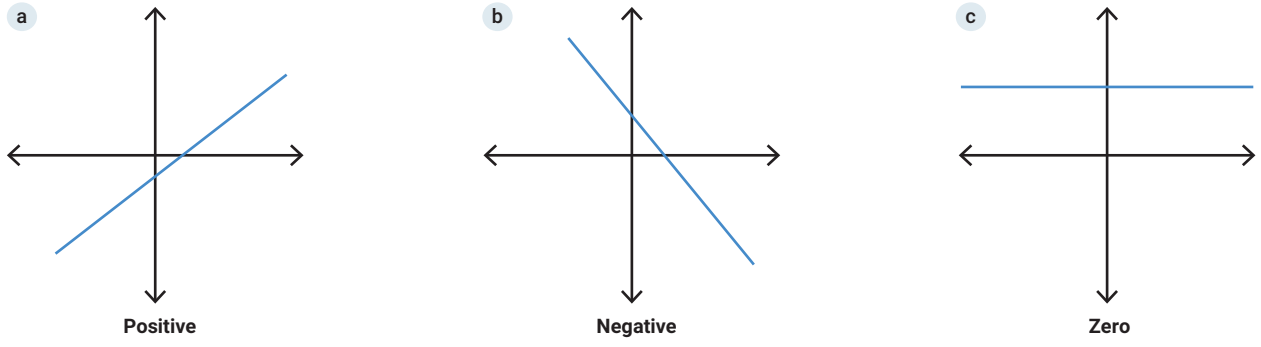


FIGURE DC.1.12 Linear graphs with (a) a positive gradient, (b) a negative gradient and (c) zero gradient

Analysing the gradient for non-linear relationships is a bit more complicated and requires us to calculate the gradient of different tangents at specific points along the graph and compare the changes.

Scatterplots

Scatterplots are similar to linear graphs in that they show individual data points, highlighting the relationship between the independent and dependent variables. However, unlike line graphs, the data points in scatterplots are not connected (Figure DC.1.13).

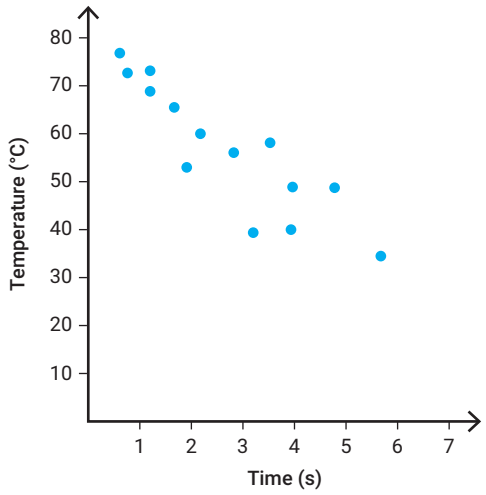


FIGURE DC.1.13 A scatterplot of changes in temperature over time

trendline a line that represents the general direction or pattern of data points

Although the points in a scatterplot are not connected, the way the data points are organised relative to each other can identify a relationship between the variables. **Trendlines** can be drawn through or near the datapoints to help make the relationship between the independent and dependent variable more visible (Figure DC.1.14) while also showing the strength of this relationship.

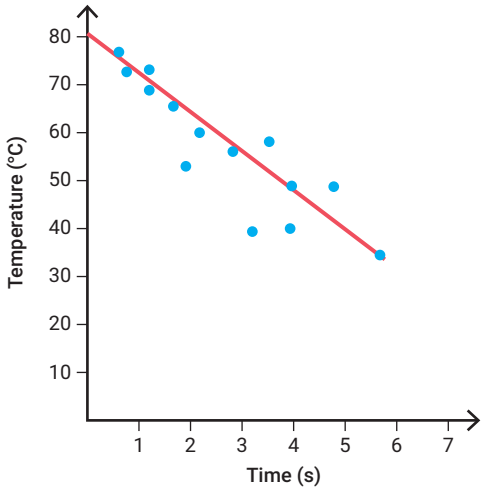


FIGURE DC.1.14 A scatterplot of changes in temperature over time including a trendline (red)

Although it's possible to draw trendlines manually, it is more accurate to use software to draw trendlines. When manually adding trendlines, the line should be drawn so that it minimises the distance between the line and the data points.

If a trend does exist, we can often easily identify whether it is positive (or positive correlation) or negative (negative correlation). In a positive trend, the dependent variable increases as the

independent variable increases (Figure DC.1.15a), whereas in a negative trend, the dependent variable decreases as the independent variable increases (Figure DC.1.15b).

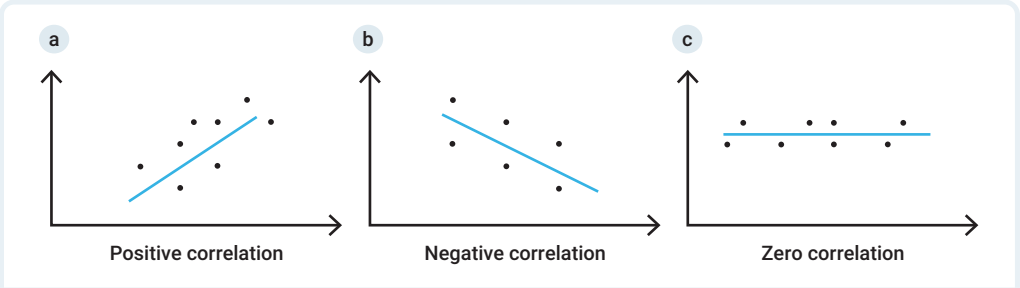


FIGURE DC.1.15 Scatterplots with trendlines showing (a) a positive trend, (b) a negative trend and (c) zero trend

Maximum and minimum trendlines are visual representations of the strength of the relationship between the variables (Figure DC.1.16). A wider range between the two suggests a greater variability of uncertainty in the data, whereas a narrow range suggests a lower variability in the measured values. Analysing **maximum trendlines** and **minimum trendlines** together can help us predict the potential range of outcomes. For example, using trendlines to forecast temperature changes as a result of emissions can help us predict and prepare for worst-case scenarios. Maximum and minimum trendlines can also help identify potential errors in the experiment. Values that fall significantly outside the area between the maximum and minimum trendlines suggest an outlier that may be due to a random error.

maximum trendline
a trendline with the greatest gradient that fits within the data within the uncertainty values

minimum trendline
a trendline with the smallest gradient that fits within the data within the uncertainty values

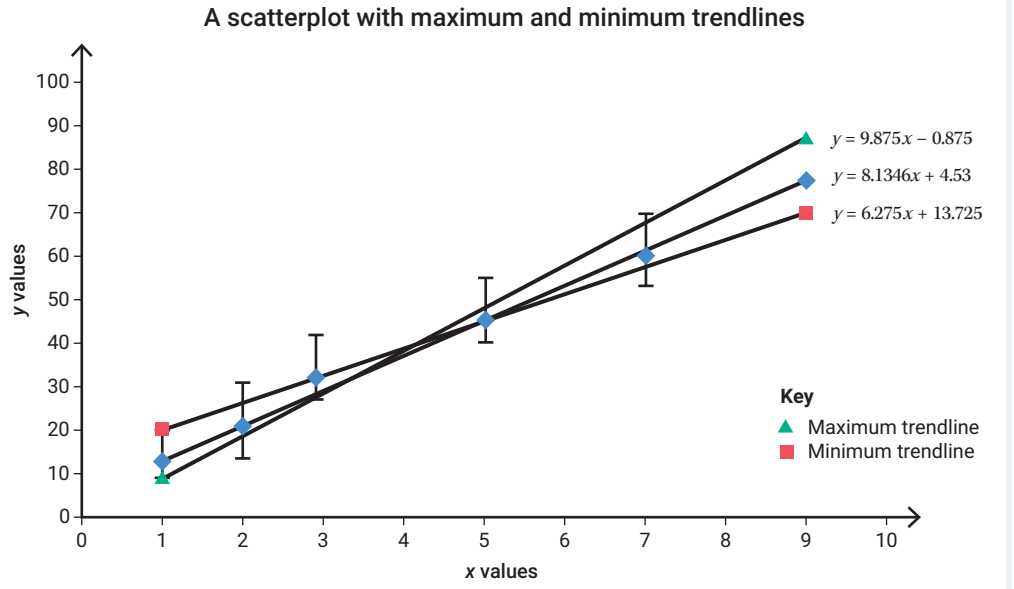


FIGURE DC.1.16 An example of a scatterplot that includes a maximum and minimum trendline

Greater variability in certain areas of the graph may also suggest error. For example, when measuring the rate of a reaction at different temperatures, it may be evident that there is a large variability in the rate of the reaction at higher temperatures. This could imply an error in temperature control at higher temperatures.

A common strategy used to draw a maximum trendline involves drawing a line from the bottom of the error bar of the starting data point to the top of the error bar of the last data

point. To draw a minimum trendline involves drawing a line from the top of the error bar of the starting data point to the bottom of the error bar of the last data point.

line of best fit a straight line through data points in a graph that best expresses the relationship shown in a scatterplot

Although trendlines are more general and can be used for different types of graphs with linear and non-linear data, the **line of best fit** is better suited for linear relationships. Since the line of best fit is used for linear relationships, the data points can be used to establish the relationship expressed as $y = mx + c$.

Although this can be done manually, the calculations can become complex and therefore it is often easier (and more accurate) to use software such as Excel, which can both draw the graph and establish the corresponding equation for the line of best fit. Lines of best fit can be used to predict values not measured in the experiment (extrapolation) or estimate values within the range of data collected (interpolation) that was not directly measured **(Figure DC.1.17)**.

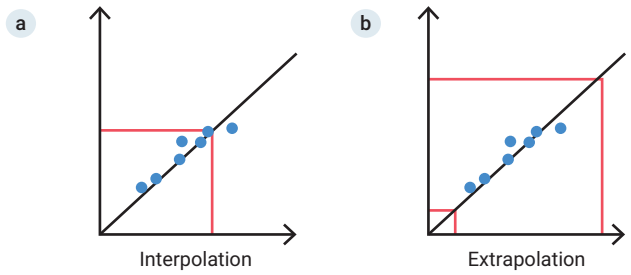


FIGURE DC.1.17 Using a line of best fit to (a) interpolate a data point within the measured values and (b) extrapolate a data point outside of the measured values

Drawing the line of best fit involves specific statistical models such as linear regression and is often accompanied by a quantifiable level of certainty, known as the *R*-squared value (R^2) (also referred to as the coefficient of determination). Regression analysis provides an equation for a graph so that predictions can be made about the data.

Linear regression is a basic and commonly used type of predictive analysis. Regression is used to examine two key questions:

1. Does a set of predictor variables do a good job at predicting an outcome (dependent) variable?
2. Which variables in particular are significant predictors of the outcome variable?

Weblink
Linear regression and Excel

These regression estimates are used to explain the relationship between one dependent variable and one or more independent variables.

This can be calculated in Excel.

Before discussing R^2 values, we must first understand the significance of R values.

Pearson correlation coefficient (*R*) a statistical measure that quantifies the direction and strength of a relationship between two variables

A method that can be used to quantitatively describe the direction and strength of a linear relationship between the independent and dependent variables is the **Pearson correlation coefficient (*R*)**, which measures the correlation between two sets of data. R values can be between –1 and 1, where:

- $R = 0$ suggests no correlation
- $R = 1$ suggests a strong positive correlation
- $R = -1$ suggests a strong negative correlation.

The formula to calculate the R value is complicated and therefore it is much easier to use software to help with this calculation. Programs such as Excel have options for calculating R when plotting a graph.

Squaring the R gives us the R^2 value. This value indicates the strength of the correlation of the linear relationship between two sets of data. In simple terms, it answers the question, 'Can I draw a line graph to represent the data?' Calculating this coefficient does not allow you to fit a line to your data (use a regression analysis for this). However, the value is not able to tell the difference between the independent and dependent variables; for example, investigating a

high-calorie diet causing diabetes might give a correlation of 0.8. However, you could also get the same result with the variables switched around – diabetes causes a high-calorie diet. Therefore, as a researcher you must be aware of the data you are putting in and note the difference between correlation and causation:

- $R > 0.8 =$ *strong* correlation.
- $R < 0.5 =$ *weak* correlation.

Non-linear graphs

Not all trends show a linear pattern. For example, graphs showing the solubility of substances at different temperatures show a non-linear relationship **(Figure DC.1.18)**.

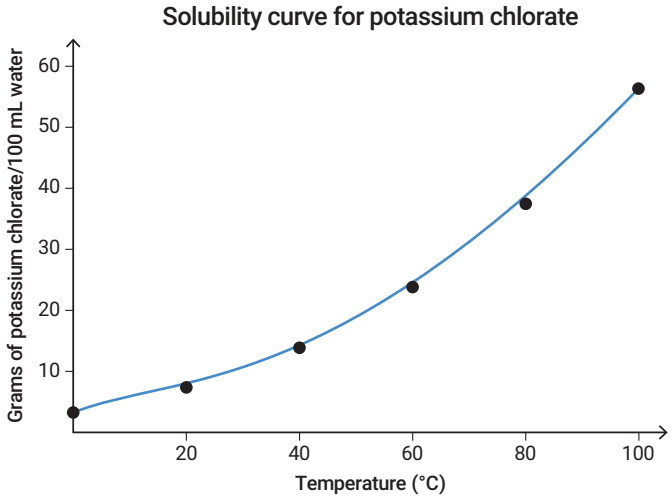


FIGURE DC.1.18 The solubility of potassium chlorate in 100 mL of water at different temperatures shows a non-linear relationship.

The simplest way to identify whether a relationship between two variables is linear or non-linear is to plot the data points on a graph to identify the overall trend. Gradient analysis can be conducted on non-linear graphs by calculating the instantaneous gradient of the tangent line at each data point and comparing the extent of the changes between each point. The tangent line is a straight line that 'touches' the data point and shares the same gradient as the curve at the given data point **(Figure DC.1.19)**.

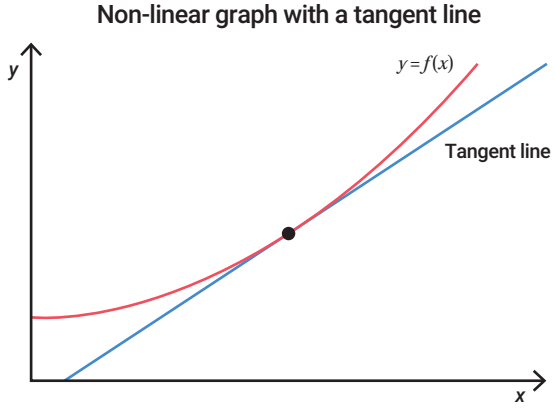


FIGURE DC.1.19 An example of a tangent touching a data point on a non-linear graph

Error bars

To illustrate uncertainty, your graphs should incorporate error bars. These extend from data points to demonstrate the uncertainty the measurement (Figure DC.1.20).

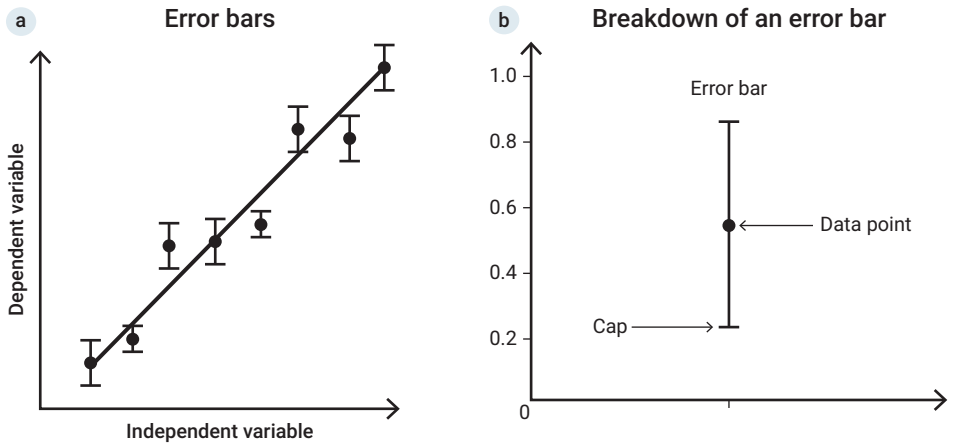


FIGURE DC.1.20 (a) A scatterplot that has incorporated error bars. (b) The structure of an error bar.

Weblinks
Error bars
Drawing graphs with error bars

The upper and lower limits of the error bars can be determined by using descriptive statistics such as standard deviation or absolute uncertainty. (Note: There are different types error bars, e.g. standard deviation, confidence intervals, absolute uncertainty, percentage uncertainty.) To draw error bars on graphs:

1. Identify the data point.
2. Calculate the uncertainty of the mean for the data point. This will determine the upper and lower limits of the error bar.
3. Use the values from step 2 to identify the maximum and minimum value for the data point. Use this to draw the error bar.

Graphing applications such as Excel have an option to include error bars in graphs. This is a faster and often more accurate method of generating graphs with error bars.

A larger error bar indicates that the values are spread out and suggests greater uncertainty than a smaller error bar, which signals that the measurements are clustered around the data point. Error bars can be drawn for different types of graphs (Figure DC.1.21).

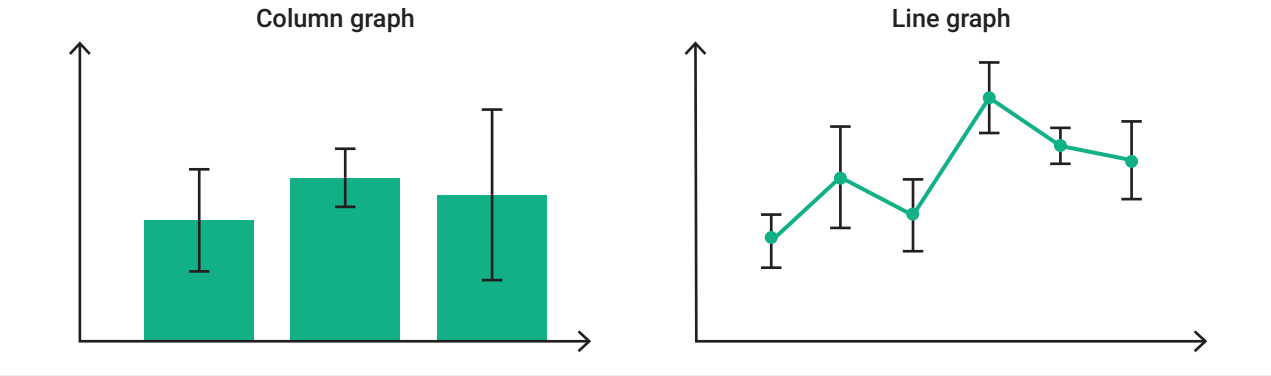


FIGURE DC.1.21 A column graph and a line graph with error bars

Other representations of data

Scientific drawings

Textbooks are full of scientific drawings that represent structures, organisms and processes. These drawings are highly detailed, accurate and clear. For example, consider the representation of covalent bonding between two hydrogen atoms in a hydrogen molecule (Figure DC.1.22).

Scientific drawings include labels and annotations and are also drawn to scale to show the relative proportions of the elements involved.

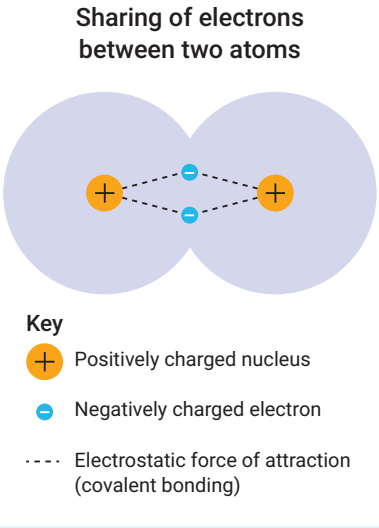


FIGURE DC.1.22 Covalent bonding in a molecule of hydrogen (H_2)

Identifying trends and relationships

The purpose of an experiment is to collect relevant data that can be analysed and used to understand the relationship between the independent and dependent variables.

Analysing graphs

When analysing graphs, it is important to consider all aspects presented in the graph. Consider the graph shown in Figure DC.1.23. What we tend to notice first is the overall trend in the data. The graph shows a negative trend where the cell potential decreases as the concentration of Zn^{2+} increases. We determine this visually based on the shape of the line; however, it is possible to also measure the negative gradient for the line. The large R^2 value of 0.9723 (very close to 1) suggests high correlation between both variables.

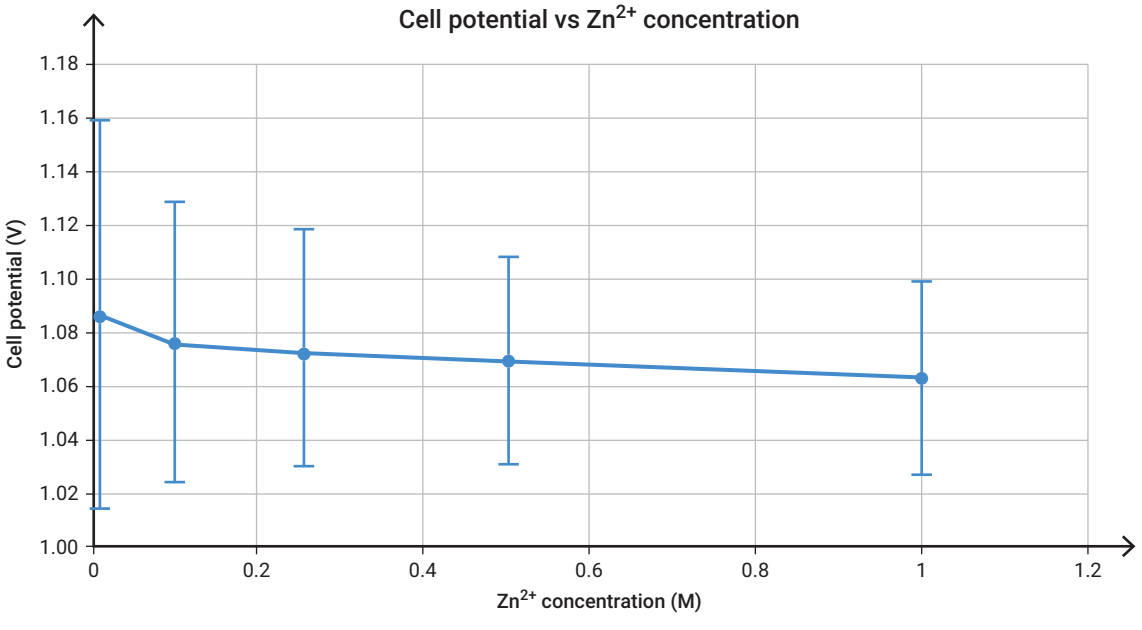


FIGURE DC.1.23 A graph showing the effect of the concentration of $ZnSO_4$ on cell voltage

The graph in Figure DC.1.23 also contains error bars showing the overlap of all data points. When this happens, it suggests that the differences between the overlapping data points are statistically insignificant and are due to random errors. As such, the trend shown may not reflect the true relationship between the concentration and cell potential.

Although not as easy to visually identify as graphs, raw data tables can also be interpreted to identify the relationship between two variables. Consider the raw data table for the graph in Figure DC.1.23 (Table DC.1.6).

TABLE DC.1.6 A data table for the experiment testing the effect of the concentration of $ZnSO_4$ on cell voltage

$ZnSO_4$ conc. (M)	Mean cell potential (V)	Absolute uncertainty (V)	Percentage uncertainty (%)	Theoretical E_{cell} (V)	Absolute error (E)	Percentage error (%)
0.01	1.087	±0.005	±0.460	1.159	±0.072	±6.249
0.10	1.077	±0.005	±0.464	1.129	±0.053	±4.681
0.25	1.073	±0.005	±0.465	1.117	±0.044	±3.977
0.50	1.070	±0	±0	1.108	±0.039	±3.506
1.00	1.063	±0.005	±0.470	1.100	±0.037	±3.333

All results have an overall low percentage error, suggesting that the experiment has high validity.

Interpreting

Resource
Sample research investigation

You need to scientifically justify the argument. This is done by referencing theory and previous studies to explain the phenomena being shown through the data. For example, in an experiment measuring the effect of temperature on enzyme function, we would want to refer to the theory relating to the current understanding of enzyme function and use that to justify the arguments made from the trends identified in the data.

The culmination of this allows us to draw well-informed conclusions that help to answer the research question.

To demonstrate that you have a robust understanding of the results of the experiment, it is important to identify the pattern/relationship between the variables and comment on the reliability and validity of the relationships using your calculations of errors and uncertainty. Although it sounds counterintuitive, highlighting sources of error in your experiment and describing its effect on your results strengthens your argument. It also allows you to identify any limitations and offer suggestions for improvements and/or extensions to your experiment. By doing so, you are demonstrating an ability to critically analyse data, which helps to develop well-informed arguments.

LEARNING CHECK DC.1

DESCRIBING

1 **Describe** the difference between:
   - **a** accuracy and precision
   - **b** reliability and validity.

2 **Identify** two strategies to improve the accuracy of data.

3 **Identify** the type of data most suited to:
   - **a** pie charts
   - **b** line graphs
   - **c** column graphs.

4 **Describe** the importance of:

a a logbook **b** MSDSs **c** ethics in experiments.

5 **Sequence** the following sections of the scientific method in the correct order: methods, materials, discussion, research question.

APPLYING

6 **Consider** the following research question:
'How does increasing the temperature (K) affect the rate of a reaction (mL s^{-1})?'
Identify the:

a dependent variable **b** independent variable.

7 A student wanted to conduct an experiment to see whether eating food before running had any effect on how far she could run. Write a research question for this experiment.

8 A student is conducting an experiment involving the use of a glass measuring cylinder to measure and pour a sample of acid into a 100 mL glass beaker. **Identify** one safety concern associated with the experiment and how the risk can be minimised.

9 In a medical experiment, a participant was asked to undergo a series of additional tests that could reveal sensitive information about their health situation. The participant refused to give consent to the tests. However, the experimenter ignored this and requested for the tests to be conducted anyway. Which ethical concept has the experimenter breached? **Explain** your answer.

10 **Identify** the number of significant figures in the following.

a 0.0023 **b** 2.43007
c 8.1005 **d** 0.7

11 A student measured a value of 20 cm in their experiment with an absolute uncertainty of 1 cm.

a **Calculate** the percentage uncertainty.
b What does this value suggest about the precision of the measurement?

ANALYSING

12 A group of students designed an experiment to measure the melting points of different substances. The students obtained five different substances: A–E. They set up a melting point apparatus and heated each substance until it melted, recording the temperature at which melting occurred.

a **Identify** an extraneous variable for this experiment.
b Each student took turns measuring the melting point of each sample each day. Students brought in their own thermometers, and it was noticed that some used digital thermometers while others used analogue thermometers. **Identify** the type of error that occurred as a result of this.

13 In a particular set of measurements, a student recorded the following measurements: 14.2 cm, 14.1 cm and 14.3 cm. **Calculate** the absolute uncertainty.

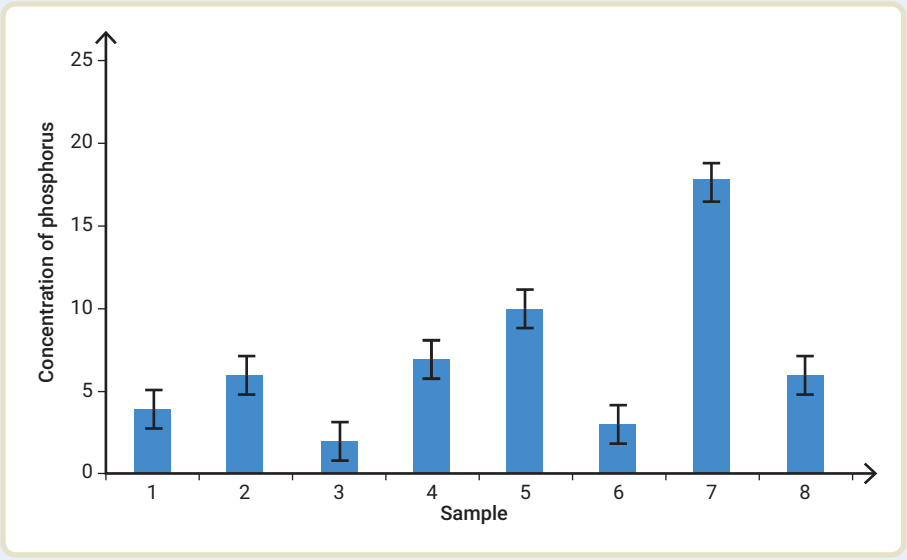
14 The results from a student's experiment are shown below.

Concentration of reactant (mol L^{-1})	Trial 1 Rate of reaction (mol L^{-1} s^{-1})	Trial 2 Rate of reaction (mol L^{-1} s^{-1})	Trial 3 Rate of reaction (mol L^{-1} s^{-1})
0.1	0.0050	0.0060	0.0050
0.2	0.010	0.011	0.0090
0.3	0.015	0.017	0.016
0.4	0.020	0.022	0.021

a **Identify** the dependent and independent variables for this experiment.
b **Calculate** the mean value for each concentration.

c Use the values to draw a graph to represent this data.
d **Determine** the correlation (if any) between the independent and dependent variables.

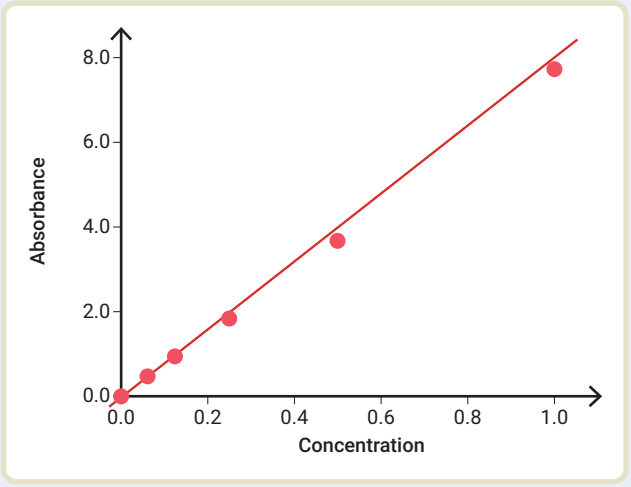
15 Consider the following graph.



a **Determine** the dependent variable.
b Which sample shows the greatest variability?

16 This graph was drawn for an experiment measuring the change of absorbance as a result of a change of concentration.

a What is the name of the type of graph drawn?
b What is the name given to the line drawn in the graph?
c **Calculate** the gradient (m) of the line.
d **Determine** the approximate absorbance at a concentration of 0.2.
e Based on the graph, would you expect the R value to be closer to 1 or to 0? **Explain** your response.



DC.2 Research investigation

To help prompt your Research Investigation (IA3) assessment, your teacher will provide a list of claims that you can investigate. These claims will be related to particular topics outlined in the syllabus. After selecting a claim, you will be required to choose a research question to investigate. Unlike the student experiment, the research investigation requires you to collect and analyse **secondary data** about your topic and particular research question.

secondary data data that is collected by someone else

Forming and finding

Researching to write a rationale

As with the Student experiment, you will need to conduct research before developing a research question. This involves reading scientific articles and books and investigating other resources to develop a solid understanding of the topic. From blogs to scientific journals, there are many resources available to help develop your understanding. These sources may be available through open access (e.g. Google Scholar) or through organisations such as government websites and local or national libraries; for example, the State Library of Queensland. Open Science, an initiative by Creative Commons, has a list of open-source scientific articles that are freely available. For scientific research, it is important to use a variety of credible resources. Therefore, you will need to be able to assess the reliability of the sources you are using. For example, blogs that can be written by anyone are not as reliable as a scientific article from a peer-reviewed journal **(Figure DC.2.1)**.

Weblink
Open Science

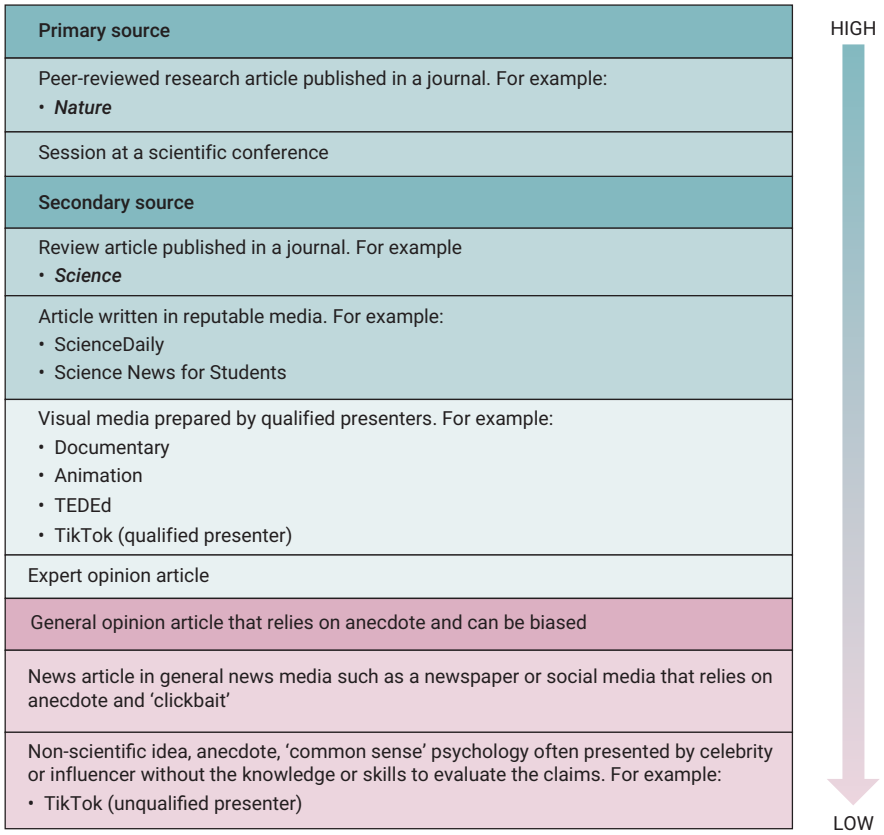


FIGURE DC.2.1 Sources of information based on their reliability

This is why the peer-review process in scientific research is so important **(Figure DC.2.2)**. For an article to be published in a journal, it must be reviewed by multiple experts, who evaluate it and make suggestions for further improvement. Before it can be resubmitted, the author must review and respond to the suggestions. This process can take months. Only once this process has been completed can the article be accepted for publication by the journal.

When using sources that are not from peer-reviewed journals, it is important to assess the reliability and validity of the information. It is helpful to ask yourself question such as:

- Is the author(s) an expert in this domain?
- Does the author use evidence to support their claims?
- Is the methodology valid?

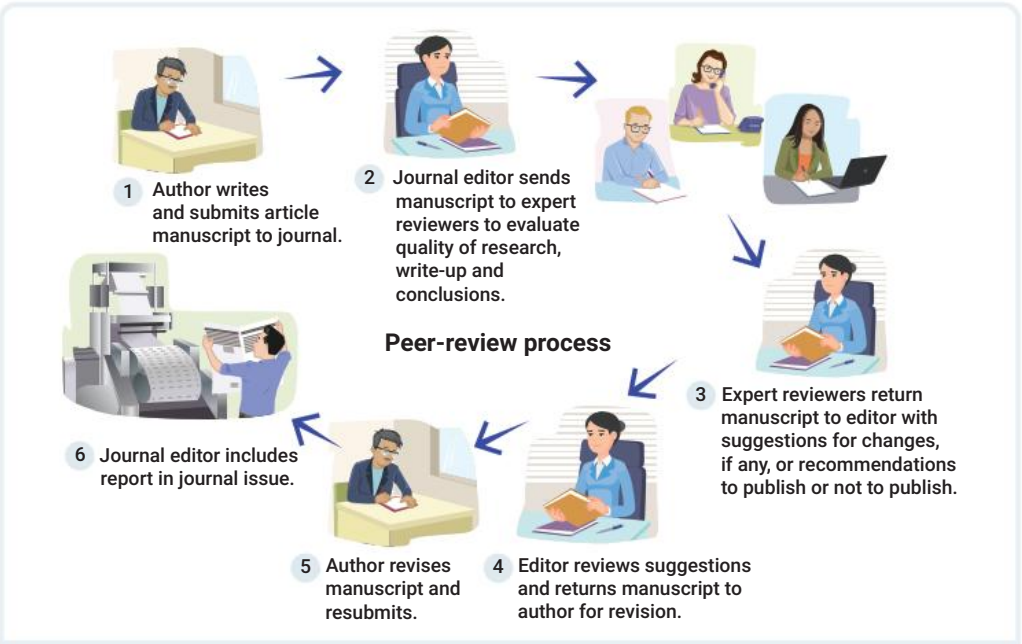


FIGURE DC.2.2 The peer-review process

- If evidence is used, where does the data come from?
- Is this publication trustworthy?
- Is there any bias; for example, is there a conflict of interest among the researchers?

It is also a good idea to cross-reference the information presented by these resources with other sources such as primary sources and textbooks. This initial research helps you to develop a rationale for your investigation, and as a result helps to craft a research question that is relevant to the claim. As with the student experiment, the research question needs to be able to be tested.

To help the reader have the necessary context for the research investigation, you need to provide a level of background. The background needs to include enough of a foundation that the reader can understand the theoretical underpinnings of the research while also showing that you have used scientific evidence to develop a research question that aligns with the claim.

Referencing conventions

Because experiments and scientific research draw on the knowledge, thoughts and ideas developed by others, we need to appropriately acknowledge the source of the information. The referencing format that is required depends on the discipline; however, in most cases, science uses the APA (American Psychological Association) referencing style.

Weblinks
Evaluating the information you find
Referencing style guides
Referencing sources

Analysing evidence

As part of your assessment, you will need to find scientific evidence from previous research related to your research question. The data derived from these studies is used in the same way as the data collected from your student experiment – to identify trends and relationships between variables to answer the research question.

Because there are multiple data points, it is important to re-organise the data and present it in a way that can be analysed. For example, **Table DC.2.1** presents a comparison of data collected from two distinct scientific experiments investigating the properties of different shampoos. The data from all three studies has been organised to make it easier to compare.

TABLE DC.2.1 Comparison of results between different studies

	(Badi 2014)			(Isaiah 2015)		(Mainkar 2001)	
	Formulated shampoo	Dove	Herbal Essence	Ego-cert	Undisclosed synthetic shampoo	Laboratory shampoo	Average of five commercial shampoos
Surface tension (dyne cm^{-1})	38.72	31.68	38.36	32	34	37.1	32.8–37.7
Wetting time (s)	187	141	157			130	159–227
Solid content (%)	22.75	25	25	25.3	26.5		
Foam description	Small dense	Small dense	Small airy			Loose open	Dense creamy
Foam height (mL)	115	92	113	165	169	158	153–168
	2% solution			1% solution			
Detergency (% sebum removal)				93	95	61.14	61.1–80.12

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Additionally, the data can be used to construct graphs **(Figure DC.2.3)**.

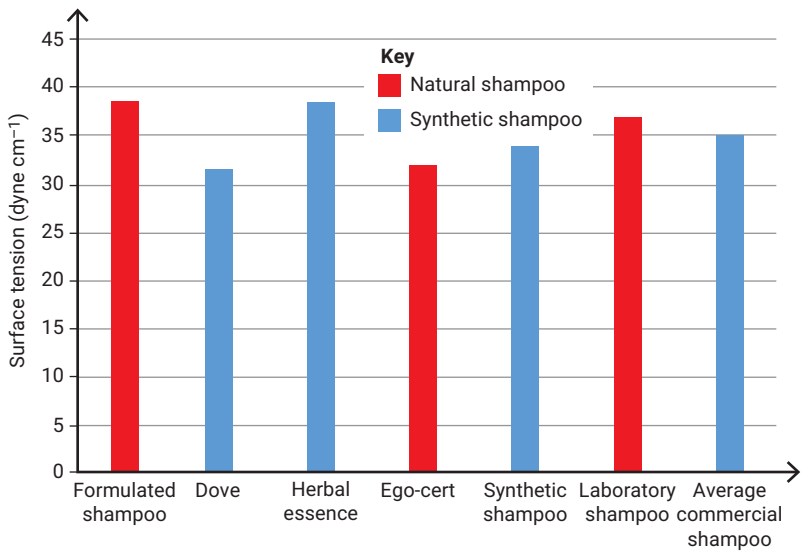

FIGURE DC.2.3 A graphical representation of the surface tension data presented In Table DC.2.1

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Organising data in this way makes it easier to identify any trends, patterns or relationships that exist between the variables being tested. As in your student experiment, you would also need to identify any sources of error and levels of uncertainty that can impact the results.

Interpreting evidence

As you now know, presenting data and describing trends and relationships on their own is not sufficient. We need to be able to use the evidence and scientific theory to justify the argument being made and to draw a conclusion.

When developing your conclusion, ensure that it directly answers the research question. Sometimes when assessing studies at an individual level, the data may point to a particular conclusion. However, when studies in the same area are evaluated together, an overall analysis may suggest a different conclusion. If your investigation shows a different conclusion from the studies used, that in itself is an important conclusion. It highlights that further investigation is required to develop a deeper understanding of the area.

Scientific language

The ability to communicate scientific understanding to an audience is often an overlooked skill. How we present the information depends on what we are sharing and the audience we are sharing with. For example, when communicating to a younger audience who are unfamiliar with many scientific concepts, it is important to use accessible language and visuals to help foster a foundational understanding of the topic. When communicating findings to those in the scientific community, we need to make sure to use scientific language, including correct nomenclature, units and symbols specific to the scientific theory.

Evaluating evidence

The quality of evidence can affect the reproducibility of the research and strength of the conclusions drawn. We can assess the quality of the evidence by identifying any limitations caused by errors and/or uncertainty **(Figure DC.2.4)**. This may include assessing:

- appropriateness of the method (where possible)
- sample size
- sources of error
- degree of uncertainty of the data.

It is also important to consider any bias (e.g. is the funding from a particular company?), recency of data and qualifications of the author(s).

> The three studies used to determine whether a natural or synthetic shampoo is better at cleaning hair have not led to any conclusive results. The characteristics used to determine whether a shampoo cleans better were limited to the surface tension of the water when the shampoo was added, wetting time, foaming ability, solid content and detergency. In all three studies, the natural shampoo performed better in some characteristics, while the synthetic shampoo in other characteristics. Therefore, the review of the studies done into cleaning ability does not support or refute the claim that natural shampoos are better cleaners than synthetic shampoos.

FIGURE DC.2.4 An excerpt evaluating the evidence provided by previous scientific studies

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This would also help to make any interpolation or extrapolations of the findings to further analyse the research claim. It is important to suggest any further improvements for future studies related to this area **(Figure DC.2.5)**. For example, identifying any changes that you would make to the methodology to improve the validity or reliability of the data from the experiment.

Further investigations required

To truly investigate whether natural shampoos are better than synthetic shampoos in terms of surface tension, wetting time, solid content, foaming ability and detergency, further testing would need to be carried out. This testing would need to involve a larger sample of both natural and synthetic shampoos. The amount of shampoo would need to remain constant in all testing and be similar to the quantity of shampoo used when washing hair, and the hardness of the water would also

FIGURE DC.2.5 Suggestions for further investigation for an experiment involving shampoos that showed inconclusive evidence

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Suggestions for improvement should also address any limitations present in the experiment including:

- experimental limitations; for example, time available to conduct the experiment, errors
- methodological limitations; for example, accuracy and reliability of measurement techniques, ethical constraints
- external limitations; for example, environmental factors that can introduce variability, access to proper equipment.

As you can appreciate, being able to interpret and evaluate data is crucial for reaching informed conclusions about your research. Not only do you need to speak about the data, you need to be able to use the evidence to justify any arguments made from the research.

LEARNING CHECK DC.2

DESCRIBING

1 **Identify** the difference between primary and secondary data.

2 **Describe** the role of the peer-review process in scientific research.

APPLYING

3 A student conducted an experiment to investigate the effect of different concentrations of hydrochloric acid on the pH of a solution. The student tested four different concentrations: 0.5 M, 1 M, 2 M and 4 M. The pH was measured using a pH meter. **Identify** one possible experimental and one methodological limitation for this experiment.

4 **Consider** the following passage:

The rate of reaction is a fundamental concept in the field of chemistry. Understanding the factors that influence reaction rates is crucial in predicting and controlling chemical reactions.

Rewrite the passage so that it can be read and understood by a primary school student who is studying science.

5 A student used the following source for their research investigation.

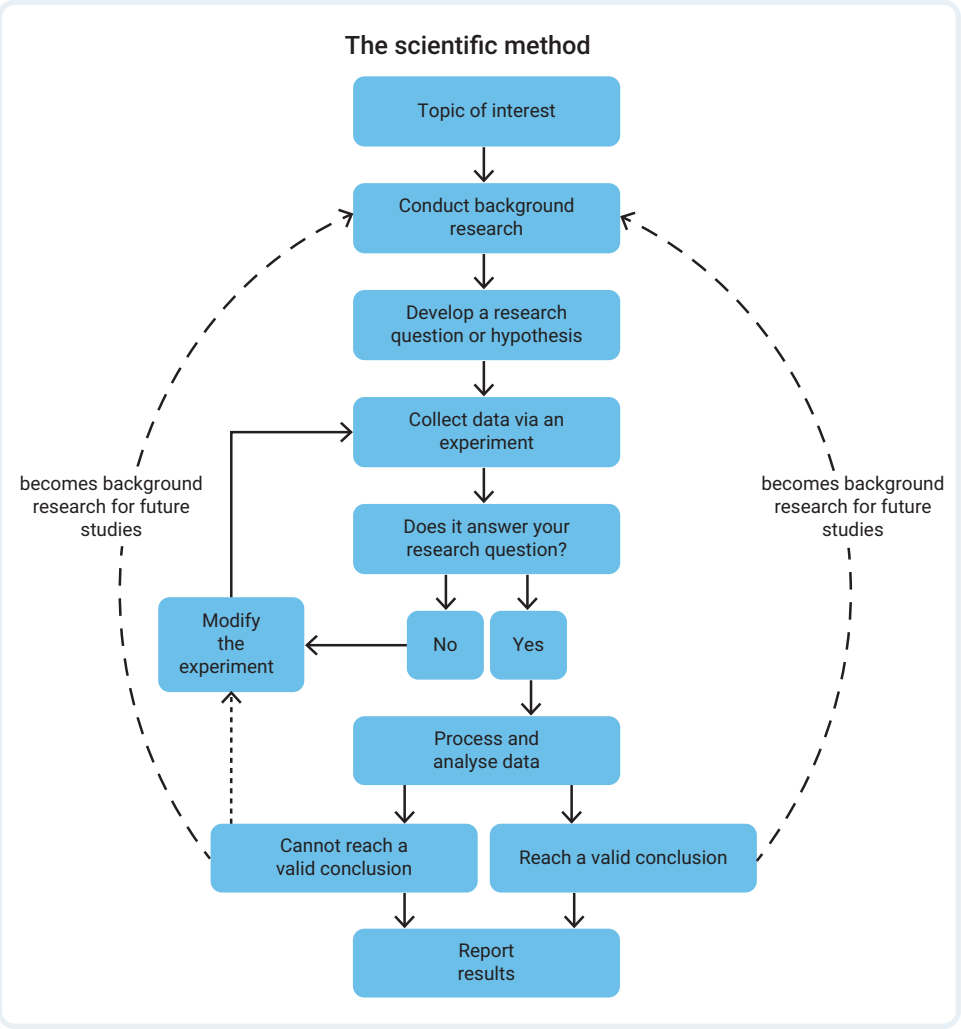
Cruzan, J. (2012). 'The most important solvent'. Retrieved from http://www.drcruzan.com/Water.html.

Use information from the 'Referencing sources' weblink to show how this resource would be referenced in the text.

CHAPTER SUMMARY

Conducting research

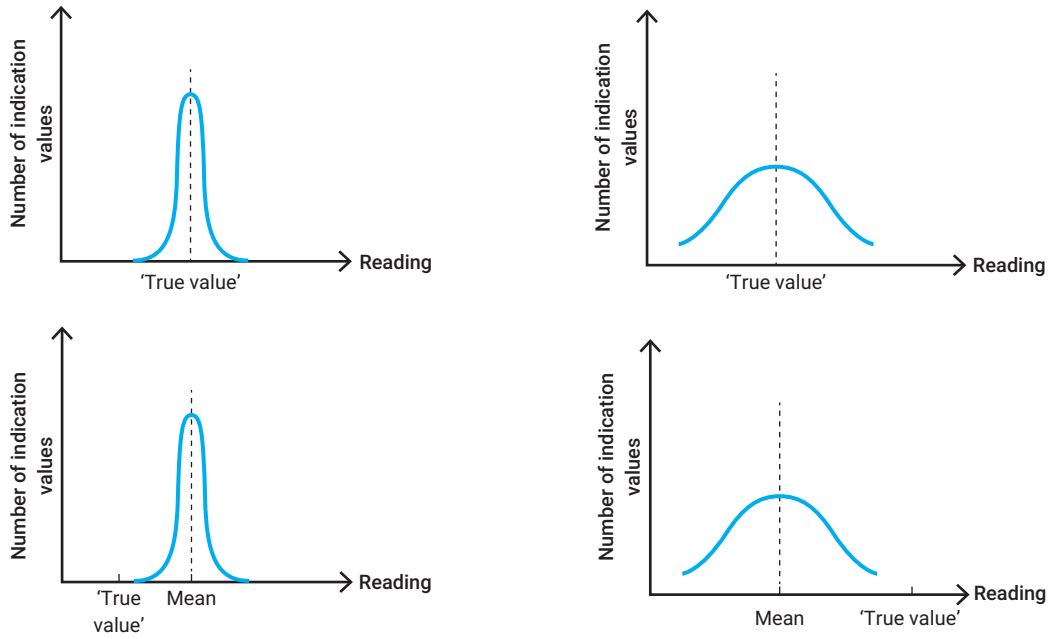
- The scientific method follows a particular process aimed to maximise accuracy, reliability and objectivity while minimising uncertainty and error.



Analysing data

- Precision describes the closeness of data, whereas accuracy describes how close the measured value is to the true value.
- The quality of data affects the validity of the experiment.
- Errors affect the accuracy and precision of data. These can be categorised into:
  - random errors
  - systematic errors.

Accuracy and precision



- Percentage error helps to indicate the accuracy of a measurement.

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

- Uncertainty describes the variability in the measured results:

$$\text{Absolute uncertainty} = \pm\frac{\text{maximum} - \text{minimum}}{2}$$

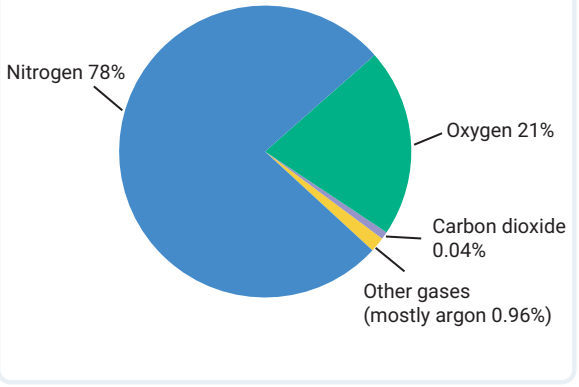
$$\text{Percentage uncertainty (\%)} = \frac{\text{absolute uncertainty}}{\text{measurement}} \times \frac{100}{1}$$

- Pearson's correlation (R) coefficient helps quantify the direction and strength of the relationships between the measured variables.
  - $R = 0$ suggests no correlation.
  - $R = 1$ suggests a strong positive correlation.
  - $R = -1$ suggests a strong negative correlation.

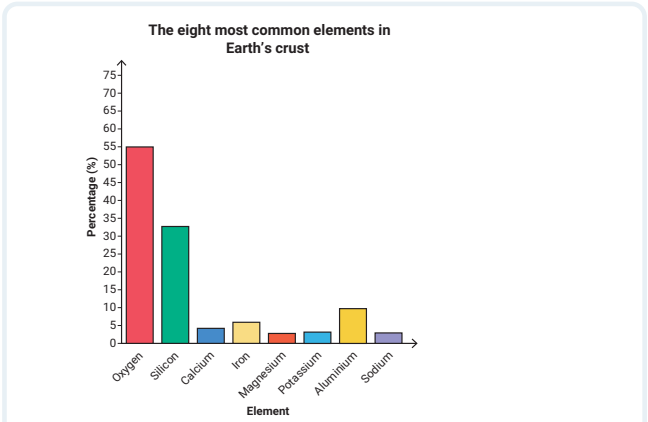
Graphs

- There are many different graphical representations of data, including:
  - linear graphs
  - column graphs
  - pie charts
  - scatterplots.

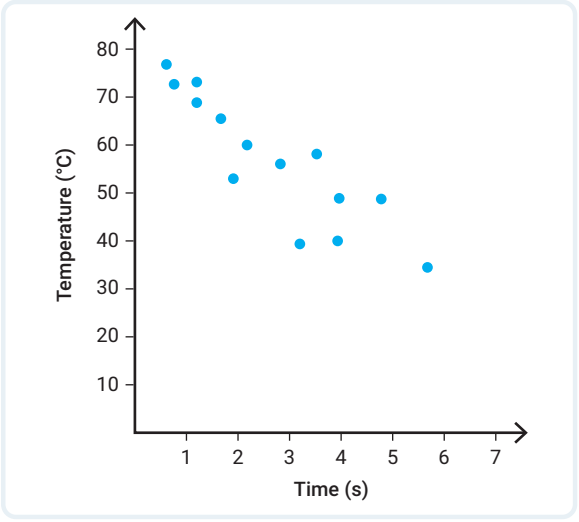
Pie charts



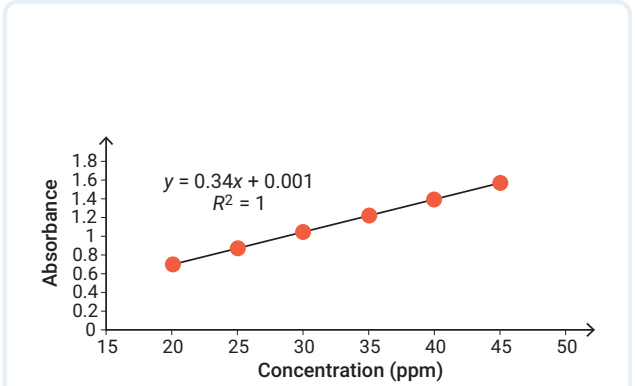
Column graphs



Scatterplots

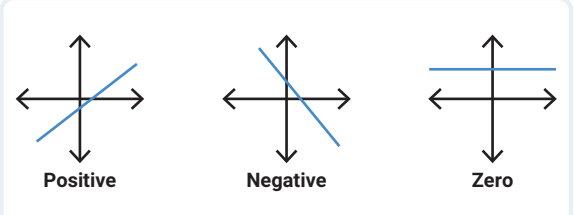


Line graphs

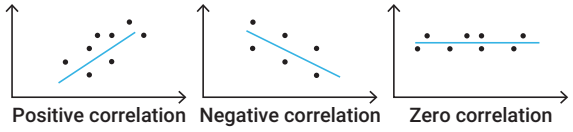


- Graphs help to show the relationship between variables. Although they can show correlation, this does not mean causation.

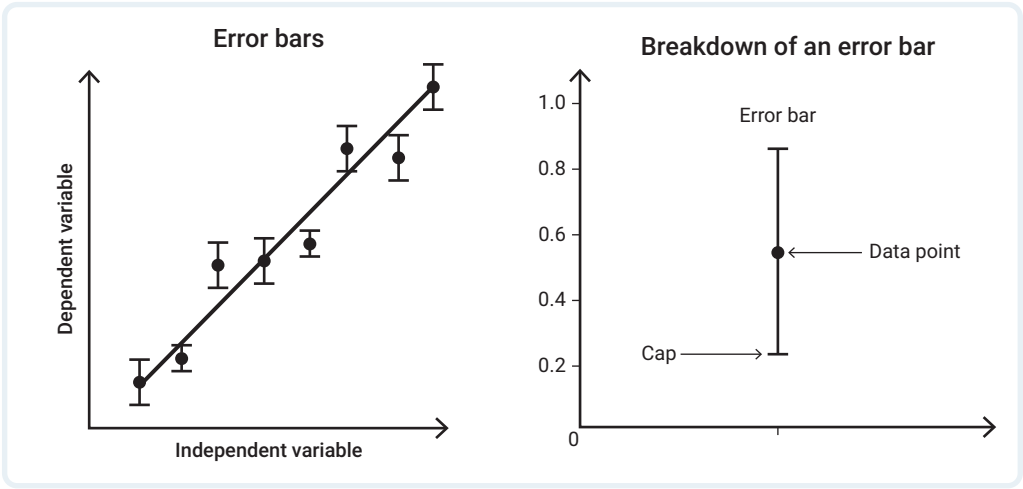
Correlation of line graphs



Correlation trends of scatterplots

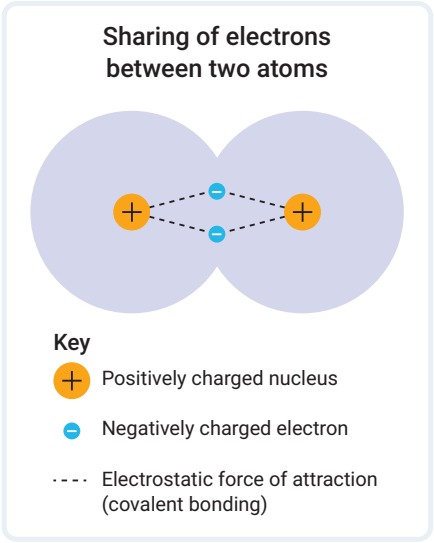


- Error bars on graphs help to visualise variability of measurements around the mean.
  - The central point shows the data point.
  - The upper and lower limits show the variability of the measured values.



Scientific drawings

- Scientific drawings are representations of scientific concepts.



Interpreting, analysing and evaluating evidence

- Apart from speaking to the trends shown in the data, when analysing data it is also important to assess:
  - appropriateness of the method
  - sample size
  - sources of error
  - degree of uncertainty of the data.
- When evaluating evidence, make sure to also address any limitations present in the experiment, including:
  - experimental limitations; for example, time available to conduct the experiment, errors
  - methodological limitations; for example, accuracy and reliability of measurement techniques, ethical constraints

- external limitations; for example, environmental factors that can introduce variability, access to proper equipment.

Communicating findings

- When communicating findings, make sure to:
  - use appropriate conventions and nomenclature
  - use language appropriate to the audience
  - reference appropriately using the relevant referencing system.

MULTIPLE CHOICE

1. Which measure provides information about the spread or variability of data points in a data set?
   - **A** Mean
   - **B** Mode
   - **C** Outlier
   - **D** Standard error

2. Which of the following data sets would be considered precise but not accurate?
   - **A** Volume of solution added to a flask using a graduated cylinder with a chipped spout (Readings: 22 mL, 21 mL, 23 mL)
   - **B** Measurements of the pH of a solution using a faulty indicator that consistently reads 0.5 units higher than the actual pH (Readings: 3.5, 3.5, 3.6)
   - **C** Mass of a metal bar measured on a balance that is not zeroed properly (Readings: 11.4 g, 15.8 g, 13.2 g)
   - **D** Temperature readings of a Bunsen burner flame measured with a thermometer that is positioned slightly farther from the flame each time (Readings: 1500°C, 1500°C, 1600°C)

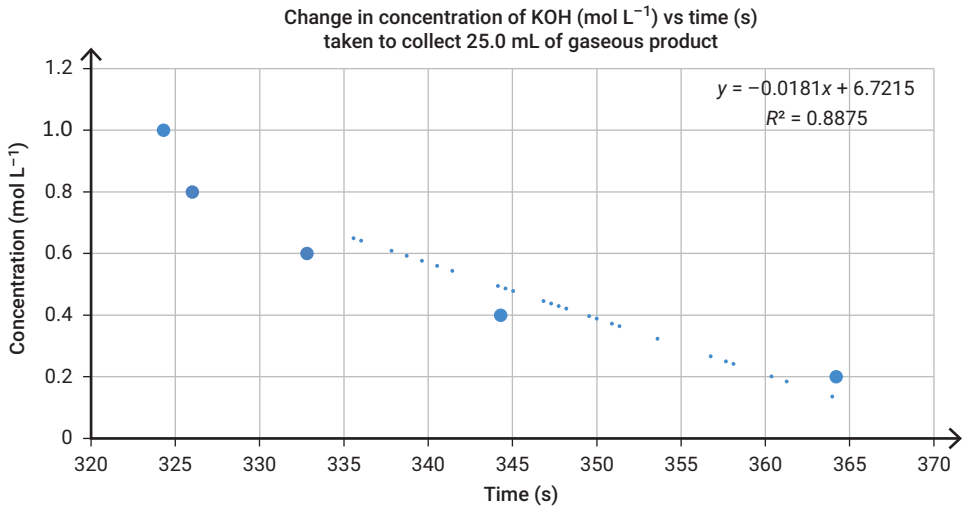
Questions 3 and 4 relate to the following information.
A Chemistry student measures the volume of a liquid using a graduated cylinder. The student reads the volume as 12.5 mL. However, a more precise instrument shows the actual volume to be 12.9 mL.

3. What is the percentage error in the student's measurement?
   - **A** 1.5%
   - **B** 2.4%
   - **C** 2.6%
   - **D** 3.1%

4. Which of the following actions would not improve the reliability of the student's results in subsequent measurements?
   - **A** Using a graduated cylinder with a smaller volume division (e.g. 0.1 mL instead of 1 mL)
   - **B** Repeating the measurement with the same graduated cylinder and averaging the results
   - **C** Calibrating the graduated cylinder by measuring a known volume of a different liquid
   - **D** Estimating the volume between the markings on the graduated cylinder

5. In a Chemistry experiment, students investigated the effect of the concentration of solutions on light absorbance. Which of the following can be considered an extraneous variable?
   - **A** Type of light source used
   - **B** Concentration of the solution
   - **C** Length of time the solution was exposed to light
   - **D** Temperature of the room during the experiment

Questions 6–8 relate to the following information.
A student conducted an experiment to measure the rate of a reaction. The rate was measured through the collection of the gaseous product.



6. The independent variable is:
- **A** concentration (mol L^{-1}).
- **B** gas (mL).
- **C** mass (grams).
- **D** time (seconds).

7. Which of the following correctly describes the trend shown by the graph?
- **A** As the concentration increases, the time taken to collect 25.0 mL of gas increases.
- **B** As the concentration decreases, the time taken to collect 25.0 mL of gas increases.
- **C** As the concentration decreases, the time taken to collect 25.0 mL of gas decreases.
- **D** As the concentration increases, the time taken to collect 25.0 mL of gas remains the same.

8. The R^2 shows:
- **A** a weak correlation between the variables.
- **B** a strong correlation between the variables.
- **C** a negative correlation between the variables.
- **D** no correlation between the variables.

9. Which of the following options can be considered a random error in a chemistry experiment?
- **A** Using a calibrated balance
- **B** Following the experimental procedure
- **C** Reading a measuring cylinder at different angles from the meniscus
- **D** Performing the experiment at a temperature higher than that outlined in the methodology

10. Which of the following cannot improve the reliability of results in an experiment measuring soil acidity levels in different areas?

A Increasing the replicates in each area
B Using various measurement techniques
C Calibrating the pH meters before taking measurements
D Reducing the number of data points collected in each area

SHORT RESPONSE

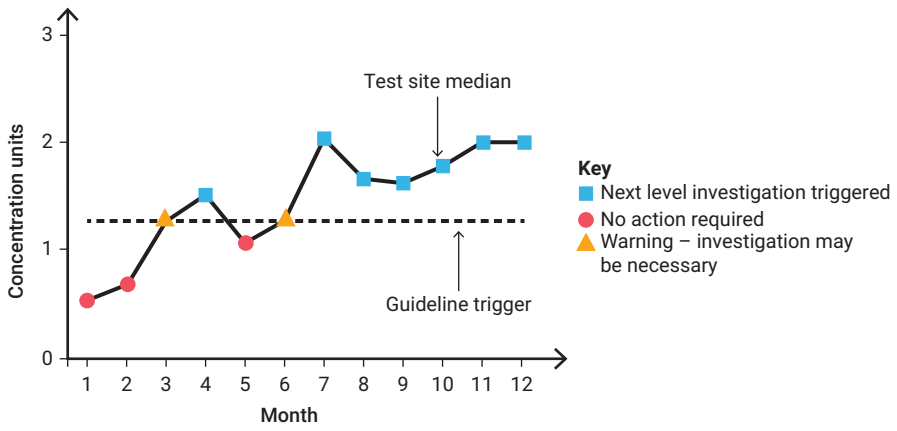
11. The following is a description of an experiment.

Students are investigating the effect of different concentrations of a chemical solution on the rate of a chemical reaction. In the experiment, the reaction is conducted with three different concentrations: 0.1 M, 0.5 M and 1.0 M.

All reactions are conducted at the same temperature and pressure, and the rate of the reaction is measured at regular time intervals.

Write an appropriate research question for this experiment.

12. Governments monitor water quality to ensure that the water is being provided to the population is safe and within guidelines. As part of ongoing monitoring, water samples are measured for the presence of different chemicals.



a **Identify** the dependent variable.
b At what point would the guideline be triggered?
c **Describe** the trend shown by the graph.

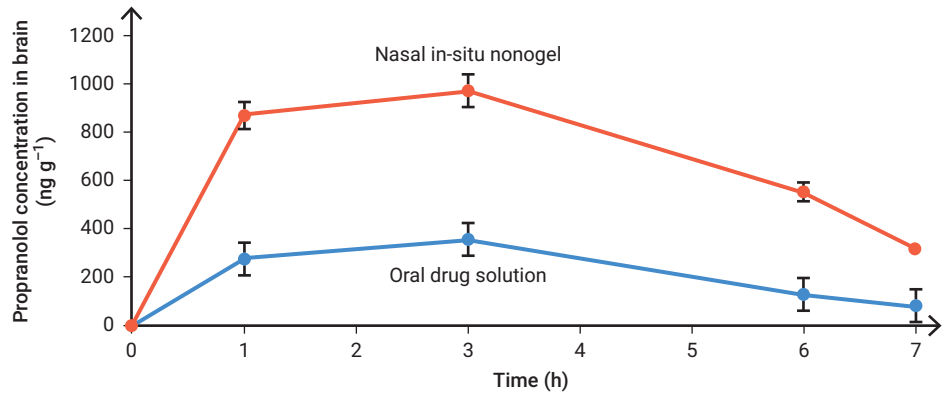
13. The data in the table was collected from an experiment testing the effect of different concentrations of a chemical solution on the rate of a chemical reaction.

Concentration of solution (%)	Time taken for a set mass of product to be produced (s)		
	Trial 1	Trial 2	Trial 3
2.0	15 ± 5%	16.8 ± 5%	16.2 ± 5%
1.5	24 ± 5%	25.8 ± 5%	25.2 ± 5%
1.0	34.8 ± 5%	36 ± 5%	35.4 ± 5%
0.5	45 ± 5%	46.8 ± 5%	46.2 ± 5

Sketch an appropriate graph to represent this data. Include error bars in your graph.

14. According to the Global Burden of Disease, neurological diseases are one of the main causes of death globally. Migraine is a neurological disease affecting the central nervous system that causes severe pain to one side of the head. Propranolol is a drug developed to help manage migraine attacks; however, multiple factors affect how much of the drug can be absorbed into and used by the body.

The following graph was taken from a study exploring the best mechanisms to deliver the drug to improve the availability of propranolol.



a **Describe** the trend seen in the graph.

b For someone suffering from migraines, which delivery method would be the preferred method? **Explain** your choice.

ANSWERS

CHAPTER DC SCIENCE RESEARCH

LEARNING CHECK DC.1

DESCRIBING

1 a Accuracy refers to how close a value is to the true value, whereas precision describes how close a set of measurements are to each other.

b Reliability refers to the consistency of measurements upon repeat experiments, whereas validity describes the extent to which the experiment measures what it is intended to measure.

2 Calibrate measuring instruments.

Record multiple measurements and take an average.

3 a Data that is in categories

b Continuous data or measurements taken over time

c Data that is in categories or discrete data

4 a A logbook contains detailed notes relating to the experiment, including observations, results and methodology. This information is important during the analysis of the results of the experiment.

b MSDSs contain information about the safe handling of any chemicals or substances used in an experiment. This ensures the safety of the researchers.

c Ethics help to ensure the safety of participants in the experiment, the integrity of the experiment and the proper use of the experimental results.

5 Research question, materials, methods, discussion

APPLYING

6 a Dependent variable: rate of reaction (mL s^{-1})

b Independent variable: temperature

7 Potential research question: Does the consumption of food (grams) before running affect the total distance a person can run (km)?

8 Potential risk: The student could drop the measuring cylinder, causing it to break and shatter. The pieces of glass could cause potential damage to the skin.

Risk minimisation – Wear gloves and closed-toe shoes to protect against pieces of glass if broken.

9 The experimenter breached informed consent. The experiment ignored the participant's refusal to be tested and performed the procedure anyway. Participants need to give formal consent to participate in experiments and the experimenter must respect their wishes, not go against them.

10 a 2 **b** 6 **c** 5 **d** 1

11 a Percentage uncertainty $= \frac{1}{20} \times 100 = 5\%$

b This suggests that the measurements are relatively imprecise.

12 a The rate of cooling of each substance – this could affect the temperature recorded when the substance melts

b Random error

13 Absolute uncertainty $= \frac{14.2 - 14.1}{2} = \pm 0.1$ cm

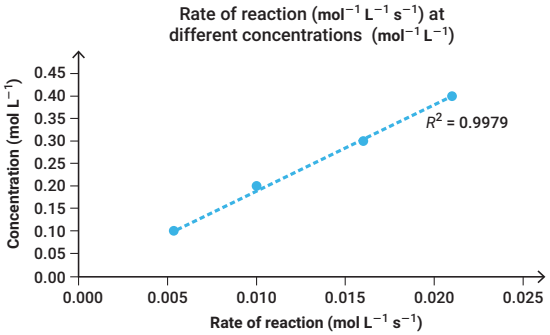
14 a Dependent variable : Rate of reaction

Independent variable: Concentration of reactant

b

Concentration (mol L^{-1})	Mean rate (mol L^{-1} s^{-1})
0.1	0.0053
0.2	0.0073
0.3	0.016
0.4	0.021

c



d There is a positive correlation between the rate of reaction and concentration of reactant.

ANALYSING

15 a Concentration of phosphorus

b Sample 3

16 a Scatterplot

b Line of best fit

c Gradient $= \frac{\Delta y}{\Delta x}$

$= \frac{4 - 2}{0.480 - 0.250}$

$= 8.70$ (approximately)

d Approximately 1.500

e Since there is a strong positive correlation between the two variables, the *R* value is likely to be closer to 1 than 0.

LEARNING CHECK DC.2

DESCRIBING

1 Primary data is firsthand data collected by the researcher, whereas secondary data refers to information collected from an experiment conducted by someone else.

2 The peer-review process helps to ensure the quality of the research and the results. It also helps to add credibility to the research investigation.

APPLYING

3 Experimental limitation: the accuracy of the pH meter

Methodological limitation: only testing three concentration levels

4 How fast a reaction occurs is the rate of reaction. Knowing how fast or slow reactions occur can help scientists with studying chemical reactions.

5 (Cruzan, 2012)

CHAPTER EXAM

MULTIPLE CHOICE

1	D	**3**	D	**5**	A	**7**	B	**9**	C
2	B	**4**	D	**6**	D	**8**	B	**10**	D

SHORT RESPONSE

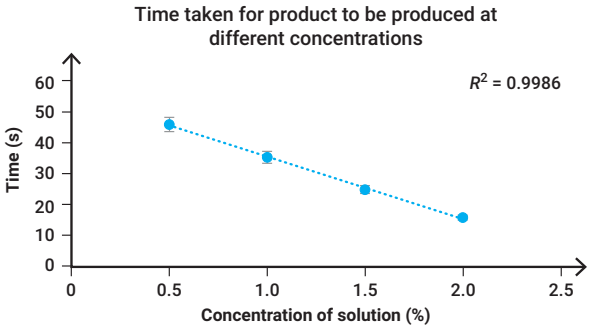
11 How does the concentration(M) of a chemical solution affect the rate of a chemical reaction(mL s^{-1})?

12 a Concentration

b At a concentration above 1.2–1.3

c In the first 4 months, the concentration increased over time. From months 3–4, the concentration increased high enough for the guideline to be triggered. From months 4–5, the concentration decreased but began to increase again from months 5–7. From months 7–9, the concentration decreased over time but began to increase again from months 9–11 after which it remained stable. For the period of months 7–12, the concentration was greater than the guideline trigger point.

13



14 a The graph shows that nasal in-situ nonogel allows for a higher concentration of propranolol in the brain over time compared to oral drug solution. For both graphs, the concentration of propranolol in the brain increases during the first 3 hours, after which the concentration decreases over time.

b For someone suffering from migraines who would want more of the migraine drug to be available quicker, nasal in-situ nonogel would be a preferred option because it allows for both a quicker and a higher concentration of medication to reach the brain than the oral drug solution. It also allows for more of the drug to be available in the brain over time.

UNIT

3

Equilibrium, acids and redox reactions

John Inns/Adobe Stock Photos

Topic 1: Chemical equilibrium systems

CHAPTERS RELATED TO THIS TOPIC AREA: 1–7

Topic 2: Oxidation and reduction

CHAPTERS RELATED TO THIS TOPIC AREA: 8–11

9780170483544

Reversible reactions occur in a variety of chemical systems, including acid–base equilibrium systems and electrochemistry. Applications include the principles of oxidation and reduction (redox) reactions and the production of electricity from electrochemical cells. Reversible processes respond to a range of factors and can achieve a state of dynamic equilibrium. Investigations explore the principles of dynamic chemical equilibrium and how these can be applied to electrochemical cells and the pH scale. The concepts of equilibrium and redox are important in the real world in terms of environmental issues, such as acid rain and oceanic acidification. These concepts can also be applied to contemporary energy use and sustainability debates. In an industrial context, applications include food and wine production, corrosion and corrosion prevention, fuel cells and uses of electrochemistry.

UNIT OBJECTIVES

By the end of this unit, students should be able to:

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.

Chemistry 2025 v1.2 General Senior Syllabus

CHAPTER 1

Chemical equilibrium

iStock.com/Nostal6ie

SYLLABUS DOT POINTS

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 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.

Introduction

In our everyday lives, there are many examples of balance or equilibrium. A see-saw is in equilibrium when the forces on either side are balanced, and the see-saw remains horizontal. A river ecosystem can be in equilibrium when the amount of water entering the river through rainfall is balanced by the amount of water leaving through evaporation or flowing downstream. This balance helps maintain stable water levels and a healthy environment for aquatic life.

Imagine you are using your phone while it is connected to the charger and the power is being added at the same rate as it is being used. The inflow and outflow rates are equal, so the power level in the phone is constant. This represents equilibrium because power is still entering and leaving the system, but the overall power level doesn't change. Similarly, in chemistry, reversible reactions (represented by double arrows) can occur in both directions simultaneously at the same rate at a molecular level, and so achieve a balance where the amounts of reactants and products remain constant and the chemical system *appears* to be unchanging.

ASSUMED KNOWLEDGE

- ✓ Chemical equations are composed of reactants and products.
- ✓ Balanced chemical equations can be determined for a range of reactions.
- ✓ Symbols are used to indicate the phases of matter (s, l, g, aq) in chemical equations.
- ✓ The rate of reaction depends on several factors.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ compare open and closed systems, and provide examples of each
- ✓ explain the difference between reversible and non-reversible reactions
- ✓ understand the difference between steady state and dynamic equilibrium systems
- ✓ describe physical equilibrium and chemical equilibrium systems, giving examples of each
- ✓ understand that reversible reactions can go in the forward or reverse direction
- ✓ analyse the rates and concentrations of products and reactants in chemical equilibrium, using equilibrium graphs
- ✓ consider the activation energies of the forward and reverse reactions as a predictor of the reversibility of a reaction.

chemical system the chemicals involved in a reaction

surroundings everything except the chemicals involved in a reaction

closed system a system in which the chemicals involved in a reaction are all contained in a fixed space

open system a system in which one or more reactants or products in a reaction can be added or lost

Worksheet
Chemical systems

Weblinks
What is equilibrium?
Equilibria

1.1 Equilibrium – systems in balance

The chemicals involved in a reaction form the **chemical system**, while anything around these chemicals but not involved in the actual reaction forms the **surroundings**. For example, in the reaction between hydrogen gas and oxygen gas to form water vapour, the molecules of hydrogen, oxygen and water make up the system, while the other molecules in the air (e.g. nitrogen, carbon dioxide) form the surroundings. In an aqueous environment, the water forms part of the system if it is involved in the reaction and it forms the surroundings if it is not involved.

If the chemicals in the reaction are all contained in a sealed system, the system is a **closed system** (Figure 1.1.1). For example, if hydrochloric acid was added to calcium carbonate in a fixed space where nothing can enter or leave the system, it is a closed system.

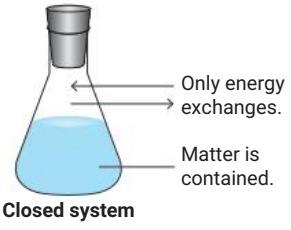


FIGURE 1.1.1 A system in which chemicals are contained is described as a closed system.

Conversely, if substances can either be added from or lost to the surroundings, then it is described as an **open system**. For example, if hydrochloric acid is added to calcium carbonate in an open beaker, then the carbon dioxide gas produced would escape into the air:

$$2HCl(aq) + CaCO_3(s) \rightarrow CO_2(g) + CaCl_2(aq) + H_2O(l)$$

It is important to note that energy, such as heat or light, can enter or leave a system, regardless of whether the system is open or closed.

Physical and chemical changes

Changes that occur in a chemical system can be described as a **physical change** or a **chemical change**. During a physical change, no new substances are formed. Instead, the physical properties of the reactant change, which can include a change of state. For example, when water is boiled, it changes from a liquid to a gas. The molecules remain the same; they are simply further apart (Figure 1.1.2). We can represent this change with the equation:

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

physical change a change in which no new substance is produced

chemical change a change in which a new substance is produced

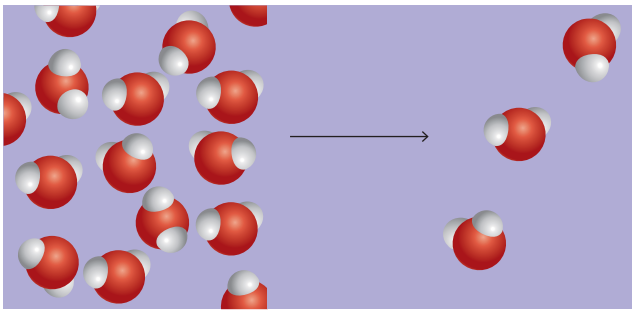


FIGURE 1.1.2 Water boiling is a physical change from liquid to gas.

Syllabus link
Chapter 8 of *Nelson QCE Chemistry Units 1 & 2* describes physical and chemical changes.

During a chemical change, the reactants produce new substances with different physical and chemical properties from those of the original substances. For this to happen, the atoms rearrange and form products that are different from the reactants. For example, a chemical change occurs when an electric current is passed through water (Figure 1.1.3). The atoms in the reactant, water, rearrange to form the new substances of oxygen gas and hydrogen gas:

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

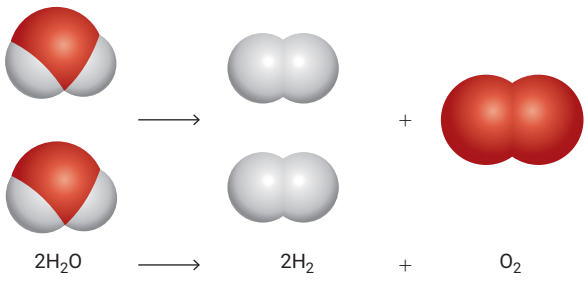


FIGURE 1.1.3 The electrolysis of water is a chemical change.

Chemical reactions are often thought of as a situation in which the reaction continues producing the products until one of the reactants is used up. However, this only happens for some reactions. In many reactions, as the products are formed, some of them react to become reactants again. This means that when the reaction appears 'complete', there are both reactants and products present, as shown in Figure 1.1.3.

Reactions in which the reactants can form products, and the products can form reactants are known as **reversible** reactions. The reaction in which the reactants form products is called the *forward reaction*, and the reaction where the products form reactants is called the *reverse reaction* (Figure 1.1.4). A double arrow $\rightleftharpoons$ is used to show that the reaction can

reversible a reaction in which the products can be converted back to the reactants

occur in both directions. All physical changes are reversible reactions. However, only some chemical changes are reversible.

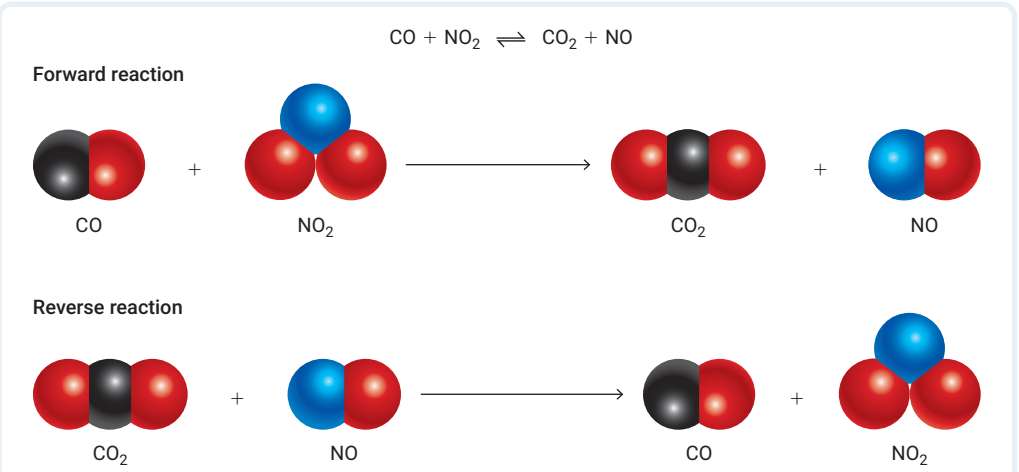


FIGURE 1.1.4 Forward and reverse reactions

The reaction between hydrogen gas and nitrogen gas is a reversible reaction and can be represented by the following equation:

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

In the example shown in Figure 1.1.4, carbon monoxide (CO) reacting with nitrogen dioxide (NO_2) is the forward reaction; carbon dioxide (CO_2) reacting with nitrogen monoxide (NO) is the reverse reaction. The double arrows indicate that the reaction can proceed in both the forward and reverse directions.

Some of these reactions show observable changes.

LEARNING CHECK 1.1

DESCRIBING

1 **Describe** the difference between a forward reaction and a reverse reaction.
2 **Describe** the requirements for a closed system.
3 **Explain** whether all chemical reactions are reversible.
4 **Explain** why double arrows are used in equations for reversible reactions.
5 **Describe** the difference between a chemical change and a physical change.

APPLYING

6 The reaction for the self-ionisation of water is an endothermic reaction:

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

a **Construct** the equation for the forward reaction.
b **Construct** the equation for the reverse reaction.
c **Identify** the distinguishing feature in the chemical equation that indicates that this is a reversible reaction.

1.2 Dynamic equilibrium

Weblink
Reversible reactions

In a closed chemical system involving a reversible reaction, as the reactants form products the products also form reactants. This means that the reaction does not go to completion. Rather, it reaches a state of *dynamic equilibrium,* where the forward and reverse reactions are occurring at the same rate.

Dynamic equilibrium is achieved when the *rates* of the forward and reverse reactions in a reversible reaction are equal. Dynamic equilibrium can only occur in a closed system. The word 'dynamic' indicates that the reactions are still occurring at the molecular level, even though the concentrations of reactants and products appear to remain the same. At dynamic equilibrium, molecules of reactants are still converting into products, and molecules of products are still converting back into reactants. In comparison, a **steady state** may be achieved in open systems with continuous inflow of reactants and outflow of products. For example, if reactants are added to a reaction mixture at the same rate that the products are removed, then a steady state will be achieved even though the system will not be at equilibrium.

dynamic equilibrium a closed system in balance in which the forward and reverse reactions occur at the same rate

steady state an open system in balance in which the inflow of materials from the surroundings equals the outflow of materials to the surroundings

Equilibrium in chemical systems

When reactants are initially placed in a system, their concentrations are high compared to the concentration of products. As there are initially no products, the reverse reaction cannot occur, and the reaction progresses towards the products. This means that the rate of the forward reaction is relatively high.

As the forward reaction progresses, the concentration of the products increases. The rate of the forward reaction begins to decrease, because there are fewer reactant molecules available. At the same time, the reverse reaction starts to occur, and its rate initally increases to produce a higher concentration of products. This rate slows over time as less reactants become available. Eventually, both the forward and reverse reactions slow until the rates of the forward and reverse reactions are equal and equilibrium is achieved.

Figure 1.2.1 shows how, in a reaction between nitrogen gas and hydrogen gas, the concentrations of the reactants and products change as an equilibrium is reached. The equation for the reaction described is:

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

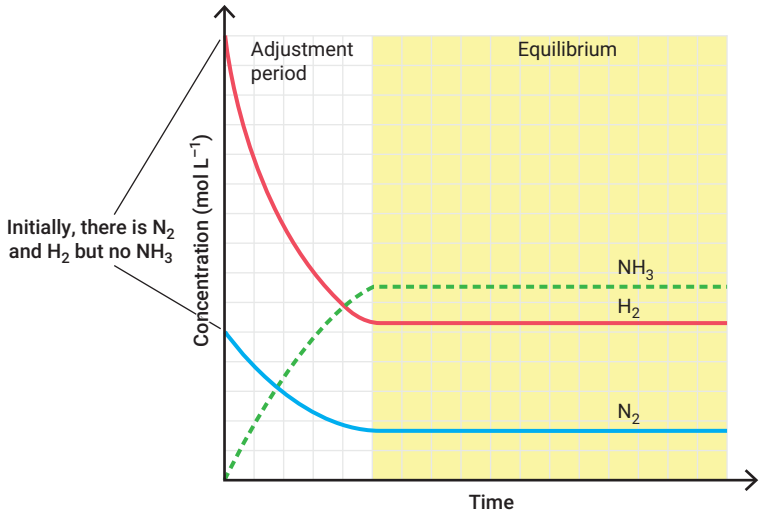


FIGURE 1.2.1 Concentration of reactants and products against time during the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Therefore, the:

- rate of the forward reaction decreases as the concentration of the reactants decreases
- rate of the reverse reaction increases as the concentration of the products increases.

The system reaches a point at which the rate of the forward reaction is the same as the rate of the reverse reaction (Figure 1.2.2). At this point, products are formed at the same rate that they are used up. Therefore, the concentrations of the reactants and products remain constant. When this happens, the system is said to be in dynamic equilibrium.

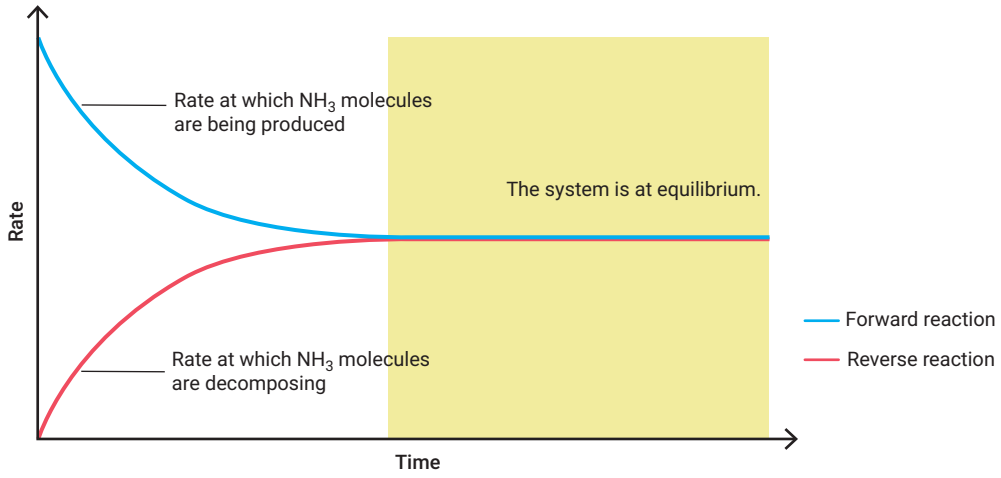


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FIGURE 1.2.2 Rates of reactions against time during the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, when N_2 and H_2 are mixed

Worksheet
Systems in equilibrium

When a system is at dynamic equilibrium, the concentrations of the reactants and products remain constant even though the reactions are still occurring in both directions. This means that the **macroscopic properties** also remain constant. For example, the colour will remain constant or the mass of a solid will stay the same. Note that although the concentrations must be constant for the system to be at equilibrium, they do not need to be equal. In fact, it is unlikely that they will be equal, as the equilibrium may favour the products or the reactants.

macroscopic property a property that is observable, e.g. pressure, temperature, colour, mass

Physical and chemical systems in equilibrium

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FIGURE 1.2.3 A system at dynamic equilibrium will maintain constant macroscopic properties, such as colour.

Physical and chemical changes may be in dynamic equilibrium, where the changes are reversible. Both types of equilibrium involve processes in which opposing actions occur at the same rate.

Physical equilibrium occurs in processes that involve a change of state (e.g. solid, liquid or gas) in a closed system with no matter or energy being lost to surroundings (Figure 1.2.3). For example, water can evaporate and condense at the same rate in a closed container, maintaining constant levels of liquid and vapour.

Chemical equilibrium occurs when reactants are transformed to products at the same rate as the reverse reaction. For example, in the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, nitrogen and hydrogen combine to form ammonia, and ammonia decomposes back into nitrogen and hydrogen at equal rates at equilibrium.

physical equilibrium a situation in which rates of opposing processes, such as phase changes (e.g. evaporation/condensation), are equal, resulting in no net change to the system

chemical equilibrium a situation in which forward and reverse reactions occur at equal rates, leading to constant concentrations of reactants and products

LEARNING CHECK 1.2

DESCRIBING

1 **Define**:
   - **a** equilibrium
   - **b** dynamic equilibrium
   - **c** steady state.

2 **Identify** the following statements as true or false.
   - **a** A chemical system will reach equilibrium if it is an open system.
   - **b** A chemical system will reach equilibrium if it involves a reversible reaction.
   - **c** At equilibrium, the rate of the forward reaction is the same as the rate of the reverse reaction.
   - **d** At equilibrium, the concentrations of the reactant and products do not remain constant.
   - **e** At equilibrium, the macroscopic (large-scale) properties are not constant.

APPLYING

3 **Describe** the process shown in Figures 1.2.1 and 1.2.2.

4 **Explain** why the initial rates of the forward reaction are faster than the reverse reaction when one reactant decomposes into two products.

5 **Describe** the trend on the graph (Figure 1.2.2) indicating equilibrium has been achieved.

1.3 Predicting reversibility

In *Nelson QCE Chemistry Units 1 & 2*, you considered collision theory to predict the rate of reactions. Collision theory states that for a reaction to occur, the particles must collide with sufficient energy to break the bonds and at the appropriate orientation to allow new bonds to form. This theory can also be used to understand why some reactions are reversible and others are not.

Recall that the amount of energy required to break the bonds of the reactants is known as the **activation energy, E_a**. This is the difference in **enthalpy** between the reactants and the **activated complex**, as shown in Figure 1.3.1. Also, recall that although atoms cannot be gained or lost in closed systems, energy can transfer.

activation energy, E_a the minimum amount of energy required for a chemical reaction to occur

enthalpy total energy content of a chemical substance

activated complex the intermediate state of a chemical reaction in which bonds are breaking and forming

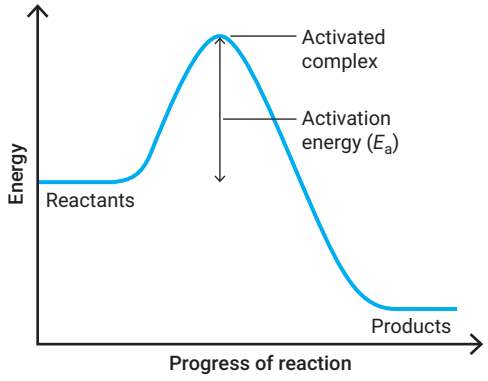

FIGURE 1.3.1 The activation energy of a reaction is the minimum amount of energy required for the chemical reaction to occur.

Syllabus link
Chapter 19 in *Nelson QCE Chemistry Units 1 & 2* explains rate of reaction and activation energy.

Weblink
What triggers a chemical reaction?

If the reactant particles in a collision do not have enough energy to break the bonds, then they are unable to form the products. If the activation energy is lower than the energy of the reactant particles, then more particles will have enough energy to break the reactant bonds and form the products. Therefore, the size of the activation energy influences the likelihood of a reaction proceeding.

In a reaction, we can consider the activation energy of both the forward and reverse reactions. If the activation energy of either of these is very high, then that reaction is unlikely to proceed because very few particles will have enough energy for a successful collision. Therefore, for a reaction to be reversible, the activation energies of both the forward and reverse reactions must be low enough that sufficient particles will have enough kinetic energy for a successful collision. **(Figure 1.3.2)**.

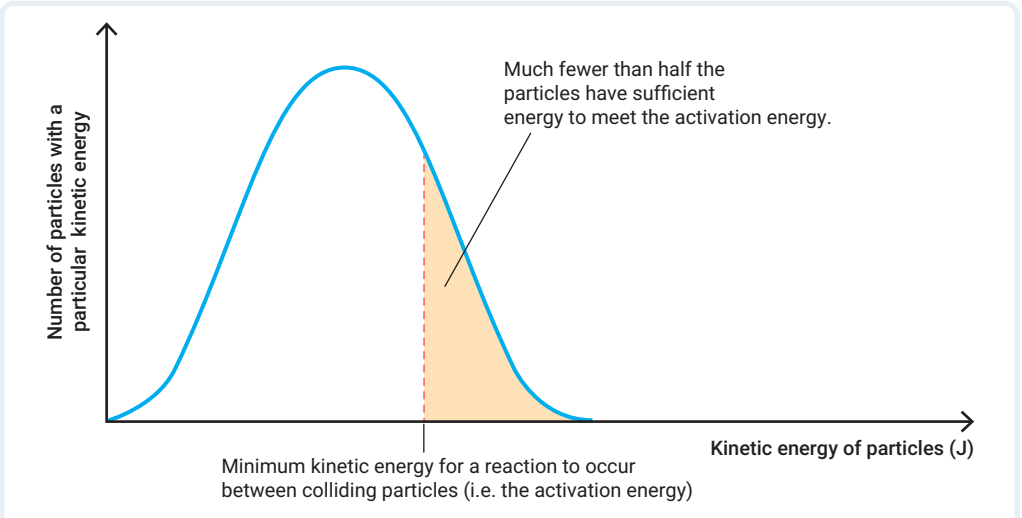

FIGURE 1.3.2 The number of particles with enough energy for a successful collision depends on the activation energy of the reaction.

An example of a reversible reaction in which the activation energies of the forward and reverse reactions is the Haber process method of synthesising and decomposing ammonia:

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

In this reaction, both the forward and reverse reactions have activation energies low enough for a reversible reaction to occur.

In comparison, the combustion of octane in petrol is non-reversible. It is represented by the equation:

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

This time, the forward reaction has a relatively low activation energy, and releases massive amounts of energy as heat. The reverse reaction has such a high activation energy, and the reactants carbon dioxide and water are so stable that the reaction will not proceed in this direction.

Syllabus link
The Haber process is discussed in more detail in Chapter 17.

LEARNING CHECK 1.3

DESCRIBING

1 **Define** 'activation energy' (E_a).
2 **Define** 'activated complex'.
3 **Describe** what the reversibility of reactions depends on.

APPLYING

4 **Explain** what will happen to a reaction if both the forward and reverse reactions have low activation energies.

5 **Compare** reversible and non-reversible reactions on the basis of activation energy.

6 **Explain** why the Haber process is reversible, but the combustion of petrol is not.

1.4 Analysing data to identify equilibrium

Graphs are used in many situations to visually represent data. When studying chemical systems involving equilibrium, graphs can be used to consider either the rates of the reactions or the concentrations of the substances over time.

Reaction rate against time

In a graph of reaction rate against time, when starting with reactants only, the following are observed.

1. The rate of the forward reaction is initially high.
2. The rate of the reverse reaction is initially zero.
3. The rate of the forward reaction decreases, initially quickly but then more slowly.
4. The rate of the reverse reaction increases, initially quickly but then more slowly.
5. The rates of the two reactions become equal – this is when dynamic equilibrium is reached.

This can all be seen in **Figure 1.4.1**.

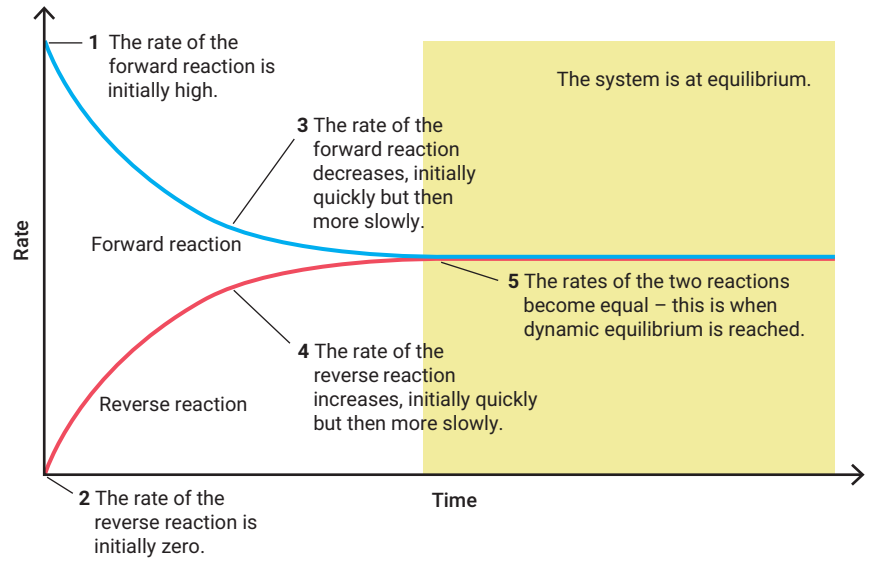

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FIGURE 1.4.1 A graph of reaction rate against time for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Weblink
Concentration vs time graphs

Concentration against time

Similarly, a graph can be used to represent the changes in concentration during a reaction as it reaches equilibrium. Typically, the reaction starts with only reactants; therefore, the concentration(s) of:

1. reactants is initially large
2. products is initially zero
3. reactants decreases, initially quickly (steep graph) but then more slowly
4. products increases, initially quickly (steep graph) but then more slowly
5. both reactants and products plateau (remain constant) when the system reaches equilibrium.

This is shown in **Figure 1.4.2**.

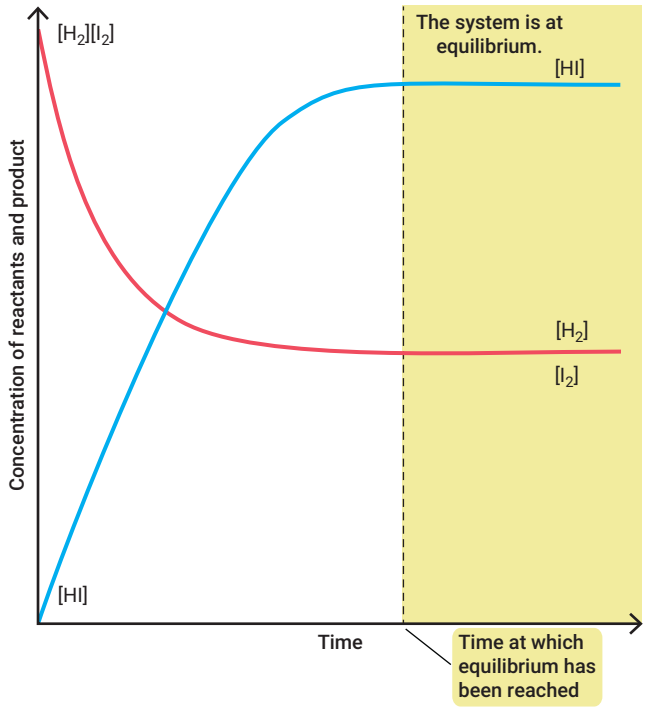


FIGURE 1.4.2 A graph of reaction rate against time for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

position of equilibrium the relative concentrations of the products and reactants are at equilibrium

The **position of equilibrium** is defined as the relative concentrations of the reactants and products become constant. Even though the concentrations are constant at equilibrium, they are not necessarily the same (Figure 1.4.2).

Table 1.4.1 summarises the features of graphs of concentration against time and reaction rate against time.

TABLE 1.4.1 Graphing concentration and reaction rate against time

Graph	Number of lines	Position of line at equilibrium
Concentration vs time	Depends on the number of reactants and products. Each may be represented on the graph by a separate line.	All lines plateau because *concentrations are constant*. They do not need to be of equal value.
Reaction rates vs time	Two lines, one each for the forward and reverse reactions.	The two lines meet and plateau because the two *rates are equal*.

LEARNING CHECK 1.4

DESCRIBING

1 **Identify** the significance of a plateau in a concentration–time equilibrium graph.

APPLYING

2 **Describe** how the concentrations of reactants and products can indicate whether equilibrium has been reached.

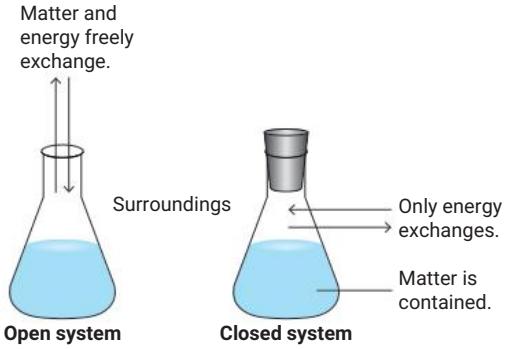
3 **Describe** how monitoring the rate of the forward and reverse reactions can determine whether equilibrium has been reached.

4 **Compare** the rates of change of the forward and reverse reactions at the beginning of a reaction to the rates when the system reaches equilibrium.

CHAPTER SUMMARY

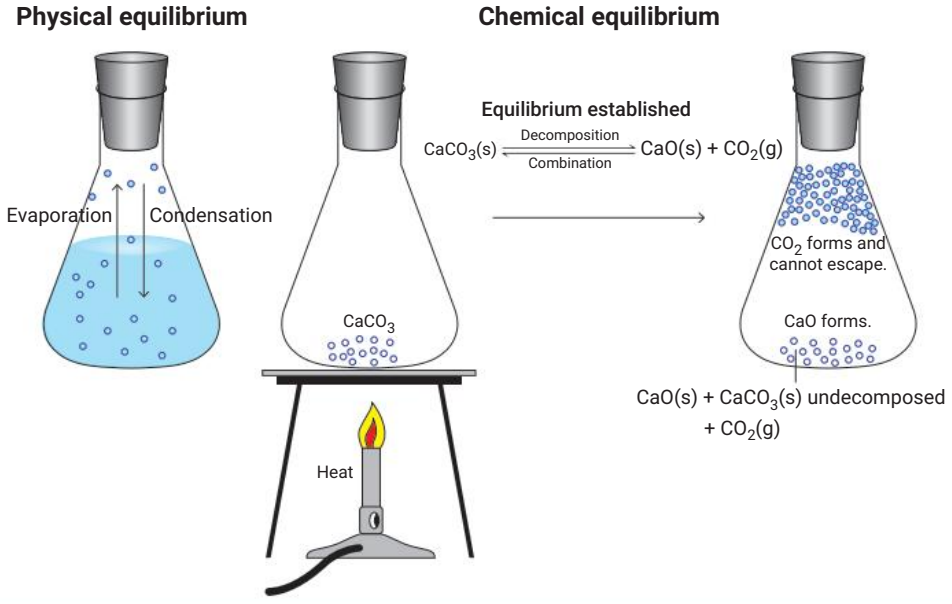
Open and closed systems

- Closed systems (e.g. a sealed reaction vessel) allow the exchange of energy but not matter. In a closed system, equilibrium can be established.
- Open systems allow the exchange of matter and energy with the surroundings (i.e. boiling water in a saucepan with no lid). In an open system, equilibrium cannot be established.



Physical and chemical changes

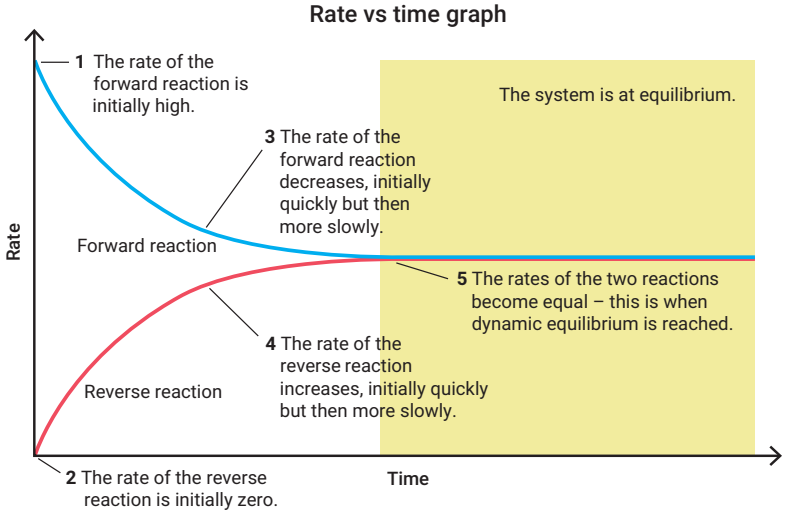
- Physical change involves phase changes and no new products (solid ⇌ liquid ⇌ gas).
- Physical changes are typically reversible because they involve phase changes only (i.e. ice melting and freezing).
- Chemical change involves reactants producing products that are new substances with different physical and chemical properties (e.g. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$).
- Chemical changes may or may not be reversible, depending on the activation energy of the forward and reverse reactions.
- Both physical and chemical reversible reactions may reach equilibrium.



Reversible reactions and dynamic equilibrium

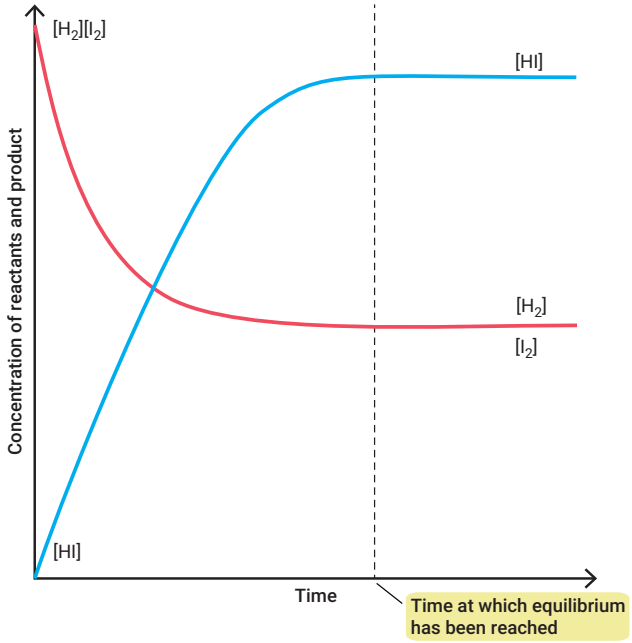
- Reactions that can go in the forward or reverse directions ($\rightleftharpoons$) are reversible.
- In dynamic equilibrium, rate of the forward reaction = rate of the reverse reaction.
- At equilibrium, the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products remain constant. The reaction still proceeds in both the forward and reverse directions.
- The reversibility of a reaction is governed by the activation energy E_a. If E_a in *both* directions is low, the reaction is likely to be reversible.
- Dynamic equilibrium may be shown on rate of reaction vs time and concentration vs time graphs.

Rate vs time graph



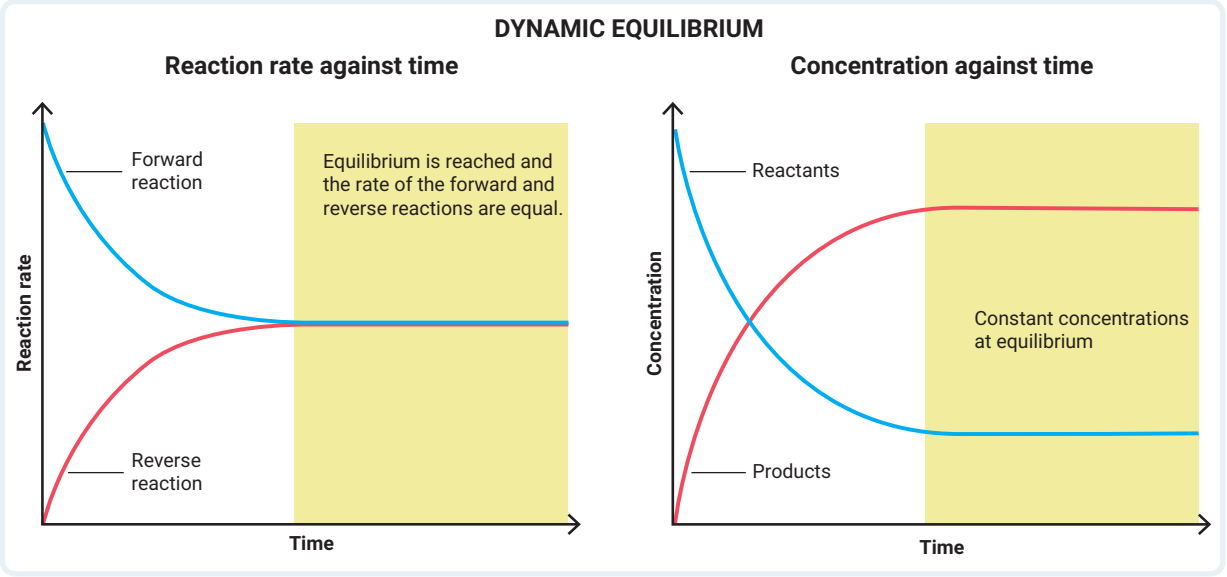
Concentration vs time graph for the reaction:

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



- Equilibrium is achieved when the rates of reaction are equal, and the concentrations remain constant.
- The initial rates of reaction are high and decrease as the reactions approach equilibrium, which is indicated on the graph as a plateau.
- The rates of reaction slow and equalise as they approach equilibrium.
- The concentrations of reactants and products plateau as they reach equilibrium.

Source: https://www.chemistrylearner.com/wp-content/uploads/2021/07/Dynamic-Equilibrium.jpg



CHAPTER EXAM

MULTIPLE CHOICE

1. Which one of the following statements about dynamic equilibrium is false?
- **A** At equilibrium, there is no net change in the system.
- **B** At equilibrium, the concentrations of reactants and products stay the same.
- **C** At equilibrium, the forward and reverse reactions cease to occur.
- **D** At equilibrium, the rates of the forward and reverse reactions are equal.

2. A system in which no reactants or products leave the reaction mixture is known as:
- **A** an open system.
- **B** a closed system.
- **C** a steady state system.
- **D** a partially closed system.

3. Chemical equilibrium is known as dynamic because, at equilibrium, the:
- **A** equilibrium temperature changes.
- **B** reactants and products continue reacting.
- **C** rates of the forward and reverse reactions change.
- **D** concentrations of the reactants and products continue to change.

4. Reactions in which products cannot turn back into reactants are called:
- **A** irreversible reactions.
- **B** reversible reactions.
- **C** equilibrium reactions.
- **D** redox reactions.

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5. In a chemical reaction at equilibrium, a reversible arrow ($\rightleftharpoons$) symbolises that:
- **A** the forward reaction has stopped but can be reversed.
- **B** the moles of reactants and products present are equal.
- **C** half of the reactants have been converted into products.
- **D** the concentrations of reactants and products remains constant.

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6. Melting is a:
- **A** physical change that is reversible.
- **B** chemical change that is reversible.
- **C** physical change that is irreversible.
- **D** chemical change that is irreversible.

7. An open system with an equal rate of inputs and outputs is known as:
- **A** chemical equilibrium.
- **B** physical equilibrium.
- **C** dynamic equilibrium.
- **D** steady state.

8. An example of a physical equilibrium is:

A a bathtub with water flowing in from a tap and out of a plughole at the same rate.
B a reaction in which chlorine gas is being given off to the surroundings.
C water being formed and decomposed at the same rate to form H_2 and O_2.
D a closed container in which water evaporates and condenses at the same rate.

9. The rate of the forward and reverse reactions:

A decreases when the system approaches dynamic equilibrium.
B increases when the system approaches dynamic equilibrium.
C remains the same as the system approaches dynamic equilibrium.
D is slow initially then is fast when the system reaches dynamic equilibrium.

10. The concentration of reactants and products at equilibrium:

A are not likely to be the same but remain constant at equilibrium.
B continuously change when the system equalises.
C are exactly half of the original concentrations.
D are exactly the same.

SHORT RESPONSE

11. The following statement is a common misconception about equilibria.
'At equilibrium, the concentrations of reactants and products will be equal.'

Explain why this statement is incorrect.

12. **Explain** why an open system can never reach equilibrium.

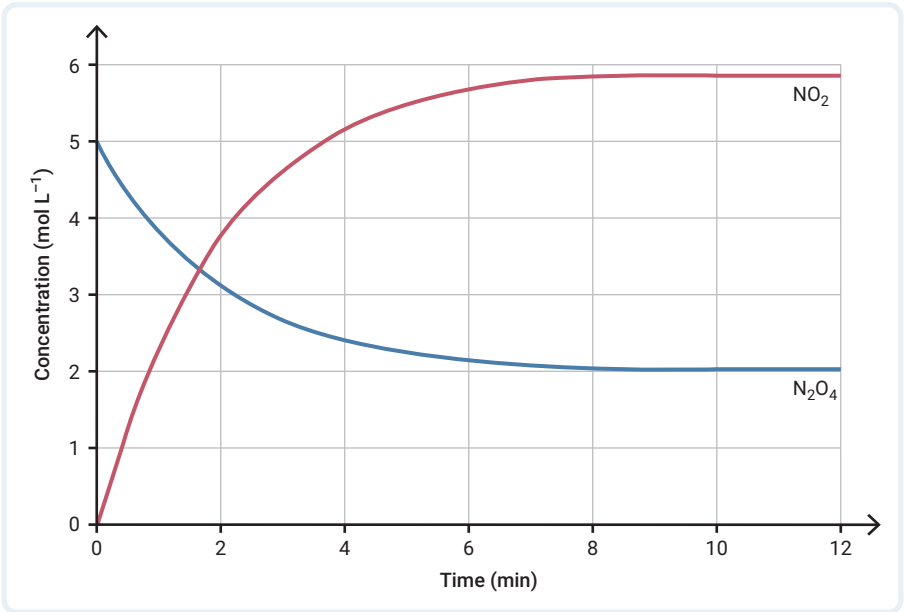
CROSS-CHAPTER QUESTION

13. A mixture of CO(g) and O_2(g) was placed into a sealed container. The gases produce CO_2(g) when mixed. This reaction was observed as it reached dynamic equilibrium.

a **Construct** a balanced equation to represent this reaction. Include all states and reversibility.
b **Identify** the reactants of the forward reaction.
c **Identify** the products of the forward reaction.
d **Describe** how the concentration of carbon dioxide would change from the initial reaction to the concentration at equilibrium.

DATA ANALYSIS

14. The following graph illustrates the concentrations of N_2O_4 and NO_2 over time as they approach equilibrium.



a **Identify** the initial concentrations of N_2O_4 and NO_2.

b **Identify** the trend that indicates when the system reached equilibrium.

c **Identify** the time at which the system first reached equilibrium.

d **Explain** why the line indicating N_2O_4 dropped so sharply in the initial stages of the reaction.

15. **Sketch** a graph showing the relative concentrations of all species over time if equal amounts of NO and O_2 are introduced to a closed container and are allowed to reach equilibrium in the following reaction:

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

Explain the shape of your graph.

CHAPTER 2

Factors that affect equilibrium

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SYLLABUS DOT POINTS

SCIENCE UNDERSTANDING

- 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.

SCIENCE INQUIRY

- Investigate factors that affect equilibrium (Le Châtelier's principle).

Introduction

When equilibrium is established in a chemical system, the rates of the forward and reverse reactions are the same and, therefore, the relative amounts of products and reactants present in the system are constant. If the rates of these reactions alter because of changes in conditions, such as temperature, concentration of chemicals or pressure, the subsequent change in rate of reaction means that the system is no longer at equilibrium. The relative amounts of products and reactants has changed and this will cause the equilibrium to be re-established and therefore it will be different from the original equilibrium due to the changes applied to the system.

Either the forward or reverse reaction is favoured as equilibrium is re-established. If the forward reaction is favoured, then we say that the position of equilibrium has shifted to the right. This is because more products will be produced, and products lie on the right-hand side of the equation. If the reverse reaction is favoured, then the position of equilibrium shifts to the left, as more reactants are produced.

By understanding what happens during a reaction, we can explain the changes in equilibrium when conditions are altered. This also allows us to choose conditions that best suit the purpose of the reaction.

ASSUMED KNOWLEDGE

- ✓ The rate of a chemical reaction depends on the frequency of collisions, the energy of the particles during collisions, and the orientation of the particles.
- ✓ Enthalpy is a measure of the energy of a system.
- ✓ Activation energy is the minimum amount of energy necessary for molecules to have a successful collision and react.
- ✓ Reversible reactions can occur in both the forward and reverse directions.
- ✓ At dynamic equilibrium, the reactions occur in the forward and reverse directions at the same rate.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ the position of equilibrium can shift to the left or right, depending on the reaction conditions
- ✓ determine the direction of shift to a new position of equilibrium resulting from temperature changes to a system at dynamic equilibrium
- ✓ use collision theory to explain how temperature, concentration and pressure create a shift to the forward and reverse reactions
- ✓ determine the effect changes of temperature, concentration of chemicals and pressure, and the addition of a catalyst, have on the position of equilibrium
- ✓ understand graphs of concentration against time and rate against time graphs to determine equilibrium processes
- ✓ apply Le Châtelier's principle to understand the shift in equilibrium reactions in theoretical, laboratory or simulated environments.

2.1 Changing temperature

Chapter 10 of *Nelson QCE Chemistry Units 1 & 2* explores how endothermic and exothermic reactions relate to the law of conservation of energy, and the relationship between temperature and enthalpy changes. In an **endothermic reaction**, the products have more enthalpy than the reactants, meaning that energy will be absorbed from the surroundings. Alternatively, in an **exothermic reaction**, the reactants have more enthalpy than the products and energy will be released to the surroundings. In a reversible reaction, the reaction in one direction is endothermic and the reaction in the opposite direction is exothermic. For example, consider the following reaction:

endothermic reaction a reaction in which energy is absorbed from the surroundings, causing temperature to decrease

exothermic reaction a reaction in which energy is released to the surroundings, causing temperature to increase

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -58 \text{ kJ mol}^{-1}$$

According to the enthalpy value, the forward reaction is exothermic. As a result, the reverse reaction will be endothermic:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +58 \text{ kJ mol}^{-1}$$

In both reactions, the activation energy (E_a) is the difference between the enthalpies of the activated complex and the reactants. The higher enthalpy of the reactants in the exothermic reaction means that the exothermic reaction has a smaller activation energy than the endothermic reaction for the same reversible reaction **(Figure 2.1.1)**.

Worksheet
Factors that affect equilibrium

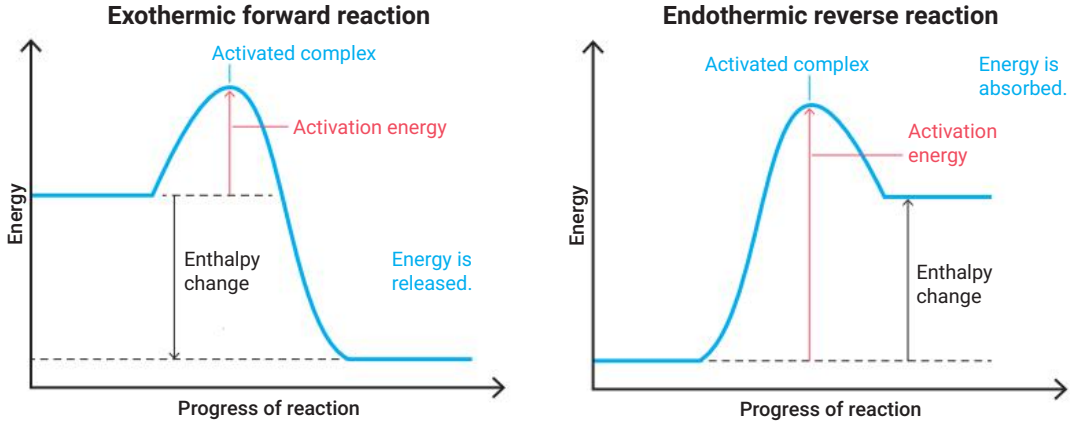


FIGURE 2.1.1 Comparing the activation energies of the forward and reverse reactions

Increasing temperature

When the temperature of a system increases, according to **collision theory**, the rates of the forward and reverse reactions increase because there are more collisions between the particles. The rate of the endothermic reaction increases more than that of the exothermic reaction. This is due to the higher energy held by the particles. The increase in temperature increases the percentage of particles able to react in the endothermic reaction more than in the exothermic reaction. This is because a greater E_a is required for endothermic reactions than for exothermic reactions. As a result, the increase in temperature means more particles that previously had insufficient energy now meet the E_a. In turn, this increases the chance of a successful collision to produce a chemical reaction (Figure 2.1.2).

collision theory for a reaction to occur, the particles must collide with sufficient energy and in the required orientation

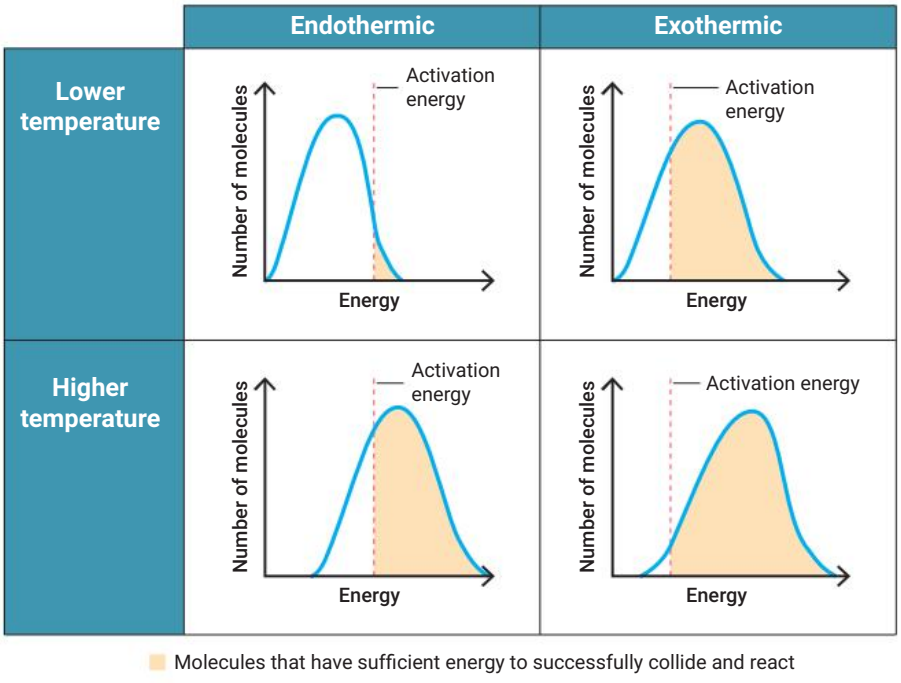


FIGURE 2.1.2 The effect of an increase in temperature on the particles with sufficient energy to react for both endothermic and exothermic reactions

As more of the products of the endothermic reaction are produced, the rate of the opposite exothermic reaction increases. At the same time, the rate of the endothermic reaction decreases as the reactants are used up. This trend will continue until the two rates are once again equal and the system is at equilibrium.

The effect of temperature changes on a chemical system can be explained by considering the enthalpy changes for the forward and the reverse reactions. For example, the reaction between sulfur dioxide (SO_2) and oxygen (O_2) to produce sulfur trioxide (SO_3) is an exothermic reaction:

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

This means that the forward reaction is exothermic and the reverse reaction is endothermic. If the temperature of the system increases, then the endothermic reaction (the reverse reaction) will be favoured because there will be energy available for a greater proportion of particles to overcome the activation energy barrier (E_a). This will result in an increase in the concentrations of $SO_2(g)$ and $O_2(g)$ and a decrease in the concentration of $SO_3(g)$ **(Figure 2.1.3a)**. Therefore, the position of equilibrium at a higher temperature is shifted to the left (towards the reactants). The impact of an increase in temperature on the same reaction can be seen in **Figure 2.1.3b**.

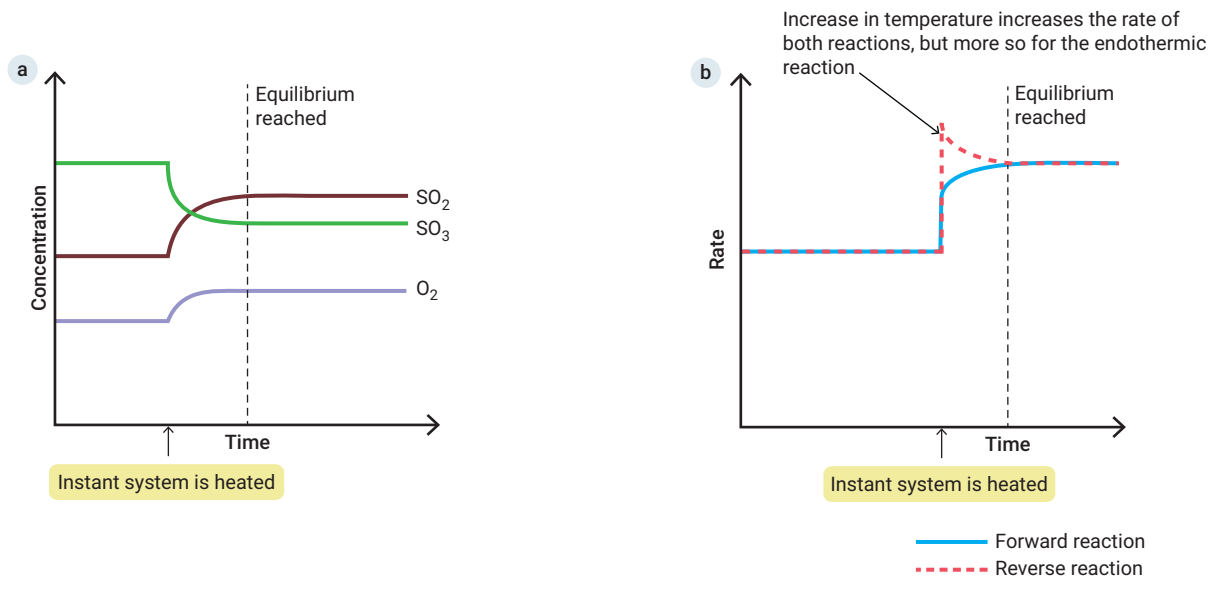


FIGURE 2.1.3 **(a) A concentration vs time graph showing the change in concentrations of reactants and products with an increase in temperature for the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$. (b) A rate vs time graph showing the impact of an increase in temperature on the rate of reaction.**

Decreasing temperature

When the temperature of a system decreases:

- the rate of both the forward and reverse reactions decreases according to collision theory
- the rate of the endothermic reaction decreases more, meaning that the rate of the exothermic reaction increases in comparison
- over time, the rate of the endothermic reaction increases while the rate of the exothermic reaction decreases until the two are equal again and equilibrium is re-established.

Consider the reaction between hydrogen gas (H_2) and nitrogen (N_2) gas to form ammonia (NH_3). This reaction is exothermic:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

If the temperature of the system decreases, the rate of both the forward and reverse reaction decreases. However, this decrease in temperature has a smaller effect on the exothermic reaction

than on the endothermic reaction. As a result, the concentration of ammonia (NH_3) increases and the concentrations of hydrogen gas (H_2) and nitrogen gas (N_2) decrease. Therefore, at the reduced temperature, the position of equilibrium shifts to the right (towards the products). This is shown in **Figure 2.1.4**.

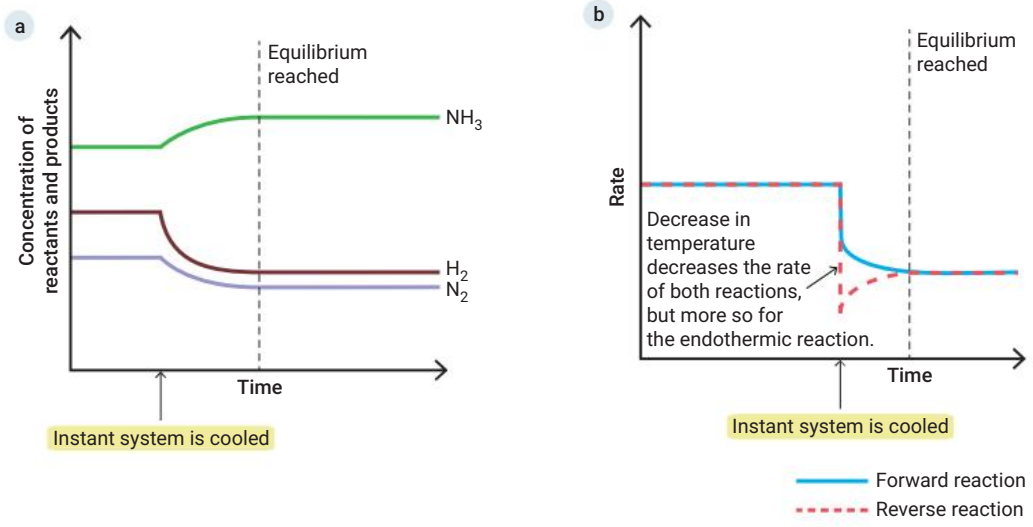


FIGURE 2.1.4 (a) A concentration vs time graph showing the change in concentrations of reactants and products with a decrease in temperature for the reaction $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$. (b) A rate vs time graph showing the impact of a decrease in temperature on the rate of reaction.

When the temperature of a system at equilibrium changes, there are no sudden initial changes in concentration. However, one reaction will be favoured as equilibrium is being re-established. Therefore, the concentrations gradually change as the system counteracts the change. This is reflected in the graph's shape in **Figure 2.1.4a**. Gradual changes in equilibrium graphs are a sign that a temperature change has taken place.

A change in temperature results in a shift in equilibrium that affects the position of equilibrium, as shown in **Table 2.1.1**. If the change in temperature favours the forward reaction, then the concentration of products will increase and the concentration of the reactants will decrease. Therefore, the position of equilibrium will shift to the right. Alternatively, if the reverse reaction is favoured, then the concentration of the reactants will increase and the concentration of products will decrease. This will shift the position of equilibrium to the left.

Weblinks
Effect of temperature at equilibrium
Equilibria: temperature

TABLE 2.1.1 The effect of a change in temperature on the position of equilibrium

Change in temperature	Forward reaction	Reverse reaction	Favoured reaction	Shift in equilibrium position
Increase	Exothermic	Endothermic	Endothermic/reverse	To the left
	Endothermic	Exothermic	Endothermic/forward	To the right
Decrease	Exothermic	Endothermic	Exothermic/forward	To the right
	Endothermic	Exothermic	Exothermic/reverse	To the left

Tip: It is sometimes easier to think of heat as a reactant or product. In endothermic reactions, heat is absorbed, so it can be considered a reactant. An increase in heat will drive the reaction forward. In exothermic reactions, heat is released, so it can be considered a product. An increase in heat will drive the reaction in the reverse direction to use up the released heat.

PRACTICAL ACTIVITY 2.1.1

EFFECT OF TEMPERATURE ON A SYSTEM AT EQUILIBRIUM (TEACHER DEMONSTRATION ONLY)

Introduction

An equilibrium will exist between $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ when they are in a solution. The equation representing this is:

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

The $[Co(H_2O)_6]^{2+}$ ion is a pink colour, whereas the $[CoCl_4]^{2-}$ ion is a deep blue colour. Therefore, the relative concentrations of the ions and the position of equilibrium will be indicated by the colour of the solution. A blue solution indicates a high concentration of $[CoCl_4]^{2-}$ compared to $[Co(H_2O)_6]^{2+}$. A pink solution indicates a high concentration of $[Co(H_2O)_6]^{2+}$ compared to $[CoCl_4]^{2-}$.

Research question

How does a change in temperature affect the position of an equilibrium reaction?

Aim

To observe the effect of changing the temperature of a system at equilibrium

Materials

- 3 g cobalt(II) chloride-6-water ($CoCl_2.6H_2O$)
- 5 mL of concentrated hydrochloric acid (HCl)
- distilled water
- 3 large test tubes
- test-tube racks
- test-tube tongs
- Bunsen burner
- heat mat
- forceps

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Concentrated HCl is very corrosive to skin and clothes.	Wear gloves and an apron. If any acid comes in contact with skin, wash it immediately with plenty of water. Teacher demonstration only.
Cobalt(II) chloride-6-water may irritate eyes, skin and respiratory systems. It may cause cancer, genetic defects and may damage fertility.	Handle with extreme care. Use in a well-ventilated area. Wear gloves, safety glasses and an apron. If any of the chemical comes in contact with skin, wash it immediately with plenty of water. This chemical should not be handled by pregnant women. Women of reproductive age should handle this chemical carefully.
Cobalt(II) hexahydrate is toxic to aquatic life.	Dispose of the solution correctly.
Heating chemicals in a test tube can be hazardous.	Always point the test tube away from people.

Copy the risk assessment table in your write-up. Add any more risks you can think of, and ways to manage them.

Online demonstration videos that illustrate this equilibrium change may be preferred if there are concerns with the safety of this demonstration.

Procedure

1 Your teacher will demonstrate this experiment.

2 Use the forceps to pick up a pea-sized amount of $CoCl_2.6H_2O$. Dissolve it in 1–2 mL of distilled water in a test tube. Observe and record the colour of the resultant solution. Place the test tube in a test-tube rack and keep it as a reference.

3 Dissolve a pea-sized amount of $CoCl_2.6H_2O$ in 1–2 mL of concentrated hydrochloric acid in a test tube. Observe and record the colour of the resultant solution. Place the test tube in a test-tube rack and keep this as a reference.

4 Dissolve a pea-sized amount of $CoCl_2.6H_2O$ in 1–2 mL of distilled water in a test tube. Gently heat the solution over the Bunsen burner until the solution is almost boiling. Place the test tube in a test-tube rack and then observe and record the colour change.

5 Allow the third test tube to cool down, observing and recording the colour change.

Results

Record your results in a carefully formatted table.

Analysis of results

1 Identify the colour change observed when the test tube was heated.

2 Identify the colour change observed when the test tube cooled down.

Interpretation

3 Explain what the colour changes indicate about the relative proportion of the two ions.

4 Identify which reaction was favoured when the test tube was heated. Classify the forward reaction as exothermic or endothermic. Explain your answer.

Evaluation

5 Predict how the equilibrium position for this reaction would change with a decrease in temperature. Explain your answer.

6 Identify other factors that may have contributed to the observations.

7 What conclusion can you draw about the effect of temperature on the equilibrium between $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$?

LEARNING CHECK 2.1

DESCRIBING

1 Complete the following statements by using the word 'exothermic' or 'endothermic'.

a Raising the temperature of a system at equilibrium will favour the _____ reaction.

b Lowering the temperature of a system at equilibrium will favour the _____ reaction.

c The activation energy of an _____ reaction is greater than that of an _____ reaction.

2 Consider the exothermic reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

a **Describe** the effect of increasing temperature on the yield of ammonia (NH_3).

b **Identify** whether the position of equilibrium shifts to the left or the right if the temperature is increased.

APPLYING

3 **Explain** why raising the temperature affects the rate of exothermic and endothermic reactions differently.

4 **Explain** why equilibrium graphs showing a temperature change shows gradual rather than sudden changes to the concentrations of reactants and products.

2.2 Changing concentration

concentration a measure of the amount of solute in a given volume of solvent

From our understanding of collision theory and reaction rates from Chapter 19 of *Nelson QCE Chemistry Units 1 & 2*, we know that increasing the **concentration** of a reactant will increase the rate of the reaction because of the increased number of collisions (given sufficient energy). In a reversible reaction, if the concentration of a reactant is increased, then the rate of the forward reaction will increase. Alternatively, if the concentration of a product is increased, then the rate of the reverse reaction will increase.

If the concentration of one chemical in a system at equilibrium is increased, then the rate of the reaction that uses that chemical will increase. This will use up some of the additional chemical, reducing the concentration, and therefore this rate will gradually decrease. At the same time, the rate of the opposite reaction will increase, as more of its reactants are produced. Eventually the rates of the two reactions once again become equal, so equilibrium is re-established. Consider the reaction between hydrogen (H_2) and iodine (I_2) to form hydrogen iodide (HI):

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

- If more I_2 is added to the system, its concentration is increased.
- Because I_2 is a reactant for the forward reaction, the rate of the forward reaction will increase.
- This means that the concentration of H_2 and I_2 will begin to decrease while the concentration of HI will increase, as shown in **Figure 2.2.1**.
- As more HI is produced, the rate of the reverse reaction will begin to increase.
- This pattern will continue until the rates of the forward and reverse reactions are once again equal. At this time, the concentrations of each chemical will remain constant.
- The new concentration of I_2 will be lower than the concentration after the addition of the extra I_2. However, it will not return to the original concentration because a new position of equilibrium has been reached.

Syllabus link
Chapter 19 of *Nelson QCE Chemistry Units 1 & 2* describes collision theory in greater detail.

Weblinks
Collision theory
Effects of changing concentration on equilibrium

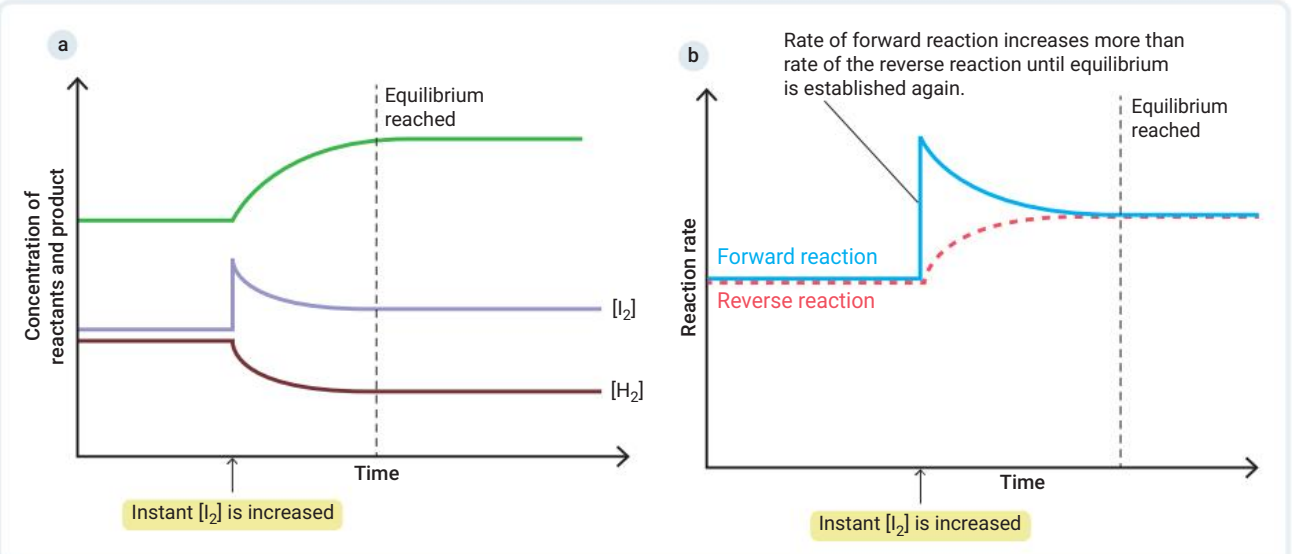


FIGURE 2.2.1 (a) A concentration vs time graph showing the change in concentrations of [HI], [I_2] and [H_2] after an increase in [I_2], (b) A rate vs time graph showing the changes in the rate of reaction when I_2 is added.

The same logic can be applied to a decrease in concentration:

- A sudden decrease in concentration will lead to a decrease in the rate of the reaction that uses that substance.
- Over time, the concentration of the reactants for that reaction will increase as less of each is used up, while the concentration of the products for that reaction will decrease.
- However, the concentration of the substance that was removed will not return to its original value.

Weblink
Chemical equilibrium demonstration – concentration

TABLE 2.2.1 The effect of a change in concentration on equilibrium

Imposed change		Reaction favoured	Shift in equilibrium	Resultant change in concentration of reactants	Resultant change in concentration of products
Product or reactant altered	Increase or decrease in concentration				
Reactant	Increase	Forward	To the right	Decrease	Increase
Reactant	Decrease	Reverse	To the left	Increase	Decrease
Product	Increase	Reverse	To the left	Increase	Decrease
Product	Decrease	Forward	To the right	Decrease	Increase

PRACTICAL ACTIVITY 2.2.1

EFFECT OF CHANGES IN CONCENTRATION ON EQUILIBRIUM (TEACHER DEMONSTRATION ONLY)

Introduction

In an aqueous solution of chromate or dichromate salts, an equilibrium will exist between the two ions:

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

Yellow Orange

The chromate ion (CrO_4^{2-}) is yellow and the dichromate ion ($Cr_2O_7^{2-}$) is orange. Therefore, the colour of the solution indicates the relative proportions of the two ions, and hence the position of equilibrium. If the solution is yellow, then there are more chromate ions than dichromate ions and the equilibrium lies more to the left. If the solution is orange, there are more dichromate ions than chromate ions and equilibrium lies to the right.

Research question

What effect does changing the concentration of hydrogen ions (H^+) have on an equilibrium reaction involving chromate ions (CrO_4^{2-})?

Aim

To observe the effect of a change in concentration of a reactant on a system at equilibrium

Materials

- 5 mL of 0.1 mol L^{-1} potassium chromate (K_2CrO_4)
- 5 mL of 0.1 mol L^{-1} potassium dichromate ($K_2Cr_2O_7$)
- 5 mL of 0.2 mol L^{-1} sodium hydroxide (NaOH) in a dropper bottle
- 5 mL of 0.2 mol L^{-1} hydrochloric acid (HCl) in a dropper bottle
- distilled water
- 4 test tubes and test-tube rack
- 2 graduated droppers

RISK ASSESSMENT

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
0.2 mol L^{-1} HCl is corrosive to skin and clothing.	Wear gloves, safety glasses and an apron.
0.2 mol L^{-1} NaOH may irritate eyes and skin.	Wear gloves, safety glasses and an apron.
Potassium dichromate and potassium chromate are oxidising agents and may cause cancer and respiratory allergic reactions. May cause genetic defects in unborn children or fertility problems.	Handle with extreme care. Wear gloves, safety glasses and an apron. Keep away from combustible materials. Do not dispose of these chemicals down the sink. These chemicals should not be handled by pregnant women. Women of reproductive age should take special care when handling these chemicals.

Copy the risk assessment table in your write-up. Add any more risks you can think of, and ways to manage them.

Online demonstration videos that illustrate this equilibrium change may be preferred if there are concerns with the safety of this demonstration.

Procedure

1. Your teacher will demonstrate this experiment.
2. Place approximately 1 mL of 0.1 mol L^{-1} potassium chromate (K_2CrO_4) into a test tube. Observe the colour and keep this test tube as a reference for the colour of the chromate ion.
3. Place approximately 1 mL of 0.1 mol L^{-1} potassium dichromate ($K_2Cr_2O_7$) into a test tube. Observe the colour and keep this test tube as a reference for the colour of the dichromate ion.
4. Place approximately 1 mL of 0.1 mol L^{-1} K_2CrO_4 into a clean test tube. Add 0.2 mol L^{-1} hydrochloric acid to the solution drop by drop until a colour change is observed. Compare this colour with your reference test tubes.
5. To the same test tube used in step 3, add 0.2 mol L^{-1} sodium hydroxide drop by drop until a colour change is observed. Compare this colour with your reference test tubes.
6. Place approximately 1 mL of 0.1 mol L^{-1} $K_2Cr_2O_7$ into a clean test tube. Add 0.2 mol L^{-1} sodium hydroxide to the solution drop by drop until a colour change is observed. Compare this colour with your reference test tubes.
7. To the same test tube used in step 6, add 0.2 mol L^{-1} hydrochloric acid drop by drop until a colour change is observed. Compare this colour with your reference test tubes.

Results

Present your observations in a simple table.

Analysis of results

1. **a** Identify what happened to the colour of the chromate solution when the hydrochloric acid was added.
   b Explain why this occurred.
2. **a** Describe what happened to the concentration of hydrogen ions when the sodium hydroxide was added to the chromate solution.
   b Construct an equation to demonstrate this reaction.
   c Describe the colour change that was observed in step 5.
   d Explain why this colour change happened.
3. Justify why the colour changed or remained the same in steps 6 and 7.

Interpretation

4 Compare the colours observed in steps 4–7 to the reference test tubes. Suggest a reason for any changes that occurred.

5 The volumes used in this experiment were approximate volumes. Identify the effect (if any) of this on the results. Explain your answer.

Evaluation

6 Draw conclusions regarding the shift in equilibrium after:

a an increase in concentration of a reactant or product

b a decrease in concentration of a reactant or product.

LEARNING CHECK 2.2

DESCRIBING

1 **Describe** what is meant by an increase in concentration.

2 **Explain** collision theory, in terms of increasing concentration and rate of reaction.

APPLYING

3 **Explain** why increasing the concentration of one reactant affects the position of equilibrium of a system.

4 **Identify** the trend that would be expected in results for all three components of the equilibrium reaction $A + B \rightleftharpoons C$ if C was suddenly removed from the system at equilibrium.

2.3 Volume, pressure and catalysts

Volume and pressure

When the volume or pressure of a gaseous system changes, the concentrations of all gaseous substances are altered. This means that the concentration of both reactants and products may change. The one that changes the most will have the greatest influence on the change of equilibrium. Volume affects the pressure of a system. As volume is decreased, pressure (and concentration of gases) increases because the same number of particles of gas are in a smaller volume. This is illustrated by **Figure 2.3.1**.

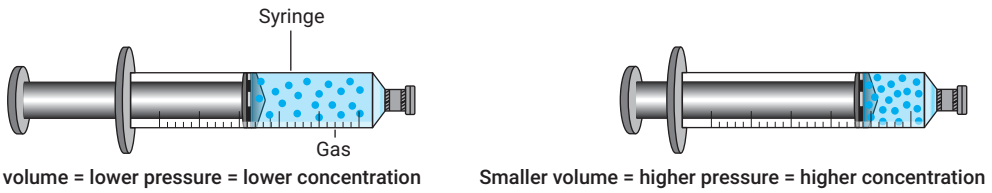


FIGURE 2.3.1 In a gaseous system, as volume decreases, pressure (and concentration of gases) increases.

For the reaction between nitrogen gas and hydrogen gas producing ammonia, three molecules of H_2 and one molecule of N_2 are used for every two molecules of NH_3 produced:

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

so there is a 4:2 ratio of gas molecules of reactants to products.

- If the volume of the system is halved, then the pressure and, therefore, the concentration of all the gases will double.
- Therefore, the rates of both the forward and reverse reactions will increase because there will be more collisions between gas particles.
- There are proportionally 4 moles of reactant gases ($3H_2 + N_2$) to 2 moles of product gases ($2NH_3$). So the rate of forward reaction will increase more than that of the reverse reaction.
- As the reactions proceed, the concentrations of hydrogen and nitrogen will decrease and the concentration of ammonia will increase.
- Similarly, the rate of the forward reaction will decrease and the rate of the reverse reaction will increase until equilibrium is re-established.
- The opposite will happen if the volume of a gaseous system is increased for the same reaction **(Figure 2.3.2)**.

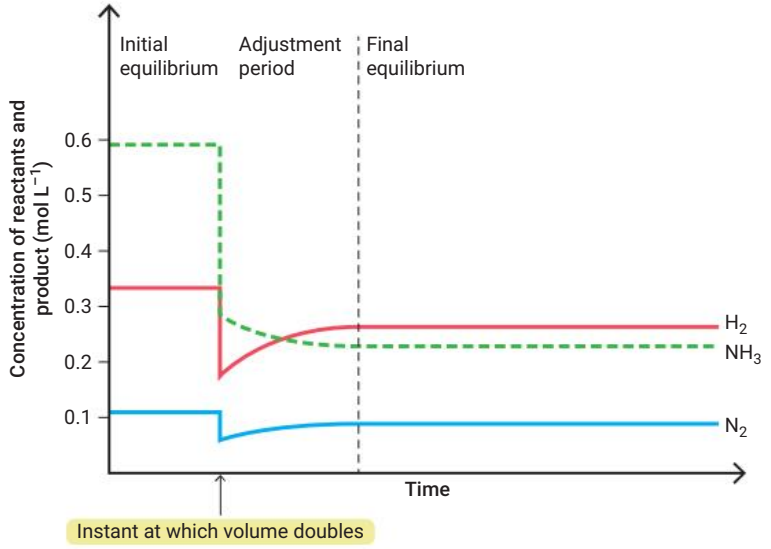


FIGURE 2.3.2 Changes in $[H_2]$, $[N_2]$ and $[NH_3]$ after an increase in volume (and therefore decrease in pressure and concentration)

Where there are equal numbers of molecules of gases in the reactants and products, and if the volume changes, the concentration of reactants and products change equally. Therefore, the rates of both the forward and reverse reactions also change equally and remain equal. Therefore, equilibrium has not been altered.

For example, in the reaction:

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

there is an equal number of moles of gas on both sides. A change in the volume of the container would not alter the position of equilibrium.

Adding an inert gas also does not alter the position of equilibrium. Although there is in overall increase in the total pressure, the particles do not take part in the reaction and therefore do not affect the equilibrium reaction.

Weblink
Volume effect on equilibrium

PRACTICAL ACTIVITY 2.3.1

CHANGING THE VOLUME OF A GASEOUS SYSTEM AT EQUILIBRIUM (TEACHER DEMONSTRATION ONLY)

Introduction

An equilibrium exists between the gases nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4):

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

Brown Colourless

Nitrogen dioxide is a brown gas, whereas nitrogen tetroxide is colourless. This means the colour can indicate the proportion of gases in the mixture. A darker brown indicates a greater concentration of NO_2 and therefore an equilibrium that lies further to the left. Conversely, a lighter brown colour indicates a lower concentration of NO_2 and therefore an equilibrium that lies further to the right.

Research question

How does decreasing the volume affect an equilibrium reaction involving nitrogen dioxide?

Aim

To observe the effect of changing the volume of a gaseous system at equilibrium

Materials

- large, transparent syringe containing NO_2/N_2O_4
- digital camera

RISK ASSESSMENT

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
NO_2/N_2O_4 is hazardous if inhaled or if it comes into contact with skin, eyes or mucous membranes.	Ensure the syringe is sealed. Conduct the experiment in a fume hood. Use small amounts only. Teacher demonstration only.

Copy the risk assessment table in your write-up. Add any more risks you can think of, and ways to manage them.

Online demonstration videos that illustrate this equilibrium change may be preferred if there are concerns with the safety of this demonstration.

Procedure

1 Your teacher will demonstrate this experiment.

2 Observe the colour of the gas mixture in the syringe.

3 Quickly push in the plunger of the syringe to reduce the volume. Observe the immediate change in the colour of the gas mixture and then the changes that occur over the next few seconds as equilibrium is re-established.

Results

Record your observations in a table or use the digital camera to video the results.

Analysis of results

1 **a** Identify what happened to the intensity of the colour when the volume was initially reduced.

b Explain why this occurred.

2 **a** Identify what happened to the intensity of the colour as equilibrium was re-established.

b Explain why this occurred.

Interpretation

3 Use your knowledge of collision theory to explain the changes that were observed.

4 Predict the changes that would be observed if the volume of the system were increased. Your teacher may demonstrate this for you so that you can see whether your prediction is correct.

5 Identify the factors that would affect the changes observed in a gaseous system when the volume is altered.

Evaluation

6 Draw conclusions about the shift in equilibrium position and colour changes observed when the volume is changed in a gaseous system.

Diluting an aqueous system

If the volume of a solution is changed by adding or removing water, then the same principles apply as for a gaseous system because the concentration of all aqueous substances will change.

- If water is added to the solution, then the concentrations of all aqueous components will decrease.
- The rate of the reaction that uses the greater proportion of aqueous molecules will initially decrease the most.
- The rate of this reaction will then gradually increase while the rate of the opposite reaction will decrease until the two are once again equal and equilibrium is re-established.

Consider the equilibrium between chromate and dichromate:

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

Figure 2.3.3 shows the changes in concentration when a mixture of chromate and dichromate at equilibrium is diluted.

- When water is added to the solution, the concentration of all the aqueous substances will decrease.
- In aqueous solution the concentration of water is assumed to be constant. Therefore, on the graph there will be sudden drops in the concentration of chromate, hydrogen ions and dichromate.
- As four aqueous molecules are used to produce only one, this will use up dichromate and produce chromate and hydrogen ions.

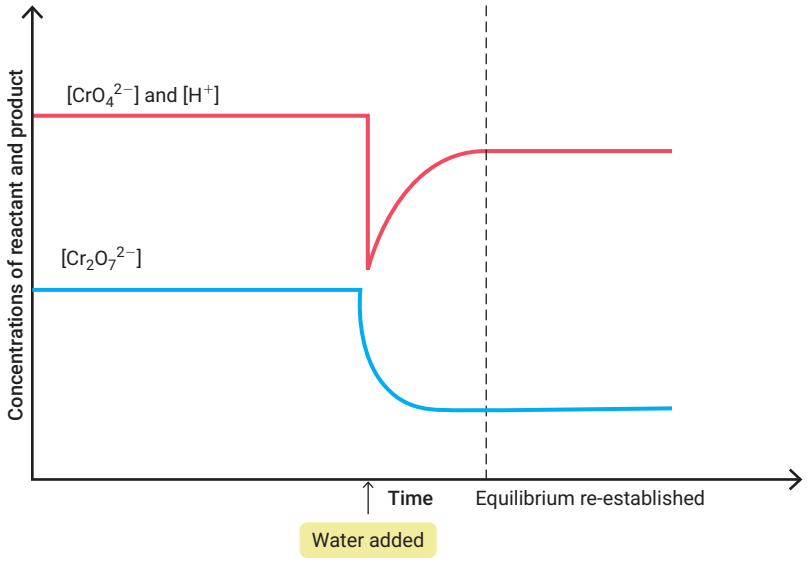


FIGURE 2.3.3 Changes in the concentration of CrO_4^{2-} and H^+ (reactants) and $Cr_2O_7^{2-}$ (product) following dilution for the reaction $2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$

- Therefore, the concentration of chromate and hydrogen ions will increase while the concentration of dichromate will decrease until the concentrations once again plateau and remain constant.

Catalysts

Catalysts speed up the rate of reaction. Adding a catalyst does not affect the position of equilibrium but it does affect how quickly equilibrium is reached. A catalyst decreases the activation energies of both the forward and reverse reactions equally. The rates of both reactions will increase; however, they change by the same proportion. Hence, the equilibrium is not disturbed.

catalyst a substance that affects the rate of certain reactions by providing an alternative pathway

LEARNING CHECK 2.3

DESCRIBING

1 Which of these reactions will not be affected in terms of equilibrium position by a reduction in total volume? **Explain** your answer.

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

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

c $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

APPLYING

2 **Explain** why altering the volume of a gaseous system affects the position of equilibrium.

3 **Explain** why diluting an aqueous system has the same effect as increasing the volume of a gaseous system.

Syllabus link
Chapter 19 of the *Nelson QCE Chemistry Units 1 & 2* describes the function of catalysts.

2.4 Le Châtelier's principle

Henri Louis Le Châtelier summarised the trends involved in a change in the conditions of a system at equilibrium in **Le Châtelier's principle**. This principle can be used to predict the changes that will occur after a change in concentration of chemicals, pressure, volume or temperature of a system.

Le Châtelier's principle the principle that states that if a change is imposed on a system at equilibrium, then the system will act to partially counteract the change

KEY CONCEPT

Le Châtelier's principle

If a system at equilibrium is subject to a change in conditions, then the system will behave in such a way so as to partially counteract the change.

Weblink
Le Châtelier's principle

To use Le Châtelier's principle to predict the outcome of a change in conditions, consider the following.

- What is the change imposed?
- What is the opposite of the change? This is what the system will do.
- Which reaction is favoured (if any) – the forward or reverse?
- Does equilibrium shift to the left or right?
- What happens to the concentration of each aqueous substance or gas?

An important part of the principle is that the system will work to only partially counteract the change. This means that the system does not fully negate the change imposed.

Using Le Châtelier's principle to predict the effect of changes in temperature

If the temperature of the system is increased, then according to Le Châtelier's principle the system will react to decrease the temperature. To do this, the endothermic reaction will be favoured because it uses energy. Alternatively, if the temperature is decreased, then the exothermic reaction will be favoured, in order to produce heat energy to increase the temperature (as seen in Table 2.1.1).

Consider again the production of ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

- This reaction as written is an exothermic reaction, which releases heat.
- Therefore, if the temperature of the system is increased, the endothermic reaction will be favoured to use up the added heat energy.
- This will favour the reverse reaction, resulting in an increase in the concentrations of hydrogen and nitrogen gas and a decrease in the concentration of ammonia **(Figure 2.4.1)**.
- Conversely, if the temperature is decreased, then the exothermic reaction will be favoured to release more heat.
- This will result in the forward reaction being favoured, increasing the concentration of ammonia and decreasing the concentrations of hydrogen and nitrogen gas.

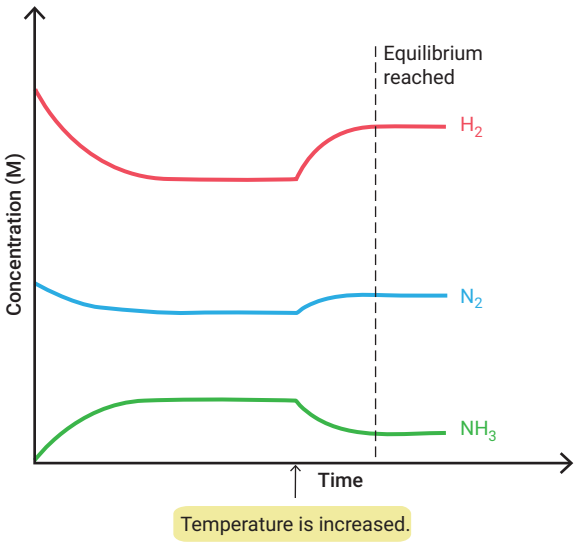


FIGURE 2.4.1 The effect of increasing temperature at equilibrium for the reaction involving the production of ammonia

Using Le Châtelier's principle to predict the effect of changes in concentration

According to Le Châtelier's principle, when the concentration of a substance involved in a reaction is altered, the system will react to counteract the change and return the concentration towards its original level.

- If the concentration of a reactant is increased, then the system will respond to decrease it by favouring the forward reaction, which uses up the reactant.
- This shifts equilibrium to the right, increasing the concentration of the products and decreasing the concentration of the reactants.
- However, the concentration of the substance added will not return to its original concentration because the system can only partially counteract the change.

Alternatively, if the concentration of a product is decreased, then the system will favour the reaction that produces products to increase the concentration again. Therefore, the forward reaction will be favoured and equilibrium will shift to the right.

Consider the equilibrium established during the production of ammonia:

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

- If more hydrogen gas is added to the container without a change in volume, then the concentration of hydrogen gas will increase.
- According to Le Châtelier's principle, the system will react to reduce this increased concentration, thus favouring the forward reaction, which uses up hydrogen gas.
- Therefore, the reaction will shift to the right, the concentrations of hydrogen gas and nitrogen gas will decrease, while the concentration of ammonia will increase (demonstrated in **Figure 2.4.2**).

Weblinks
Le Châtelier's principle in chemical equilibrium
Applying Le Châtelier's principle

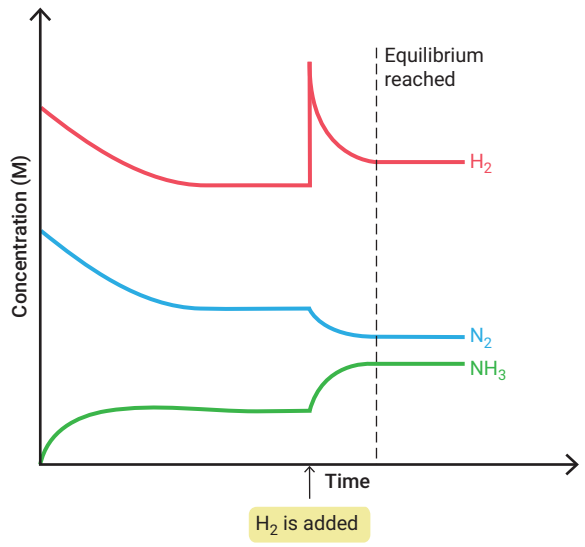


FIGURE 2.4.2 The effect of adding H_2 at equilibrium for the reaction involving the production of ammonia

Using Le Châtelier's principle to predict the effect of changes in volume

If the volume of a gaseous system is changed, then the concentration of all the gaseous substances will be altered.

According to Le Châtelier's principle, the system will react to reverse the change in the total concentration (or pressure). To determine whether the forward or reverse reaction will achieve this change, consider the number of gaseous molecules in the reactant and products. The reaction that produces more molecules of gaseous substances will increase the total concentration or pressure, while the reaction that uses more molecules will decrease the total concentration or pressure.

Worksheet
Le Châtelier's principle

For example, in the reaction between nitrogen gas and hydrogen gas to produce ammonia, four gaseous molecules are used to make two gaseous molecules:

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

- If the volume of the system is decreased, then the total pressure will increase.
- According to Le Châtelier's principle, the system will react to decrease the total pressure.
- In this reaction, the forward reaction uses more molecules than it produces, thus decreasing the total number of particles and therefore the pressure. Therefore, the forward reaction will be favoured if the pressure increases.

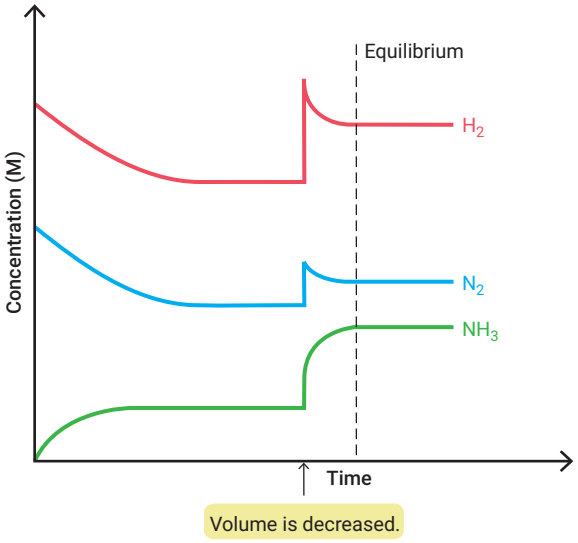


FIGURE 2.4.3 The effect of decreasing volume at equilibrium for the reaction involving the production of ammonia

LEARNING CHECK 2.4

DESCRIBING

1 **Define**:
- **a** endothermic reaction
- **b** Le Châtelier's principle.

2 The following equilibrium reaction shows carbonic acid forming in soda water when carbon dioxide is added.

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \qquad \Delta H = -15\ kJ\ mol^{-1}$

Describe the direction of the shift of an equilibrium reaction according to Le Châtelier's principle for the following changes.
- **a** The amount of carbon dioxide increases.
- **b** The product is removed.
- **c** The soda water is cooled.

APPLYING

3 Silver ions can be removed from solution by adding carbonate ions:

$2Ag^+(aq) + CO_3^{2-}(aq) \rightleftharpoons Ag_2CO_3(s)$

Describe one change to the equilibrium reaction that would increase the amount of silver ions removed from the solution.

4 Soluble sodium hypochlorite (NaClO) pellets are used in swimming pools to help kill bacteria and algae:

$ClO^-(aq) + H^+(aq) \rightleftharpoons HClO(aq) + \text{heat}$

Use Le Châtelier's principle to **predict** the changes that would occur for each of the following. (Assume the pool is covered and is therefore a closed system.)

a Adding more sodium hypochlorite pellets
b Adding sodium hydroxide
c The pool warming up on a hot day

5 The graph in **Figure 2.4.4** shows the concentration of the reactant and product for the reaction:

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

Use Le Châtelier's principle to **explain** the changes seen in the graph.

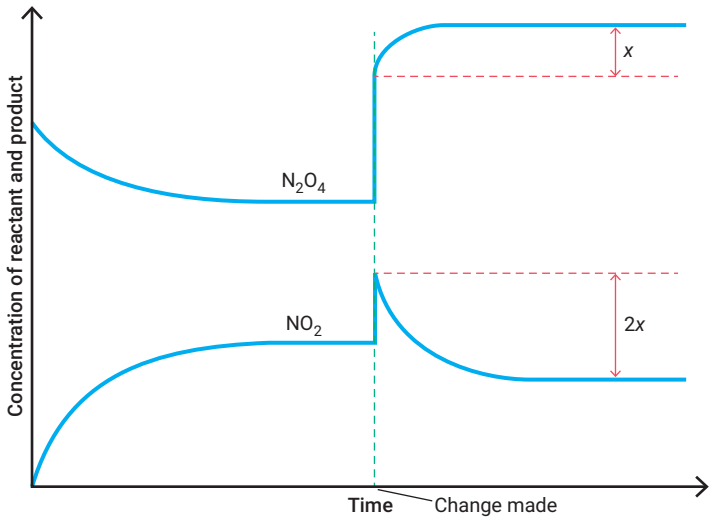


FIGURE 2.4.4 The concentration of the reactant and product for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

CHAPTER SUMMARY

Effect of temperature, concentration, volume and pressure (collision theory)

- **Temperature:** Higher temperatures increase the kinetic energy of particles, causing more frequent and energetic collisions. This typically speeds up both forward and reverse reactions, but the effect on equilibrium depends on whether the reaction is endothermic or exothermic.
  - For an **endothermic** forward reaction ($\Delta H > 0$), increasing temperature shifts the equilibrium towards the **products** (to the right).
  - For an **exothermic** forward reaction ($\Delta H < 0$), increasing temperature shifts the equilibrium towards the **reactants** (to the left).
- **Concentration:** Increasing reactant concentration shifts equilibrium towards the products as the reactants have more frequent collisions. Increasing product concentration shifts it towards the reactants because the products have more frequent collisions.
- **Pressure:** For reactions involving gases, increasing pressure (by decreasing volume) shifts the equilibrium towards the side with fewer moles of gas because the side with more moles of gas collide and react.
- **Volume:** Changing volume affects the overall concentration and pressure of the reaction. An increase in volume decreases pressure and the overall concentration of species. The reaction will shift to the side with more moles of substance. A decrease in volume increases the pressure and concentration of all species. The reaction will shift to the side with fewer moles of substance.

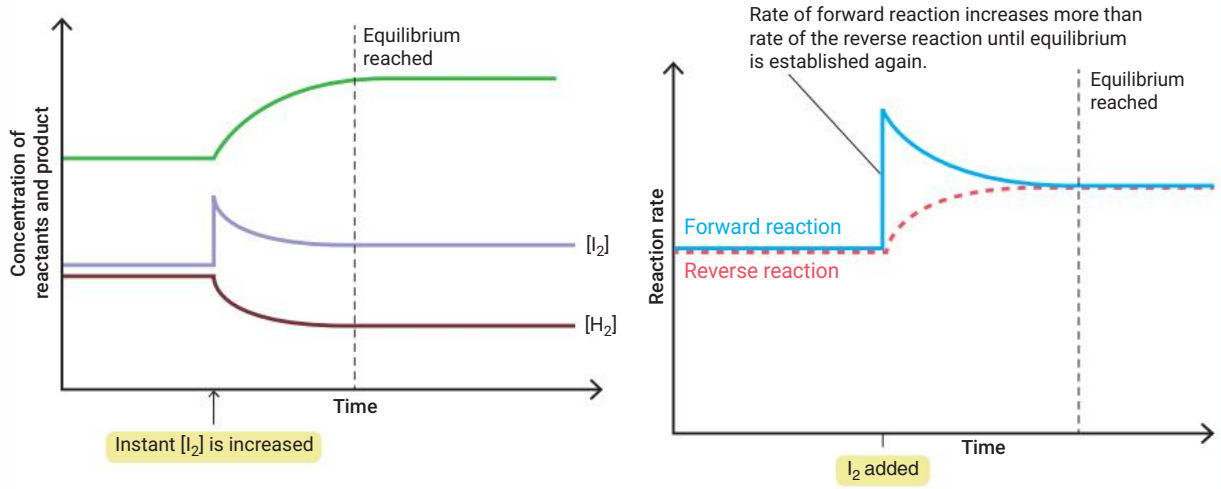
Le Châtelier's principle – changes in temperature, concentration, pressure and catalysts

- Le Châtelier's principle: 'If a system at equilibrium is subject to a change in conditions, then the system will behave in such a way so as to partially counteract the change'.
- **Temperature:** An increase in temperature favours the endothermic reaction to counteract the change. A decrease in temperature favours the exothermic reaction to counteract the change.
- **Concentration:** If reactants are added, the equilibrium shifts towards the products. If products are added, the equilibrium shifts towards the reactants.
- **Pressure:** In reactions involving gases, increasing pressure shifts the equilibrium towards the side with fewer gas molecules. Decreasing pressure favours the side with more gas molecules.
- **Catalysts:** Catalysts do not shift the position of equilibrium but speed up both the forward and reverse reactions equally, helping the system reach equilibrium faster.

Equilibrium graphing

- Graphs of concentration against time and rate against time are ways of visualising changes to a system at equilibrium.
- At equilibrium, the rates are equal, and the concentrations are constant. A disturbance to the equilibrium is represented as changing concentrations and rates until the system re-establishes equilibrium again.

Concentration versus time and rate versus time graphs showing changes to systems at equilibrium for the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$



CHAPTER EXAM

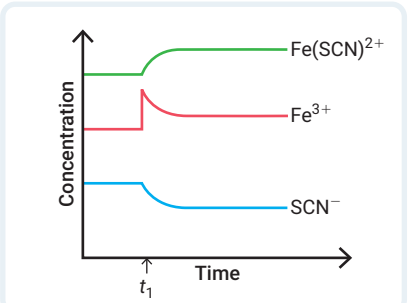
MULTIPLE CHOICE

Question 1 relates to the following information.

The following equation describes a system at equilibrium:

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

The following graph reflects what happens when a change is made to the equilibrium system in the reaction at time t_1.



1. Which one of the following would be a valid reason for the changes at time t_1?

A An increase in temperature
B A decrease in temperature
C Addition of Fe^{3+}
D Removal of $Fe(SCN)^{2+}$

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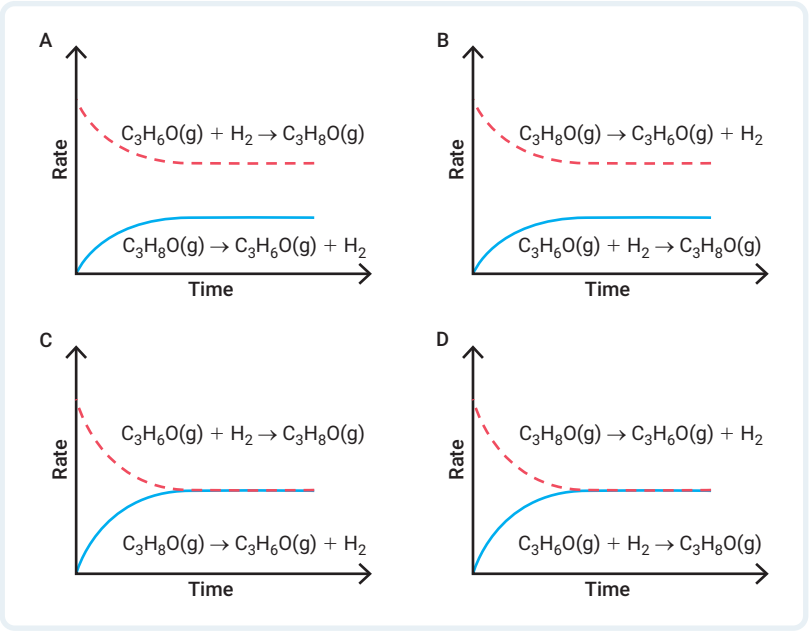
2. When 2-propanol reacts to form an equilibrium mixture with propanone and hydrogen, which one of the following best represents how the rates of the forward and back reactions change over time?



3. The following reaction is used in the contact process to produce sulfur trioxide:

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)\, 3\Delta H = -197 \text{ kJ mol}^{-1}$

The equilibrium yield of sulfur trioxide can be increased by:

A increasing the temperature.
B removing sulfur trioxide as it forms.
C increasing the pressure at constant temperature.
D increasing the volume of the container.

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4. **Identify** which change would shift the system from light purple to dark purple.

$$\underset{\text{Colourless}}{2HI(g)} \rightleftharpoons \underset{\text{Colourless}}{H_2(g)} + \underset{\text{Purple}}{I_2(g)} \qquad \Delta H = +53.6 \text{ kJ mol}^{-1}$$

A Adding HI(g)
B Adding a catalyst
C Decreasing the temperature
D Increasing the concentration of $H_2(g)$

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5. **Determine** which system at equilibrium will shift to the right (products) if the total pressure on the system is increased.

A $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
B $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$
C $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
D $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

6. According to Le Châtelier's principle, what happens when the concentration of a reactant is increased in a system at equilibrium?

A The equilibrium position shifts towards the left (reverse reaction).
B The equilibrium position remains unchanged.
C The equilibrium position shifts towards the right (forward reaction).
D The rate of the reverse reaction increases permanently.

7. **Identify** which of the following does not have an effect on the position of equilibrium.

A Adding a catalyst to the system
B Adding more reactants to the system
C Increasing the pressure of the system
D Decreasing the temperature of the system

8. A reaction mixture of $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is at equilibrium. The forward reaction is endothermic. **Identify** the effect on the position of equilibrium if the temperature is increased.

A The equilibrium shifts to the left.
B The equilibrium shifts to the right.
C The equilibrium position remains unchanged.
D Both the forward and reverse reactions stop.

Questions 9 and 10 relate to the following information.

The following reaction is studied in a laboratory:

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$

A mixture of hydrogen, nitrogen and ammonia is held in a sealed container at equilibrium.

9. **Identify** which direction the equilibrium will shift if the volume of the system is doubled.

A Right, to form more $NH_3(g)$
B Left, to form more $NH_3(g)$
C Right, to form more $H_2(g)$ and $N_2(g)$
D Left, to form more $H_2(g)$ and $N_2(g)$

10. **Identify** which direction the equilibrium will shift if the temperature is increased.

A Right, to form more $NH_3(g)$
B Left, to form more $NH_3(g)$
C Right, to form more $H_2(g)$ and $N_2(g)$
D Left, to form more $H_2(g)$ and $N_2(g)$

SHORT RESPONSE

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11. When heated in a sealed container, solid mercury(II) oxide (HgO) decomposes to form metallic mercury (Hg) and oxygen gas (O_2).

$2HgO(s) \rightleftharpoons 2Hg(l) + O_2(g)$

Orange Silver Colourless

a **Identify** whether the reaction occurs in an open or closed system.
b **Explain** why the colour of the system does not change once equilibrium is established.
c **Identify** which colour will be seen in the system if the equilibrium shifts to the left.

12. For the reaction:

$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +57.2\ kJ$

Predict the effect of each of the following changes on an equilibrium mixture of N_2O_4 and NO_2.

a Adding N_2O_4
b Adding NO_2
c Adding heat
d Removing N_2O_4
e Increasing the pressure

CROSS-CHAPTER QUESTION

13. In the reaction:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.4\ kJ\ mol^{-1}$

a **Explain** how an increase in temperature would affect the position of equilibrium, according to Le Châtelier's principle.
b **Identify** and **explain** how the enthalpy change (ΔH) of the forward reaction influences the energy profile of the reaction and its activation energy.
c **Predict** the effect on the reaction rate if the reaction took place at a lower temperature.

DATA ANALYSIS

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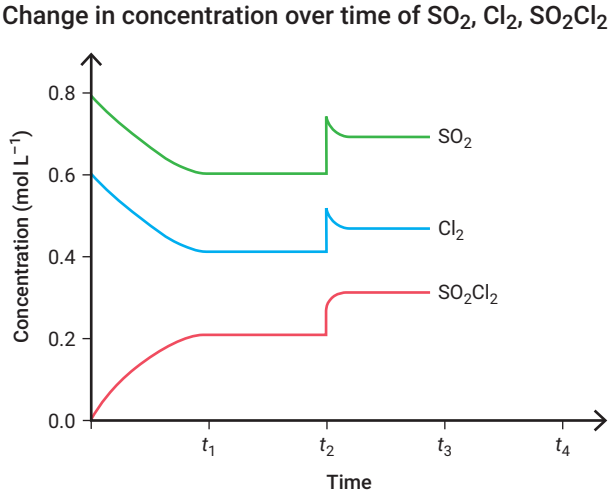
14. Interpret evidence

The following equation represents the reaction between sulfur dioxide gas (SO_2) and chlorine gas (Cl_2).

$SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g) \qquad \Delta H = -67 \text{ kJ mol}^{-1}$

The concentration versus time graph for the reaction system is shown below.



a **Identify** the initial concentration of the three gases.

b **Identify** the change applied at t_2.

c **Contrast** the change in concentration of SO_2Cl_2 with Cl_2 from t_2 to t_3. Explain why these gases behaved in this way.

d **Predict** what would happen to the gases if the temperature of the system increased at t_4.

 Modified from SCSA 2022 SA Q26

15. Interpret evidence

Consider the following system at equilibrium:

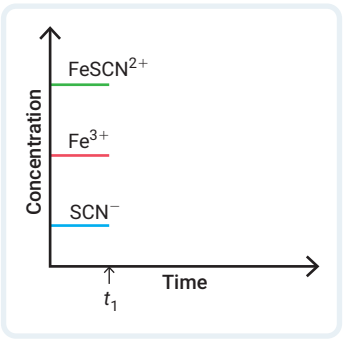
$$\underset{\text{pale brown}}{Fe^{3+}(aq)} + \underset{\text{colourless}}{SCN^{-}(aq)} \rightleftharpoons \underset{\text{deep red}}{FeSCN^{2+}(aq)} \qquad \Delta H = -\text{ve}$$

a For each of the applied changes after equilibrium is re-established, **predict** the:

- shift in equilibrium position (left, right or no change)
- rate of the forward reaction compared to the original rate (increase, decrease or no change)
- colour of the reaction mixture.

Change	Shift in equilibrium position (left, right or no change)	Rate of the forward reaction compared to original rate (increase, decrease or no change)	Colour of reaction mixture
The reaction mixture is heated.			
A few crystals of $FeCl_3$ are added.			
Water is added to the reaction mixture.			
A few drops of concentrated Na_3PO_4 are added.			

b Consider the concentration–time graph shown.



At t_1, the temperature of the system is increased. **Predict** the effect of an increase in temperature by **sketching** the change that would occur as the system re-establishes equilibrium.

CHAPTER 3

Equilibrium constants

Martyn F. Chillmaid/Science Photo Library

SYLLABUS DOT POINTS

SCIENCE UNDERSTANDING

- Identify that the equilibrium constant (K_c) indicates the relationship 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 INQUIRY

Investigate:

- solubility

Introduction

A chemical system involving a reversible reaction is said to have reached a state of equilibrium when the rates of the forward and reverse reactions are equal, and the concentrations of the reactants and products are therefore constant.

Importantly, these concentrations do not need to be equal. There is a mathematical relationship between the concentrations of the reactants and products. This relationship is known as the equilibrium constant or K_c. Understanding K_c allows scientists to manipulate equilibrium reactions, optimise reaction products and determine solubility conditions in various applications.

ASSUMED KNOWLEDGE

- ✓ Reactions have reached equilibrium when the forward and reverse rates of reaction are equal.
- ✓ Chemical equations need to be balanced.
- ✓ Stoichiometry is a technique that involves using mole ratios to calculate unknown values.
- ✓ Le Châtelier's principle states that when an equilibrium system is disturbed, it will respond in a way that will partially oppose the change.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ understand the K_c relationship between products and reactants at equilibrium
- ✓ determine the K_c expressions for various chemical reactions
- ✓ predict the extent and direction of a chemical reaction by using K_c
- ✓ use K_c to calculate the concentrations of products and reactants at equilibrium
- ✓ compare Q with K_c to determine whether a reaction has reached equilibrium
- ✓ use RICE tables to determine K_c at equilibrium from an initial reaction mixture and understanding the assumptions to make when K_c is very small
- ✓ use K_{sp} values to describe and calculate the solubility of a substance.

3.1 The equilibrium constant (K_c)

When a system is at equilibrium, at a fixed temperature, the concentration of the products divided by the concentrations of the reactants, each being raised to the coefficient of the substance in the equation, must be equal to a constant.

For the reaction:

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

the equilibrium expression is:

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

equilibrium constant the value of the ratio between the concentrations of the reactants and products, represented as K_c

equilibrium expression the ratio of the concentrations of products to reactants used to calculate the equilibrium constant

This constant is known as the **equilibrium constant**, and is represented as K_c. It can be calculated from the concentrations of the reactants and products at equilibrium, using the **equilibrium expression**.

KEY FORMULA

Equilibrium expression

For the reaction:

$aA + bB \rightleftharpoons cC + dD$

the equilibrium expression is:

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

Because the equilibrium expression is determined from the way the equation is written, the magnitude of K_c also depends on the equation.

The equilibrium constant is based on the ratio of the concentrations of reactants and products. Consider the reaction where nitrogen (N_2) and hydrogen gas (H_2) form ammonia (NH_3):

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

The equilibrium expression for this reaction can be written as:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Notice that the coefficients for each species in the balanced equation have become the 'power' for each species in the expression.

Equilibrium constants are generally reported as numbers without units. However, the concentrations for all species in the equilibrium expression must be in mol L^{-1} (or molarity, M). If concentrations are expressed in other units, they must be converted to mol L^{-1} before substituting in the expression.

Because the equilibrium constant is a fixed value for a particular reaction at a specific temperature, any disturbance to the system at that temperature does not change the value of the equilibrium constant. However, if temperature is changed, the value of the equilibrium constant will also change.

Homogeneous and heterogeneous equilibria

partial pressure the pressure exerted by an individual gas in a gaseous mixture

heterogeneous system a system in which there is a mixture of phases of reactants and products

homogeneous system a system in which all the reactants and products are in the same phase

Solutions and gases vary in concentration and therefore are included in the equilibrium expression. With gases, the **partial pressure** (the pressure of the individual gas) is proportional to the concentration of the gas and therefore can also be used in the equilibrium expression for a gaseous system.

However, solids and pure liquids do not vary in their concentration. Therefore, in a **heterogeneous system** where the substances are in more than one phase, solids and pure liquids are not included in the equilibrium expression. Only the concentrations of solutions or gases are included. In a **homogeneous system**, where all substances are in the same phase, solids and liquids are included because the relative proportions are important.

For example, the equilibrium system between nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4) is homogeneous, because all species are in the gaseous phase.

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

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

The following equilibrium system is heterogeneous because calcium carbonate ($CaCO_3$) and its dissolution products are a mix of gas and solid. The $CaCO_3(s)$ and $CaO(s)$ are therefore not included in the K_c expression.

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

$$K_c = [CO_2]$$

WORKED EXAMPLE 3.1.1

Construct the equilibrium expression for the reaction:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

ANSWER

1 **Check that the equation is balanced.**
The equation is balanced.

2 **Put the products on top of the expression and the reactants on the bottom.**

$$\frac{PCl_3Cl_2}{PCl_5}$$

3 **Add square brackets around each substance to indicate concentration.**

$$\frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

4 **Add the coefficient for each species from the balanced equation so that it becomes the power in the expression.**
The coefficient is 1 for all species, so it is not added.

5 **Multiply concentrations if there is more than one reactant or product.**

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

WORKED EXAMPLE 3.1.2

Construct the equilibrium expression for the reaction:

$$CaCl_2(s) \rightleftharpoons Ca^{2+}(aq) + 2Cl^-(aq)$$

ANSWER

1 **Exclude any solids and liquids present in the heterogeneous equilibria.**
Because the reactant is a solid, we will not consider it in the expression.

2 **Put the products on top of the expression and the reactants on the bottom.**
Because $CaCl_2$ is a solid, we do not have a reactant for this expression.
$Ca^{2+}\ Cl^-$

3 **Add square brackets around each substance to indicate concentration.**
$[Ca^{2+}][Cl^-]$

4 **Add the coefficient for each species from the equation so that it becomes the power in the expression.**
$[Ca^{2+}][Cl^-]^2$

5 **Multiply concentrations if there is more than one reactant or product.**
$[Ca^{2+}][Cl^-]^2$

6 **Write the equilibrium expression.**
Because the reactant is a solid, we remove the species from the expression.
$K_c = [Ca^{2+}][Cl^-]^2$

Calculating K_c values

Values for K_c can be calculated by substituting in the concentrations for all reaction species at equilibrium. K_c is temperature specific so its value will change with the temperature, as the reaction shifts towards the right or the left.

WORKED EXAMPLE 3.1.3

Calculate the magnitude of the equilibrium constant for the reaction:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

given that, at equilibrium, $[CH_3COOH] = 0.92$ M, $[CH_3COO^-] = 1.62 \times 10^{-2}$ M and $[H^+] = 1.02 \times 10^{-3}$ M.

ANSWER

1 Write the equilibrium expression.

$$K_c = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

2 Substitute the given concentrations into the expression.

$$K_c = \frac{(1.62 \times 10^{-2})(1.02 \times 10^{-3})}{0.92}$$

3 Calculate the answer.

$K_c = 1.8 \times 10^{-5}$

Weblink
Calculating equilibrium constants

LEARNING CHECK 3.1

DESCRIBING

1 Define:

- **a** equilibrium expression
- **b** equilibrium constant
- **c** homogenous system
- **d** heterogeneous system.

2 State the equilibrium expression for each of the following reactions.

- **a** $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
- **b** $H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$
- **c** $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
- **d** $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$
- **e** $2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$

APPLYING

3 Calculate the magnitude of the equilibrium constant for each of the following reactions.

- **a** $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$, given that the concentrations at equilibrium are: $[CO_2] = 2.00$ mol L^{-1}, $[H_2] = 3.00$ mol L^{-1}, $[CO] = 0.17$ mol L^{-1}, $[H_2O] = 0.17$ mol L^{-1}
- **b** $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$, given that the concentrations at equilibrium are: $[H_2S] = 0.2$ mol L^{-1}, $[H_2] = 7.0 \times 10^{-3}$ mol L^{-1} and $[S_2] = 3.5 \times 10^{-3}$ mol L^{-1}
- **c** $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, given that the concentrations at equilibrium are: $[SO_2] = 0.75$ M, $[O_2] = 0.62$ M and $[SO_3] = 1.70$ M
- **d** $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, given that the concentrations at equilibrium are: $[N_2] = 1.25$ M, $[O_2] = 1.70$ M and $[NO] = 2.0$ M

3.2 Describing the position of equilibrium (K_c and Q)

The magnitude of K_c can tell us whether there are more products or reactants at equilibrium. Since the products are on top of the fraction, a large K_c indicates the concentration of products is much greater than the concentration of reactants. Therefore, a:

- **large K_c** indicates that the reaction goes towards completion, meaning that nearly all of the reactants become products. We say that equilibrium lies to the right, as there are more products than reactants at equilibrium.
- **small K_c** indicates that the reaction only occurs to a small extent. We say that equilibrium lies to the left, as there are more reactants than products at equilibrium.
- **value of K_c** close to 1 indicates that there are significant concentrations of both reactants and products at equilibrium.

For example, the equilibrium constant for the 'pop test', which is the reaction between hydrogen and oxygen gas to form water vapour, is 2.4×10^{47} at 500 K.

The equation for this reaction is:

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

Therefore, the equilibrium expression is:

$$K_c = \frac{[H_2O]^2}{[H_2]^2\,[O_2]} \leftarrow \frac{\text{large amount}}{\text{small amount}} = \text{large } K_c$$

The very high value of the equilibrium constant shows that, at equilibrium, there is a large amount of product ($H_2O(g)$) and only a very small amount of reactants ($H_2(g)$ and $O_2(g)$). This indicates that most of the reactants react to become products, so the reaction occurs to a large extent. In this case, we say that the position of equilibrium is to the right.

In contrast, the reaction for hydrogen molecules splitting into hydrogen atoms has an equilibrium constant of 1.2×10^{-42} at 500 K.

$$H_2(g) \rightleftharpoons 2H(g)$$

$$K_c = \frac{[H]^2}{[H_2]} \leftarrow \frac{\text{small amount}}{\text{large amount}} = \text{small } K_c$$

The very low value for the equilibrium constant indicates that, at equilibrium, there is a large proportion of the reactant, H_2 molecules, compared to the product, H atoms. This shows the reaction only occurs to a very small extent. In this case, we say that the position of equilibrium is to the left.

FORMULA AND DATA BOOK

Reaction quotient (Q)

The ratio of products to reactants $\frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$ will only equal the equilibrium constant (K_c) when the system is at equilibrium. The **reaction quotient (Q)** is also calculated from the same ratio and gives a mathematical value for the reaction concentrations *at any point in time*. This can be compared with the equilibrium constant and can indicate whether the reaction has reached equilibrium.

reaction quotient (Q) the value of the equilibrium expression when calculated, Q

- If $Q = K_c$, then the system is at equilibrium.
- If $Q < K_c$, then there are less products and more reactants than at equilibrium. This indicates that the forward reaction will be favoured for the system to reach equilibrium.

- If $Q > K_c$, then there are more products and less reactants than at equilibrium. This indicates that the reverse reaction will be favoured for the system to reach equilibrium.

$Q < K_c$	$Q = K_c$	$Q > K_c$
Forward reaction favoured	At equilibrium	Reverse reaction favoured

WORKED EXAMPLE 3.2.1

The equilibrium constant (K_c) for the reaction:

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

is 14.5 at 483 K. If the concentrations of CO and H_2 are both 0.5 mol L^{-1} and the concentration of CH_3OH is 5 mol L^{-1}, determine if the system is at equilibrium.

ANSWER

1 Determine the expression for the reaction quotient.

$$Q = \frac{[CH_3OH]}{[CO][H_2]^2}$$

2 Using the values stated, calculate *Q* at 483 K.

$$Q = \frac{5}{0.5 \times 0.5^2}$$

$$= 40$$

3 Compare *Q* and K_c.
Since Q is not equal to K_c, the system is not at equilibrium.

LEARNING CHECK 3.2

DESCRIBING

1 Describe what the following Q and K_c values indicate, in terms of the relative amounts of products and reactants at equilibrium, and whether the system favours the forward or reverse reaction.

a $Q = K_c$
b $Q < K_c$
c $Q > K_c$

2 Explain what a K_c of close to 1 means in terms of the concentrations of reactants and products at equilibrium.

3 Explain what a high K_c of 2.4×10^{47} indicates about the extent of the reaction of hydrogen and oxygen to make water:

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

APPLYING

4 Compare the calculated reaction quotient of $Q = 15$ with the equilibrium constant $K_c = 22$ to determine which reaction is favoured in order for the system to reach equilibrium.

5 a Calculate the reaction quotient for the reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ if the system has the following concentrations: $[CO] = 0.5$ M, $[H_2] = 1.0$ M and $[CH_3OH] = 18.0$ M.

b Determine whether the reaction is at equilibrium, if $K_c = 14.5$.

Weblinks
Calculating reaction quotients
Comparing *Q* and *K*
Worksheet
Equilibrium constants dominoes

3.3 Calculating equilibrium concentrations

We can determine K_c if the starting concentrations of the reactants and products are given as well as the equilibrium concentration of at least one reactant or product. A RICE table (**r**eaction species, **i**nitial concentration, **c**hange to concentration, **e**quilibrium concentrations) is a useful way to summarise this information.

WORKED EXAMPLE 3.3.1

Hydrogen and fluorine react together to form hydrogen fluoride in a reversible reaction:

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$$

1 mol of H_2 and 2 mol of F_2 are introduced to a 1 L container and the system is left to reach equilibrium. When equilibrium is reached, 0.032 mol of H_2 remain in the container.

a Calculate the equilibrium concentrations of F_2 and HF.

b Calculate the equilibrium constant.

ANSWERS

a **1** **Use a RICE table to write what is known and calculate the concentrations.**

Reaction species	H_2	F_2	HF
Initial concentration	1 mol in 1 L $C = \frac{1\text{ mol}}{1\text{L}}$ $= 1\text{ M}$	2 mol in 1 L $C = \frac{2\text{ mol}}{1\text{L}}$ $= 2\text{ M}$	0
Change in concentration			
Equilibrium concentration	0.032 mol in 1 L $C = \frac{0.032\text{ mol}}{1\text{L}}$ $= 0.032\text{ M}$		

2 **Examine the mole ratio from the equilibrium equation.**
According to the balanced equation, the mole ratio is:

H_2		F_2		HF
1	:	1	:	2

3 **Calculate the change in the number of moles.**
Because the system has reached equilibrium, the change in number of moles of H_2 is $1 - 0.032 = 0.968$ mol.

4 **Calculate the change in the concentration of each species.**
The change in concentration of H_2 can be calculated as:

$$[H_2] = \frac{0.968\text{ mol}}{1\text{ L}}$$
$$= 0.968\text{ M}$$

According to the mole ratios, the number of moles of H_2 and F_2 reacting will be the same, and the number of moles of HF formed will be twice that of reactants lost.

$$[HF] = \frac{0.968 \times 2}{1\,L}$$
$$= 1.936\ M$$

Reaction species	H_2	F_2	HF
Initial concentration	1 M	2 M	0
Change in concentration	–0.968 M	–0.968 M	+1.936 M
Equilibrium concentration	= 0.032 M		

5 Calculate the concentration of each species at equilibrium.

Reaction species	H_2	F_2	HF
Initial concentration	1 M	2 M	0
Change in concentration	–0.968 M	–0.968 M	+1.936 M
Equilibrium concentration	1 – 0.968 = 0.032 M	2 – 0.968 = 1.032 M	0 + 1.936 = 1.936 M

b Substitute the final concentrations into the equilibrium constant expression.

$$K_c = \frac{[HF]^2}{[H_2][F_2]}$$
$$= \frac{1.936^2}{0.032 \times 1.032}$$
$$= 113.5$$

Calculating equilibrium concentrations from initial solutions

The equilibrium concentrations of reactants and products can be calculated by using K_c and the initial concentrations of a starting mixture. In this case, the mole ratios in the equilibrium equation are considered. Again, RICE tables are useful in these types of calculations.

WORKED EXAMPLE 3.3.2

PCl_5 gas decomposes into PCl_3 and Cl_2 according to the following equation, with $K_c = 0.019$.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Calculate the final concentrations, if the initial concentrations of PCl_5 was 0.025 M and of PCl_3 and Cl_2 was 0.00 M.

ANSWER

1 Examine the mole ratio from the equilibrium equation.

According to the balanced equation, the mole ratio is:

PCl_5		PCl_3		Cl_2
1	:	1	:	1

2 Use a RICE table to summarise this information.

Reaction species	PCl_5	PCl_3	Cl_2
Initial concentration	0.025 M	0.00 M	0.00 M
Change in concentration			
Equilibrium concentration			

3 Represent the unknown change with *x*.
PCl_5 decreases by x; PCl_3 and Cl_2 increase by x.

Reaction species	PCl_5	PCl_3	Cl_2
Initial concentration	0.025 M	0.00 M	0.00 M
Change in concentration	$-x$	$+x$	$+x$
Equilibrium concentration	$0.025\ M - x$	x	x

4 Write the equilibrium expression.

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

5 Substitute the values into the expression.

$$0.019 = \frac{[x][x]}{[0.025 - x]}$$

6 Solve for the unknown concentration.
Rearrange the equation.

$$0.019 = \frac{[x][x]}{[0.025 - x]}$$

$0.000\,475 - 0.019x = x^2$
Make the equation equal to 0 to solve a quadratic equation.
$0 = x^2 + 0.019x - 0.000\,475x$
Solve for x using the quadratic formula.
$x = 0.014275$ or -0.033275

(Do not use the negative number because we cannot have a negative concentration.)

Reaction species	PCl_5	PCl_3	Cl_2
Initial concentration	0.025 M	0.00 M	0.00 M
Change in concentration	− 0.014 M	+ 0.014M	+ 0.014 M
Equilibrium concentration	0.025 M − 0.014 M = 0.011 M	0.00 M + 0.014 M = 0.014 M	0.00 M + 0.014 M = 0.014 M

Worksheet
Using K_c to solve problems

Assumption for small K_c

In cases where K_c is very small, the calculation can be simplified. We assume that a very small K_c means that very little of the reaction will proceed in the forward direction towards the products. We can therefore assume that x is negligible compared to the original concentrations of the reactants. This is quite often the case with weak acids and bases, which have K_c values typically of the order of 10^{-4} or less.

WORKED EXAMPLE 3.3.3

Consider the following equilibrium equation for hypochlorous acid (HClO), with a $K_c = 3.7 \times 10^{-8}$. Calculate the concentrations of all species at equilibrium, if the initial reaction mixture had a concentration of 0.10 M for HClO, and 0.00 M for ClO^- and H^+.

$$HClO(aq) \rightleftharpoons ClO^-(aq) + H^+(aq)$$

ANSWER

1 Use a RICE table to summarise the information given.

Reaction species	HClO	ClO^-	H^+
Initial concentrations	0.10 M	0.00 M	0.00 M
Change in concentration			
Equilibrium concentration			

2 Examine the mole ratio from the equilibrium equation.

HClO : ClO^- : $H^+(aq)$
1 1 1

Each mole of HClO that ionises is equal to an increase of 1 mol of ClO^- and H^+ ions.

3 Represent the unknown change with *x*.

Reaction species	HClO	ClO^-	H^+
Initial concentrations	0.10 M	0.00 M	0.00 M
Change in concentration	$-x$ Assume ***x*** is negligible.	$+x$	$+x$
Equilibrium concentration	0.10 M	x	x

However, since K_c is so small ($10^{-8} < 10^{-4}$), we assume that the reduction in x is negligible in comparison to the initial concentration.

4 Write the equilibrium expression.

$$K_c = \frac{[ClO^-][H^+]}{[HClO]}$$

5 Substitute the values into the expression.

$$3.7 \times 10^{-8} = \frac{[x][x]}{0.10}$$

$$3.7 \times 10^{-8} = \frac{x^2}{0.10}$$

6 Solve for the unknown concentration.

Rearrange the equation.

$$3.7 \times 10^{-8} = \frac{x^2}{0.10}$$

$$x^2 = 3.7 \times 10^{-9}$$

$$x = 6.1 \times 10^{-5}$$

Reaction species	HClO	ClO^-	H^+
Initial concentrations	0.10 M	0.00 M	0.00 M
Change in concentration	x is negligible.	$+x$	$+x$
Equilibrium concentration	0.10 M	$0.00\ M + 6.1 \times 10^{-5}\ M = 6.1 \times 10^{-5}\ M$	$0.00\ M + 6.1 \times 10^{-5}\ M = 6.1 \times 10^{-5}\ M$

LEARNING CHECK 3.3

DESCRIBING

1 **Explain** how the value of the equilibrium constant describes the position of equilibrium.

2 Where K_c is very small, **explain** why it is acceptable to assume x is negligible compared to the initial concentrations.

APPLYING

3 Nitrogen and oxygen react to form nitrogen monoxide in a reversible reaction:

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

1 mol of N_2 and 1 mol of oxygen are introduced to a 2 L container and the system is left to reach equilibrium. When equilibrium is reached, there is still 0.25 mol of N_2 left in the container.

- **a** **Calculate** the equilibrium concentrations of O_2 and NO.
- **b** **Calculate** the equilibrium constant.

4 **Calculate** the concentrations of the reactants and products in the following reactions at equilibrium:

- **a** $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, given that $K_c = 53.25$ at 300°C, with initial concentrations of $[HI] = 1.5$ M, $[H_2] = 0.0$ M and $[I_2] = 0.0$ M.
- **b** $HCN(aq) \rightleftharpoons CN^-(aq) + H^+(aq)$, given that $K_c = 4.97 \times 10^{-10}$, with initial concentrations of $[HCN] = 1.25$ M, $[CN^-] = 0.0$ M and $[H^+] = 0.0$ M. State any assumptions used.

5 When 0.40 mol of PCl_5 is heated in a 10.0 L container, an equilibrium is established in which 0.25 mol of Cl_2 is present:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

- **a** **Determine** the number of moles of PCl_5 and PCl_3 at equilibrium.
- **b** **Calculate** the equilibrium concentrations of all three components.
- **c** **Calculate** K_c for this equilibrium.

3.4 Solubility equilibrium and K_{sp}

solubility product a type of equilibrium constant used to indicate the relative solubility of a precipitate in a solvent to form a saturated solution at a particular temperature

An important application of equilibrium constants is the **solubility product** (K_{sp}). Even if a chemical is described as insoluble or partially soluble, a small component of the substance will dissolve to reach an equilibrium concentration. A similar format for the K_{sp} equation is used:

$$\left(\frac{\text{products}}{\text{reactants}}\right)$$

However, because one of the components is a solid, it is not included in the equation.

For the reaction $aA(s) \rightleftharpoons cC(aq) + dD(aq)$:

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

Another way to look at it is if the salt A dissolves to form ions C^+ and D^-, the equilibrium chemical formula is:

$$A(s) \rightleftharpoons C^+(aq) + D^-(aq)$$

and the equilibrium expression for K_{sp} becomes:

$$K_{sp} = [C^+][D^-]$$

Recall that temperature affects solubility; therefore, K_{sp} is specific to the substance dissolving at a particular temperature.

FORMULA AND DATA BOOK

Weblink
Solubility equilibria

Comparing and predicting solubility

K_{sp} can be used to compare the solubilities of different substances at a particular temperature. A larger K_{sp} indicates greater solubility, whereas a smaller K_{sp} indicates low solubility.

For example, the K_{sp} values for silver chloride and iron(III) hydroxide are:

Silver chloride (AgCl) $K_{sp} = 1.8 \times 10^{-10}$ at 25°C

Iron(III) hydroxide ($Fe(OH)_3$) $K_{sp} = 2.0 \times 10^{-39}$ at 25°C

Silver chloride has a much higher K_{sp} than iron(III) hydroxide, so we can conclude that iron hydroxide is far less soluble. This type of comparison is particularly useful in industries such as water treatment, where certain ions are removed by precipitating them as insoluble compounds.

Table 3.4.1 shows some common sparingly soluble substances and their K_{sp} at 25°C.

TABLE 3.4.1 K_{sp} values of a selection of common sparingly soluble salts

Salt	Chemical formula	K_{sp} at 25°C
Silver bromide	AgBr	5.0×10^{-13}
Silver chloride	AgCl	1.8×10^{-10}
Calcium fluoride	CaF_2	3.2×10^{-11}
Calcium carbonate	$CaCO_3$	3.3×10^{-9}
Copper sulfide	CuS	8.0×10^{-37}
Magnesium hydroxide	$Mg(OH)_2$	7.1×10^{-12}

Syllabus link
Chapter 16 of *Nelson QCE Chemistry Units 1 & 2* describes solubility in more detail.

Worksheet
Equilibrium constants

Quantifying ion concentrations at equilibrium

By using K_{sp} values, we can calculate the maximum concentrations of ions in a saturated solution. To calculate these concentrations, we use K_{sp} and the solubility expression. The equilibrium chemical equation is used to determine the relative moles of ions that will dissolve.

WORKED EXAMPLE 3.4.1

Calculate the solubility of Ca^{2+} ions in a saturated solution of calcium fluoride (CaF_2), where $K_{sp} = 3.2 \times 10^{-11}$.

ANSWER

1 Determine the solubility equilibrium for this substance dissolving.

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

2 Examine the mole ratios from the equilibrium equation

CaF_2	:	Ca^{2+}	:	F^-
1		1		2

3 Determine the K_{sp} expression.

Since solids are not included in the K_{sp}:

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

4 Represent the unknown change with *x*.

According to the mole ratio of the equilibrium equation, if *x* mol of CaF_2 dissolves, then *x* mol of Ca^{2+} and 2*x* mol of F^- are formed. Substitute these values into the equation, remembering that K_{sp} has already been given to us.

5 Substitute the values into the expression.

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

$3.2 \times 10^{-11} = x \times (2x)^2$

6 Solve for the unknown concentration.

$3.2 \times 10^{-11} = 4x^3$

Solve for x^3.

$$x^3 = \frac{3.2 \times 10^{-11}}{4} = 8.0 \times 10^{-12}$$

Take the cube root to solve for x.

$$x = \sqrt[3]{8.0 \times 10^{-12}}$$

$$\approx 2.0 \times 10^{-4} \text{ M}$$

PRACTICAL ACTIVITY 3.4.1

DETERMINING THE SOLUBILITY CONSTANT OF SILVER ACETATE

Introduction

When silver acetate (ethanoate) is dissolved in a solution, acetate and silver ions are formed according to the equation:

$$AgCH_3COO(s) \rightleftharpoons Ag^+(g) + CH_3COO^-(aq)$$

The amount of silver ions in the solution can be determined indirectly by reaction with copper according to the equation:

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

Research question

How can the solubility constant of silver acetate be experimentally determined?

Aim

To determine the solubility constant of silver acetate

Materials

- 100 mL saturated silver acetate solution
- 50 mL acetone
- distilled water in a wash bottle
- 2 × 150 mL beakers
- 1 test tube
- 20 cm copper wire
- electronic balance
- steel wool
- 100 mL measuring cylinder
- thermometer

RISK ASSESSMENT

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Glassware may break and cut you.	Handle glass with care. Inspect and discard any chipped or cracked beakers, no matter how small the damage. Sweep up broken glass with a dustpan and brush; do not use your fingers.
Silver acetate can irritate eyes and skin.	Wear goggles, lab coat and gloves when handling.

Copy and complete the risk assessment table in your write-up. Add any more risks you can think of, and ways to manage them. Ask your teacher to check your risk assessment before you proceed.

Procedure

1 Measure 100 mL of silver acetate and pour it into a 150 mL beaker. Measure and record the temperature of the solution.

2 Using steel wool, clean the surface of the copper wire.

3 Carefully wrap the copper wire around a pencil to create a coil, leaving a small portion of the copper unwound so that it can be used as a hook.
4 Measure and record the mass of the copper wire.
5 Carefully place the coiled copper wire into the silver acetate solution. Use the portion of uncoiled wire to create a hook and hang the coil off the rim of the beaker.
6 Leave the experiment overnight.
7 Shake the coil to dislodge attached silver crystals. Remove it from the solution and wash it with distilled water.
8 Pour some acetone into a clean 150 mL beaker.
9 Dip the copper in the acetone to rinse the coil to remove any silver crystals that are still attached.
10 Allow the coil to air dry.
11 Measure and record the mass of the copper wire.

Results

Record your results in a carefully formatted table.

Analysis of results

1 Calculate the number of moles of copper that reacted, using the change in mass from the copper wire in the experiment.
2 Calculate the number of moles of silver that reacted.
3 Calculate the concentration of silver ions in the original solution.
4 Determine the K_{sp} expression.
5 Calculate the K_{sp} of silver acetate.

Evaluation

6 Compare your value with that obtained by other class groups, identifying possible reasons for any differences.
7 Compare your value with the theoretical value of 1.9×10^{-3} at 25°C, identifying possible reasons for any differences.

LEARNING CHECK 3.4

DESCRIBING

1 **Describe** how the value of K_{sp} gives an indication of the solubility of the particular substance.
2 **Describe** why the temperature conditions should be given when stating K_{sp}.

APPLYING

3 **Compare** the K_{sp} values in Table 3.4.1 to determine which of the following pairs of substances is the *least* soluble.
   a AgBr and CuS
   b CaF_2 and $CaCO_3$
   c Silver chloride and copper(II) sulfide
   d Calcium carbonate and copper(II) sulfide
4 **Calculate** K_{sp} of AgI at 25°C if there are 9×10^{-9} M of Ag^+ and I^- ions in solution at equilibrium.
5 **Calculate** the solubility of copper(II) sulfide using the K_{sp} values in Table 3.4.1.

Weblink
The solubility product constant

CHAPTER SUMMARY

Equilibrium constant, K_c

- The equilibrium constant K_c shows the relationship between the concentration of products and reactants at equilibrium.

  This can be calculated using the equilibrium expression:

  For the reaction:

  $aA + bB \rightleftharpoons cC + dD$

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

- Solids and pure liquids are not included in the equilibrium expression.

K_c and Q

- The reaction quotient (Q) is calculated in the same way as K_c and helps to show where the reaction is at any point in time. This can be used to compare against K_c to indicate whether the reaction is at equilibrium.
- Depending on the relative values of Q and K_c, we can determine which reaction is favoured in order to reach equilibrium:
  - If $Q = K_c$, the system is at equilibrium.
  - If $Q < K_c$, the forward reaction will be favoured.
  - If $Q > K_c$, the reverse reaction will be favoured.

Calculating constants and concentrations

- The RICE table is a strategy for calculating the concentration of species and/or K_c. For $A \rightleftharpoons B + C$:

Reaction species	A	B	C
Initial concentration			
Change in concentration			
Equilibrium concentration			

Solubility product, K_{sp}

- The solubility product (K_{sp}) indicates the solubility of a substance.
- The smaller the K_{sp}, the less soluble the substance.

  K_{sp} is calculated in a similar way to K_c. Remember that solids are not included in the expression; for example:

  $K_{sp} = [C]^c[D]^d$ for the reaction $aA(s) \rightleftharpoons cC(aq) + dD(aq)$

CHAPTER EXAM

MULTIPLE CHOICE

1. Hydrogen chloride (HCl) can decompose to form an equilibrium mixture of HCl, Cl_2 and H_2, according to the equation:

$$2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

At 30°C, $K_c = 6.2 \times 10^{20}$ and at 60°C, $K_c = 7.4 \times 10^{18}$. What valid conclusion can be drawn from this finding?

A The forward reaction is exothermic.
B HCl is less stable at the higher temperature.
C The equilibrium concentrations of H_2 and Cl_2 are equal.
D The equilibrium concentration of HCl is lower at 30°C than at 60°C.

2. An important stage in the production of sulfuric acid is the reaction of sulfur dioxide and oxygen to form sulfur trioxide:

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

In an investigation of this reaction, 2 mol of SO_3 are placed in an empty 1 L flask and allowed to reach equilibrium. The temperature is kept constant. If $[O_2] = 0.3$ M at equilibrium, what is the equilibrium concentration of SO_3?

A 0.80 M
B 1.00 M
C 1.10 M
D 1.40 M

3. Hydrogen iodide can be formed in the following reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_c = 200 \text{ at } 50°C$$

In an experiment, gases were added to a sealed container in the following concentrations:

$[H_2] = 0.04$ M, $[I_2] = 0.02$ M and $[HI] = 0.8$ M

What will the concentration of HI be when the reaction reaches equilibrium at 50°C?

A 0.80 M
B 1.00 M
C Less than 0.80 M
D Between 0.80 M and 1.00 M

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4. Ammonia gas reacts with oxygen gas in the following equilibrium reaction.

$$4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g)$$

The equilibrium expression for the reaction is:

A $\dfrac{[NH_3][O_2]}{[N_2][H_2O]}$

B $\dfrac{[N_2][H_2O]}{[NH_3][O_2]}$

C $\dfrac{[NH_3]^4[O_2]^3}{[N_2]^2[H_2O]^6}$

D $\dfrac{[N_2]^2[H_2O]^6}{[NH_3]^4[O_2]^3}$

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5. Phosgene gas ($COCl_2$) is formed by the following reaction.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad \Delta H = -110 \text{ kJ mol}^{-1}$$

At a certain temperature, the equilibrium constant K_c for this reaction is 5.0. A student calculates the value of Q as 0.83 M.
Based on the K_c and Q values, predict what is happening to the system.

A The system is at equilibrium and will not shift.
B The reverse reaction is favoured, producing more CO and Cl_2.
C The forward reaction is favoured, producing more $COCl_2$.
D The reaction will stop completely.

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6. The equilibrium constants of four different reactions are given.
In which reaction does the equilibrium lie furthest to the left?

	Reaction	K_c
A	$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$	2.4×10^{1}
B	$AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$	3.0×10^{-8}
C	$Cl_2(g) + H_2O(l) \rightleftharpoons HOCl(aq) + H^+(aq) + Cl^-(aq)$	4.0×10^{-4}
D	$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_3^{2-}(aq)$	6.3×10^{-8}

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7. Determine the equilibrium expression (K_c) for the reaction.

$$\underset{\text{Colourless}}{2HI(g)} \rightleftharpoons \underset{\text{Colourless}}{H_2(g)} + \underset{\text{Purple}}{I_2(g)} \qquad \Delta H = +53.6 \text{ kJ mol}^{-1}$$

A $K_c = \dfrac{[H_2][I_2]}{2[HI]}$

B $K_c = \dfrac{[H_2][I_2]}{[HI]^2}$

C $K_c = \dfrac{2[H]2[I]}{2[HI]}$

D $K_c = \dfrac{2[H]2[I]}{[HI]^2}$

8. Identify which of the following substances is the *least* soluble at 25°C.

A PbS with K_{sp} 8×10^{-28}
B AgCl with K_{sp} 1.8×10^{-10}
C CuS with K_{sp} 8.0×10^{-37}
D $CaCO_3$ with K_{sp} 1.3×10^{-9}

9. When PbS was dissolved in water, it formed 1.7×10^{-6} M of Pb^{2+} and S^{2-} ions, according to the equation:

$$PbS(s) \rightleftharpoons Pb^{2+}(aq) + S^{2-}(aq)$$

What is the K_{sp} of PbS at this temperature?

A 1.7×10^{-6}
B 2.4×10^{-5}
C 2.9×10^{-12}
D 3.4×10^{-6}

10. A larger K_{sp} indicates:

A equal solubility.
B lesser solubility.
C greater solubility.
D no change to equilibrium.

SHORT RESPONSE

11. Sodium chloride dissolves in water:

$$NaCl(s) \rightleftharpoons Na^{+}(aq) + Cl^{-}(aq)$$

Given that the concentration of Na^+ and Cl^- are 6.13 M, **calculate** K_{sp} of sodium chloride.

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12. 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.

b **Determine** if the relative position of equilibrium lies towards the products or reactants if the molar concentration 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.

CROSS-CHAPTER QUESTION

13. This graph shows how the concentration of reactants and products for the decomposition of phosgene ($COCl_2$) changes over time.

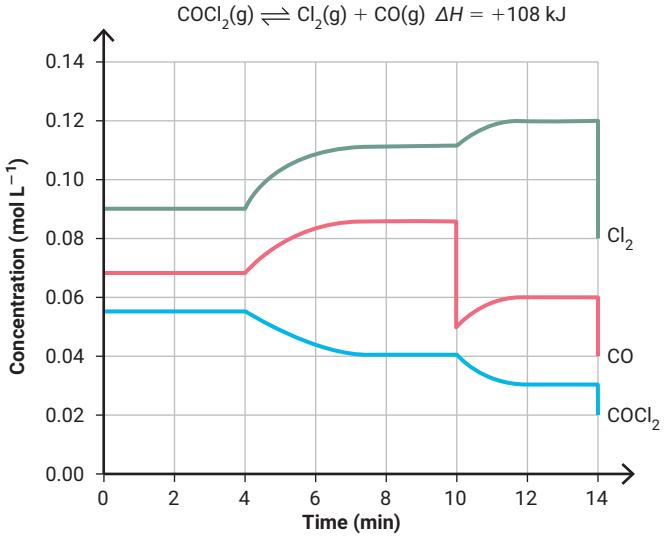
a **Identify** the equilibrium concentrations of all three species between 12 and 14 minutes.

b **Calculate** K_c for the equilibrium between 12 and 14 minutes.

c **Identify** whether the reaction moved in the forward or reverse direction from 4 to 8 minutes.

d **Calculate** the equilibrium constant from 8 to 10 minutes.

Equilibrium graph for phosgene undergoing different disturbances



DATA ANALYSIS

 QCAA paper 2 2022 SA Q2

14. Analyse data

The reaction shows part of the contact process used to produce sulfuric acid.

$$2SO_2(g) + O_2 \rightleftharpoons[V_2O_5] 2SO_3(g)$$

The equilibrium constant (K_c) for this reaction at different temperatures is shown.

Temperature (K)	Equilibrium constant (K_c) (mol L^{-1})
298	9.77×10^{25}
500	8.61×10^{11}

a **Deduce** if the forward reaction is exothermic or endothermic. Explain your reasoning.

b **Calculate** the equilibrium concentration of SO_3 at 500 K given the equilibrium concentrations $[SO_2] = 0.860$ M, $[O_2] = 0.330$ M.

c **Apply** Le Châtelier's principle to **explain** whether halving the reaction vessel's volume at 500 K would affect the position of the equilibrium or the value of the equilibrium constant.

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15. Analyse data

Two experiments were conducted to investigate the effect of temperature on the equilibrium formed during the decomposition of hydrogen iodide (HI).

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad \Delta H = +53.6 \text{ kJ mol}^{-1}$$

Experiment	Initial concentration (mol L^{-1})			Equilibrium concentration (mol L^{-1})			K_c
	[HI]	[H_2]	[I_2]	[HI]	[H_2]	[I_2]	
1	0.08	0.00	0.00		0.01		2.78×10^{-2}
2	0.00	0.06	0.06	0.06	0.03	0.03	

a **Determine** the concentration of HI(g) and I_2(g) at equilibrium for experiment 1.

b **Calculate** the equilibrium constant (K_c) for experiment 2.

c **Determine** which experiment was conducted at a higher temperature. **Explain** your reasoning.

CHAPTER 4

Acids, bases and pH

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SYLLABUS DOT POINTS

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

SCIENCE INQUIRY

- Investigate properties of acids and bases.

Introduction

Early chemists could identify an acid or a base from its properties. But to develop a conceptual definition of an acid requires an understanding of the structure of the molecules or ions of acids and bases and the mechanism of acid–base reactions. Arrhenius defined acids in terms of their ability to produce H^+ ions in solution. Understanding the strength of an acid is complicated by the fact that an acid can be monoprotic, diprotic or triprotic and that acids and bases dissociate or break apart to differing degrees. Concentration and strength can also be easily confused when referring to acids and bases. The pH scale is a useful way of comparing substances of varying degrees of acidity and basicity depending on the number of hydrogen ions they release into solution. While this gives us an idea of the amount of H^+ ions involved, it is important to be able to determine quantitatively the concentrations of hydrogen ions and hydroxide ions in solutions.

An appreciation of the concepts of chemical equilibria and Le Châtelier's principle can be useful in our understanding of the interaction of acids and bases.

ASSUMED KNOWLEDGE

- ✓ Atoms consist of protons, neutrons and electrons, and ions are atoms or molecules that have gained or lost electrons.
- ✓ Atoms that lose electrons form positive ions (cations) and atoms that gain electrons form negative ions (anions).
- ✓ Balanced chemical equations can be written from descriptions of reactions and obey the law of conservation of matter.
- ✓ The pH scale goes from 0 to 14; acids have a pH < 7, bases have a pH > 7, and a neutral substance has a pH of 7.
- ✓ Common properties of acids include sour taste and a corrosive nature, and bases have a slippery feel and a bitter taste.
- ✓ The number of moles can be calculated by using the mass and molar mass of a substance: $n = \frac{m}{M}$.
- ✓ Concentration can be calculated by using number of moles and volume: $c = \frac{n}{V}$.
- ✓ In equilibrium reactions, the forward and reverse reactions occur simultaneously.
- ✓ Le Châtelier's principle helps us identify the changes that would occur in an equilibrium reaction as a result of changing conditions.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ identify that acids are substances that can act as proton donors
- ✓ identify acids as monoprotic, diprotic or triprotic and how they ionise
- ✓ identify that bases are substances that dissociate and release OH^- in solution
- ✓ discriminate between the terms 'strong' and 'weak' for acids and bases
- ✓ identify examples of strong and weak acids and bases
- ✓ discriminate between strong and weak acids and bases in terms of extent of dissociation, rate of reaction, pH and electrical conductivity
- ✓ identify that water is a weak electrolyte and the self-ionisation of water is represented by K_w
- ✓ calculate pH, hydrogen ion concentration, pOH and hydroxide ion concentration of solutions.

Syllabus link
Chapter 17 of *Nelson QCE Chemistry Units 1 & 2* introduces the reactions of acids and bases.

Syllabus link
Chapter 18 of *Nelson QCE Chemistry Units 1 & 2* introduces the properties of acids and bases.

electrolyte a substance that dissociates into ions when dissolved in a solvent

ionisation reaction the process in which a molecular substance, often an acid, dissolves in water and separates into ions by the gain or loss of an electron

4.1 What is an acid?

Recall from Chapter 18 of *Nelson QCE Chemistry Units 1 & 2* that acids have common properties: they have a sour taste, can sting or burn the skin, conduct electricity in solution and turn blue litmus red. Acids also have a pH below 7. A pH of 7 indicates a neutral substance. Recall from Chapter 17 of *Nelson QCE Chemistry Units 1 & 2* that acids neutralise bases to produce salt and water. They also react with metals to produce a salt and hydrogen gas and metal carbonates to produce a salt, carbon dioxide and water.

Svante Arrhenius (1859–1927) proposed that acids are substances that ionise in an aqueous solution to produce hydrogen (H^+) ions. Because of this property, acids are **electrolytes**. The reaction of the acid with water is called an **ionisation reaction**, as ions are formed. Ionisation of acids is a two-step process.

For example, the two steps for the ionisation of hydrochloric acid (HCl) are:

Step 1. Hydrogen chloride dissociates in water:

$$HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$$

Step 2. The H^+ ions combine with water molecules to form the **hydronium ion** (H_3O^+) in the ionisation reaction:

$$H^+(aq) + H_2O(l) \rightarrow H_3O^+(aq)$$

hydronium ion the ion that forms when a proton is donated to a water molecule (H_3O^+)

Overall, this can be written as:

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

Hydronium ion

The hydrogen ion in an aqueous solution (Step 1) is no more than a proton, a bare nucleus that carries a single unit of positive charge. This proton is strongly attracted to any part of a nearby atom or molecule in which there is an excess of negative charge. In the case of water, this is the unshared (lone) pair electrons of the oxygen atom of the water molecule. The proton forms a shared-electron bond with oxygen, producing a hydronium ion (Figure 4.1.1).

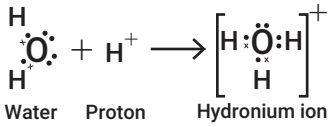


FIGURE 4.1.1 Formation of the hydronium ion

In 1923, chemists Johannes Nicolaus Brønsted (1879–1947) and Thomas Martin Lowry (1874–1936) independently developed definitions of acids based on the compounds' ability to donate protons (H^+ ions). This took the Arrhenius definition one step further and this will be looked at in Chapter 5. A Brønsted–Lowry acid is a proton (hydrogen ion) donor.

A base can be considered as a substance that produces a hydroxide ion in solution; for example, soluble salts containing the oxide (O^{2-}) ion or hydroxide (OH^-) ion. A soluble base is called an alkali. Bases have common properties such as a bitter taste and can feel slippery in aqueous solution. They have a pH above 7.

Figure 4.1.2 shows some examples of common acids and bases.

Weblink
Acids, bases and pH

FIGURE 4.1.2 Acids and bases are everyday items. Examples of substances that contain acids are vinegar (ethanoic acid), lemon juice (citric acid) and aspirin (acetylsalicylic acid). Examples of substances that contain bases are oven cleaners (sodium hydroxide), some detergents and bicarbonate of soda.

PRACTICAL ACTIVITY 4.1.1

TESTING THE PROPERTIES OF ACIDS AND BASES

Introduction

In Year 11 you learnt that:

- acids have a sour taste, sting or burn the skin, conduct electricity in solution and turn blue litmus red
- bases have a bitter taste, have a slippery feel in aqueous solution, conduct electricity in solution (not all bases are soluble) and turn red litmus blue.

These properties can help distinguish between different acids and bases.

Research question

How do properties such as reaction with litmus, and electrical conductivity help to distinguish between common acids and bases and common chemicals around the home?

Aim

To test for most of the properties listed above, using common acids and bases and some common chemicals around the home

Materials

- 50 mL of 0.1 mol L^{-1} hydrochloric acid solution
- 50 mL of 0.1 mol L^{-1} citric acid solution
- 50 mL of 0.1 mol L^{-1} sodium hydroxide solution
- 50 mL of 0.1 mol L^{-1} sodium bicarbonate (sodium hydrogencarbonate) solution
- distilled water
- 2 × 50 mL samples of any common chemicals such as detergent, coffee, lemon juice, milk
- 6 × 50 mL beakers (one for each solution)
- litmus paper (red and blue)
- 9 V battery/powerpack
- 6 alligator clips and 3 leads
- 2 graphite rods
- light bulb
- light bulb holder
- 50 mL measuring cylinder

RISK ASSESSMENT

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Glassware may break and cut you.	• Handle glass with care. • Inspect and discard any chipped or cracked beakers, no matter how small the damage. • Sweep up broken glass with a dustpan and brush; do not use your fingers.
Litmus paper is flammable.	Store in a dry location, keep away from fire.
The powerpack may give an electrical shock.	Do not use if the cord is damaged or loose. Only use the powerpack if it is tagged as safe.
0.1 mol L^{-1} sodium hydroxide is slightly toxic.	Never ingest any laboratory chemicals.
Household chemical 1 (your choice)	
Household chemical 2 (your choice)	

Copy and complete the risk assessment table in your write-up. Add any more risks you can think of, and ways to manage them. Ask your teacher to check your risk assessment before you proceed.

Procedure

Part A: pH

1. Predict whether each of your common chemicals will be acidic, basic or neither.
2. Test each of the six samples with a small strip of red litmus. Record the results.
3. Test each of the six samples with a small strip of blue litmus. Record the results.

Part B: Conductivity

1. Attach an alligator clip and lead to the positive terminal of the powerpack and another to the negative terminal.
2. Place the light bulb in its holder.
3. Connect the lead from the negative terminal to one terminal of the light bulb holder with another alligator clip.
4. Use a new alligator clip and lead to connect the other terminal of the light bulb holder to one graphite rod.
5. Connect the positive terminal lead to the other graphite rod using another alligator clip.
6. Measure and add 50 mL of 0.1 mol L^{-1} HCl into a beaker.
7. Place the two graphite rods into the beaker. Make sure they do not touch. Record your observations.
8. Repeat steps 6 and 7 for the remaining solutions (including the chosen household substances). Make sure to clean the graphite rods with distilled water between each test.

Results

Record your results in a carefully formatted table.

Analysis of results

1. Use the evidence you obtained to classify each substance as acidic or basic.
2. Identify the difficulties you experienced when testing the common chemicals.
3. Were your predictions correct?
4. What trends did you observe?

Interpretation

5. How useful are the common properties for distinguishing acids from bases?
6. Do these descriptions allow you to distinguish other solutions as neither acid nor base?
7. What would be the advantage of having alternative ways of distinguishing acids and bases?
8. Why shouldn't you test for some of the properties of acids, such as sour taste, stinging or burning the skin, or for the bitter taste or slippery feel of bases in aqueous solution?

Types of acids

Acids such as hydrochloric acid (HCl), ethanoic (acetic) acid (CH_3COOH) and nitric acid (HNO_3) will give up one proton (H^+ ion) per molecule. These are called **monoprotic** acids. Ethanoic (acetic) acid can often be confusing because of the number of hydrogens present in the compound; however, it can only donate a proton from the carboxyl –COOH group.

monoprotic a substance that can donate one proton

Other acids, such as sulfuric acid (H_2SO_4) and carbonic acid (H_2CO_3), can give up two protons per molecule of acid. These are called **diprotic** acids. The ionisation of sulfuric acid is shown below:

diprotic a substance that can donate two protons

$$H_2SO_4(l) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H_3O^+(aq)$$

The complete ionisation of sulfuric acid occurs in two steps:

Step 1: $H_2SO_4(l) + H_2O(l) \rightarrow \mathbf{HSO_4^-}(aq) + H_3O^+(aq)$

Hydrogen sulfate ion

Step 2: $HSO_4^-(aq) + H_2O(l) \rightarrow \mathbf{SO_4^{2-}}(aq) + H_3O^+(aq)$

Sulfate ion

triprotic a substance that can donate three protons

Phosphoric acid (H_3PO_4) is a **triprotic** acid and ionises in three steps:

Step 1: $H_3PO_4(s) + H_2O(l) \rightarrow \mathbf{H_2PO_4^-}(aq) + H_3O^+(aq)$

Dihydrogen phosphate ion

Step 2: $H_2PO_4^-(aq) + H_2O(l) \rightarrow \mathbf{HPO_4^{2-}}(aq) + H_3O^+(aq)$

Hydrogen phosphate ion

Step 3: $HPO_4^{2-}(aq) + H_2O(l) \rightarrow \mathbf{PO_4^{3-}}(aq) + H_3O^+(aq)$

Phosphate ion

Weblink
Polyprotic acids and bases

When polyprotic acids ionise, they form several different ions. For example, when sulfuric acid ionises, it can form the sulfate ion (SO_4^{2-}) or the hydrogen sulfate ion (HSO_4^-). The hydrogen sulfate ion can combine with a cation to produce a hydrogen sulfate salt such as potassium hydrogen sulfate ($KHSO_4$). This is an example of what are called hydrogen salts or acid salts.

Table 4.1.1 shows some common polyprotic acids and the anions they can form.

TABLE 4.1.1 Some common diprotic and triprotic acids and the anions they can form

Acid	Formula	Anions formed	Formula
Sulfuric	H_2SO_4	Hydrogen sulfate	HSO_4^-
		Sulfate	SO_4^{2-}
Carbonic	H_2CO_3	Hydrogencarbonate	HCO_3^-
		Carbonate	CO_3^{2-}
Sulfurous	H_2SO_3	Hydrogen sulfite	HSO_3^-
		Sulfite	SO_3^{2-}
Phosphoric	H_3PO_4	Dihydrogen phosphate	$H_2PO_4^-$
		Hydrogen phosphate	HPO_4^{2-}
		Phosphate	PO_4^{3-}
Citric	$C_6H_8O_7$	Dihydrogen citrate	$C_6H_7O_7^-$
		Hydrogen citrate	$C_6H_6O_7^{2-}$
		Citrate	$C_6H_5O_7^{3-}$

LEARNING CHECK 4.1

DESCRIBING

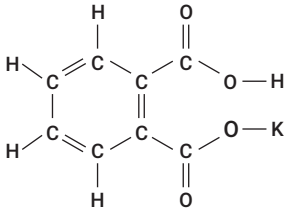
1 Define:

a acid
b base
c hydronium ion
d monoprotic acid
e diprotic acid
f triprotic acid.

APPLYING

2 Write equations to show the complete ionisation steps of the following acids.
- **a** Carbonic acid
- **b** Citric acid

3 Potassium hydrogen phthalate ($KC_8H_5O_4$) has the structure shown below. **Identify** if this acid is monoprotic, diprotic or triprotic. **Justify** your answer with appropriate ionisation equations.



Potassium hydrogen phthalate

4.2 Acid and base strength

Acids in which almost all the molecules ionise are defined as **strong acids**. Examples of strong acids are hydrochloric acid (HCl) (Figure 4.2.1), nitric acid (HNO_3) and sulfuric acid (H_2SO_4). Acids in which only some of the molecules ionise are defined as **weak acids** (Figure 4.2.2). The ionisation of weak acids is reversible; they can reach a dynamic equilibrium where the rates of the forward and reverse reactions are equal. The chemical equation is written with a reversible arrow (⇌), as introduced in Chapter 1. Examples of weak acids are carboxylic acids such as vinegar (a solution containing ethanoic (acetic) acid (CH_3COOH), citric acid ($C_6H_8O_7$) and lactic acid ($C_3H_6O_3$), and hydrofluoric acid (HF) and carbonic acid (H_2CO_3).

strong acid an acid that readily donates a proton to water

weak acid an acid in which only a small proportion of the molecules donate a proton to water

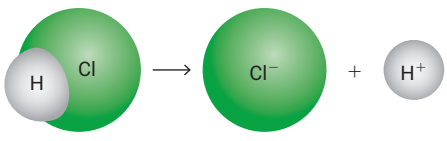


FIGURE 4.2.1 Strong acid ionisation: $HCl(aq) \rightarrow Cl^-(aq) + H^+(aq)$. The dominant species in the solution are Cl^- and H^+.

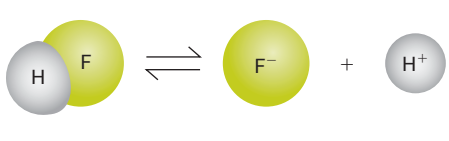


FIGURE 4.2.2 Weak acid ionisation: $HF(aq) \rightleftharpoons F^-(aq) + H^+(aq)$. The dominant species in the solution is HF.

Figure 4.2.3 shows a comparison of the extent to which HCl and HF molecules ionise.

Strong bases always dissociate in water to form separate ions. They are not reacting with water, only dissolving in the water. This reaction is called a **dissociation reaction**. Examples of strong bases are sodium hydroxide (NaOH) and potassium hydroxide (KOH). Weak bases, such as ammonia (NH_3), have only a few ions dissociated in water. Since bases also form ions when dissolved in a solvent, they are also considered to be electrolytes.

dissociation reaction a reaction in which an ionic substance separates in a solution

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

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

Weblinks
Strong and weak acids

Acid–base solutions simulation

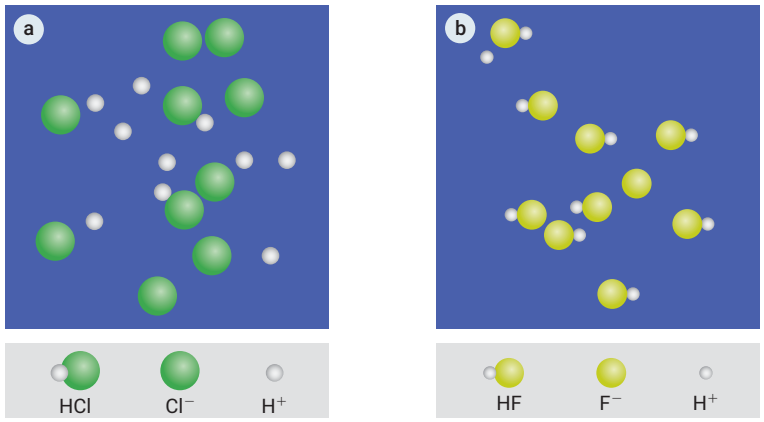


FIGURE 4.2.3 A comparison of the extent to which strong acid (HCl) and weak acid (HF) molecules ionise in water. (a) Almost all the HCl molecules are ionised. (b) Only some HF molecules are ionised.

Table 4.2.1 lists some examples of acids and bases.

TABLE 4.2.1 Examples of acids and bases

Strong acids	Strong bases
Hydrochloric acid (HCl(aq))*	Group 1 hydroxides* Sodium hydroxide (NaOH) Potassium hydroxide (KOH)
Nitric acid (HNO_3)*	
Sulfuric acid (H_2SO_4)*	Barium hydroxide ($Ba(OH)_2$)*
	Sodium oxide (Na_2O)
Weak acids	**Weak bases**
Carboxylic acids* Ethanoic acid (CH_3COOH) (vinegar or acetic acid) Citric acid ($C_6H_8O_7$) Lactic acid ($C_3H_6O_3$)	Ammonia (NH_3)*
Carbonic acid ($H_2CO_3(aq)$)*	Amines* Methylamine (CH_3NH_2) Propylamine ($CH_3CH_2CH_2NH_2$)
Hydrofluoric acid (HF)	
Sulfurous acid (H_2SO_3) Phosphoric acid (H_3PO_4) Oxalic acid ($H_2C_2O_4$) Nitrous acid (HNO_2) Arsenic acid (H_3AsO_4) Potassium hydrogen phthalate (KHP) ($KC_8H_5O_4$)	Sodium hydrogencarbonate ($NaHCO_3$)

*These are the acids and bases stated in the syllabus. You must know these acids and bases.

Concentration versus strength

The strength of an acid or base refers to its ability to ionise in solution. Stronger acids ionise completely in solution. If the concentrations of a strong acid and a weak acid are the same, the concentration of hydronium ions [H_3O^+] is higher in the strong acid solution than in the weak

acid solution. (Recall from Year 11 that the square brackets [ ] mean 'molar concentration of'.) Only a few molecules of weak acid ionise, so there is a lower concentration of hydronium ions in aqueous solution.

As discussed in Year 11, the definitions of concentrated and dilute relate to the amount of solute per unit of solution. The most convenient measure of concentration used in chemistry is molarity.

- A concentrated solution is one in which a large amount of solute is dissolved in a given volume of solvent.
- A dilute solution is one in which a small amount of solute is dissolved in a given volume of solvent.

It is possible to have a dilute solution of a strong acid and a concentrated solution of a weak acid. This is also true of strong and weak bases. 'Concentrated', 'dilute', 'strong' and 'weak' have independent meanings in chemistry, as shown in **Figure 4.2.4**.

Worksheet
Acids and bases

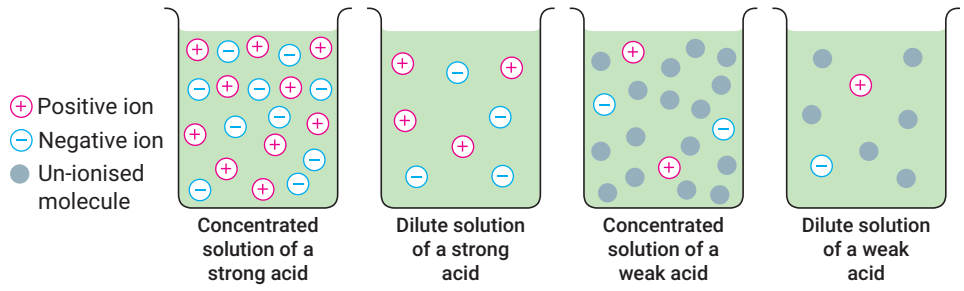


FIGURE 4.2.4 Concentrated and dilute solutions of a strong acid and a weak acid.

When distinguishing between strong and weak acids, it is useful to think of the reaction between an acid and water as an equilibrium reaction, as shown in the formula:

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

HCl is a strong acid and so every HCl molecule ionises to give a proton that attaches to a water molecule to give a hydronium ion. At equilibrium, there are no HCl molecules and so the equilibrium is shifted to the right. This can be represented with an arrow showing only the forward direction of the reaction.

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$
$$0\% \qquad\qquad 100\%$$

Ethanoic acid (CH_3COOH) is a weak acid and so only about 1% of the ethanoic acid molecules ionise:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$
$$\approx 99\% \qquad\qquad \approx 1\%$$

Similarly, strong and weak bases can be represented using equilibrium equations. Sodium hydroxide (NaOH) is a strong base and so dissociates fully:

$$NaOH(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + H_2O(l)$$
$$0\% \qquad\qquad 100\%$$

Methylamine (CH_3NH_2) is a weak base and only some of the molecules dissociate:

$$CH_3NH_2(l) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$
$$\approx 99\% \qquad\qquad \approx 1\%$$

Syllabus link
Chapters 14 and 18 of *Nelson QCE Chemistry Units 1 & 2* explained the concept of strong/weak acids and bases and molarity.

From the equilibrium equations above, it can be seen that a strong acid such as hydrochloric acid will have many more ions in solution than a weak acid such as ethanoic acid. The same can be said for strong and weak bases.

A simple way to differentiate between a strong acid (or base) and a weak acid (or base) is to measure their relative electrical conductivities by using the simple apparatus shown in **Figure 4.2.5**. A solution's ability to conduct electricity is determined by the number of ions it contains. The more ions, the greater the conductivity. A strong acid solution contains more ions and so will have a higher electrical conductivity than a weak acid.

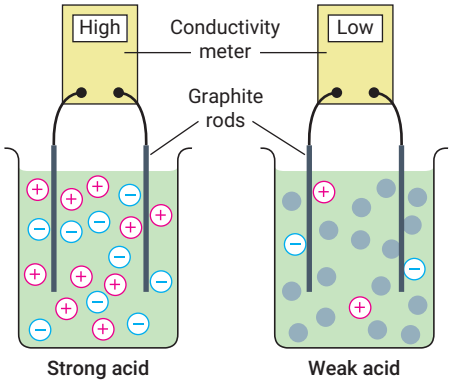


FIGURE 4.2.5 Apparatus for measuring the conductivity of strong and weak acids

Another way to differentiate between a strong acid and a weak acid is to look at the rate of reaction with metals. Magnesium reacts with an acid and produces hydrogen gas. The more concentrated the acid, the faster the magnesium will react, and you will see lots of bubbles of hydrogen being produced quickly. A strong acid and weak acid of the same concentration will react at different rates with the same metal. As shown in **Figure 4.2.6**, a strong acid has more hydrogen ions in the same concentration as the weak acid and will react faster than the weak acid. The weak acid will eventually produce the same amount of hydrogen gas as the strong acid from the same amount of magnesium; it will just take longer. At the same concentration, the stronger acid will also have a lower pH.

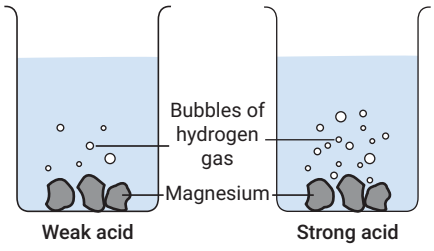


FIGURE 4.2.6 Reactions between strong and weak acids with magnesium metal. The strong acid produces more bubbles of hydrogen gas than the weak acid at the start of the reaction.

Discriminating between strong and weak acids and bases involves understanding how they differ in their behaviour in aqueous solutions. **Table 4.2.2** summarises how they can be differentiated on the basis of extent of dissociation, rate of reaction, pH and electrical conductivity.

TABLE 4.2.2 Properties to discriminate between strong and weak acids and bases

Property	Strong acids/bases	Weak acids/bases
Extent of dissociation/ ionisation Note: There is a relationship between dissociation and strength.	All molecules ionise (dissociate) in water.	Only some molecules ionise (dissociate) in water.
Rate of reaction	The reaction occurs more rapidly with other substances because of the high concentration of ions in solution.	The reaction occurs slowly with other substances because of the low concentration of ions in solution.
pH Note: There is a relationship between pH and concentration. This will be explored further in section 4.4.	Strong acids have a very low pH because of the high concentration of hydrogen ions. Strong bases have a very high pH because of the higher concentration of hydroxide ions (lower concentration of hydrogen ions).	Weak acids have a higher pH than strong acids of the same concentration because they release fewer hydrogen ions. Weak bases have a lower pH than strong bases of the same concentration because they release fewer hydroxide ions.
Electrical conductivity	They are good conductors of electricity because they completely ionise (dissociate) into ions, which carry electric current. They are strong electrolytes.	They are poor conductors of electricity because only some molecules dissociate, resulting in fewer ions in solution. They are weak electrolytes.

These differences are crucial when predicting and explaining the behaviour of acids and bases in various chemical reactions and practical applications.

LEARNING CHECK 4.2

DESCRIBING

1 **Define**:

a strong acid
b weak acid
c concentrated acid
d dilute acid.

APPLYING

2 Write chemical equations to show the ionisation/dissociation of the following substances in water.

a Nitric acid (HNO_3)
b Oxalic acid ($H_2C_2O_4$)
c Barium hydroxide ($Ba(OH)_2$)
d Propylamine ($CH_3CH_2CH_2NH_2$)

ANALYSING

3 Sulfuric acid (H_2SO_4) and carbonic acid (H_2CO_3) are diprotic acids. **Identify** which acid has the higher conductivity (assume the two acids are of the same concentration). **Justify** your answer with equilibrium equations.

4 **Analyse** the data in Table 4.2.3 to **determine** the strengths of bases X and Y.

TABLE 4.2.3 Data for two bases X and Y

Base	Concentration (mol L^{-1})	pH	Electrical conductivity (mS cm^{-1})
X	0.01	11.98	2.36
Y	0.01	8.74	0.90

5 Table 4.2.4 shows relative conductivity values for five substances, all of 1 mol L^{-1} concentration. The substances tested were, in no particular order, carbonic acid (H_2CO_3), hydrochloric acid (HCl), ethanoic acid (CH_3COOH), phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4).

From the results, **identify** each substance. **Explain** your reasoning.

TABLE 4.2.4 Relative conductivity values for five substances

Substance	Relative conductivity
A	8.0×10^{-4}
B	2.0
C	9.2×10^{-4}
D	1.7×10^{-3}
E	1.0

4.3 Self-ionisation of water

There is experimental evidence to show that in extremely pure water, some water molecules react with each other to produce hydronium ions ($H_3O^+(aq)$) and hydroxide ions ($OH^-(aq)$). This is shown in Figure 4.3.1. This is an equilibrium reaction.

Water undergoes self-ionisation according to the equation:

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

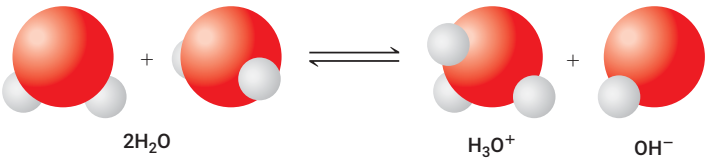


FIGURE 4.3.1 Water reacts with itself in an equilibrium reaction to form hydronium and hydroxide ions.

self-ionisation constant (K_w) the equilibrium expression that shows water ionising into two ions

This reaction occurs only to a very, very small extent; it is reversible, and the equilibrium constant is small. Only a small proportion of water molecules ionise; therefore, water is considered a weak electrolyte. The concentration of water is very large (approximately 55 M) and so effectively does not change significantly when it self-ionises. To represent this, we use the **self-ionisation constant (K_w)**, the ionic product constant for water, where $K_w = [H^+][OH^-]$. Since $[H_2O(l)]$ does not change significantly, it can be removed from the self-ionisation constant.

FORMULA AND DATA BOOK

In pure water, the concentration of H^+ equals the concentration of OH^-:

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

This means that:

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 25°C \text{ (or } 298 \text{ K)}$$

$$\text{Therefore, } [H^+]^2 = 10^{-14}$$

$$\text{Therefore, } [H^+] = \sqrt{10^{-14}}$$

$$= 10^{-7} \text{ M}$$

So, at 25°C, when water is neutral, $[H^+] = [OH^-] = 10^{-7}$ M. This is true *only* when the temperature is 25°C.

When $[H^+] > [OH^-]$, the solution is acidic. At 25°C, this is when $[H^+] > 10^{-7}$ M. When $[H^+] < [OH^-]$, the solution is basic or alkaline. At 25°C, this is when $[H^+] < 10^{-7}$ M.

KEY FORMULA

Ionic product constant for water

$K_w = [H^+]\,[OH^-]$, where $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 25°C (or 298 K)

Weblinks

Self-ionisation of water and the pH scale

Self-ionisation of water

Water autoionisation and K_w

WORKED EXAMPLE 4.3.1

Calculate the concentrations of H^+ ions and OH^- ions in a 3.48 M solution of HCl.

ANSWER

1 **Write the ionisation equation.**
$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

2 **Determine [H⁺] from the acid concentration.**
HCl is a strong acid and so every HCl molecule will dissociate.
Since the relationship between HCl and H_3O^+ is 1:1, if [HCl] is 3.48 M, then $[H^+] = 3.48$ M

3 **Determine the formula.**
Use $K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$ to determine $[OH^-]$.

4 **Substitute the known values.**

$$3.48 \times [OH^-] = 1.00 \times 10^{-14}$$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{3.48} = 2.87 \times 10^{-15} \text{ M}$$

The concentration of OH^- in this HCl solution is *very* small. We would expect this for a solution of a strong acid.

WORKED EXAMPLE 4.3.2

A solution of potassium hydroxide (KOH) is prepared in a volumetric flask. 150 g of KOH is dissolved in de-ionised water and the solution is made up to 250.00 mL. Calculate the concentrations of the H_3O^+ ions and OH^- ions in this solution.

ANSWER

1 **Determine the formula to calculate the concentration of the potassium hydroxide solution.**
Remember that volume is calculated in litres.

$$c(KOH) = \frac{n}{V}$$

2 **Calculate the amount of KOH.**

$$n(KOH) = \frac{m}{M} = \frac{150}{56.11} = 2.673 \text{ mol}$$

3 Calculate the concentration of KOH.

$c(\text{KOH}) = \dfrac{2.673}{0.250} = 10.69\ \text{M}$

4 Write the dissociation equation.

$\text{KOH(s)} \rightarrow \text{K}^+\text{(aq)} + \text{OH}^-\text{(aq)}$

5 Determine [OH⁻] from the KOH concentration and substitute the known values.

KOH is a strong base and so every KOH molecule will dissociate.

Since the relationship between KOH and OH^- is a 1:1, if [KOH] is 10.69 M, then $[OH^-] = 10.69$ M

Use $K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$ to determine $[H^+]$.

$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$

$[H^+] \times 10.69 = 1.00 \times 10^{-14}$

$[H^+] = \dfrac{1.00 \times 10^{-14}}{10.69} = 9.35 \times 10^{-16}\ \text{M}$

Again, this is a *very* small number, which is to be expected in a concentrated alkaline solution.

LEARNING CHECK 4.3

DESCRIBING

1 a Explain what is meant by the self-ionisation of water.

b Define K_w.

APPLYING

2 Calculate the concentrations of the H^+ ions and OH^- ions in the following solutions.

a 1.45 M HNO_3

b 0.89 M NaOH

c 1.50 M H_2SO_4 (consider the number of H^+ that will be produced when ionised)

d 0.89 M $Ba(OH)_2$ (consider the number of OH^- that will be produced when dissociated)

e 25 g of KOH dissolved in 50 mL of water (Recall that $n = \dfrac{m}{M}$.)

f 2.76 g of HCl dissolved in 125 mL of water

4.4 pH scale

Weblink
What is the pH scale?

The pH scale is a measure of the concentration of hydronium ions. The concentration can vary widely, generally from 1 M to 1.00×10^{-14} M. Because this range is so large, chemists introduced the pH scale to measure the concentration. The pH scale can indicate the acidic or basic nature of substances.

KEY FORMULA

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

The pH of a solution is defined as the negative logarithm (to the base 10) of the hydrogen ion concentration: $\text{pH} = -\log_{10}[H^+]$

Sometimes, you may see the concentration of hydronium ions $[H_3O^+]$ used to calculate pH or when discussing acids; however, $[H^+]$ is generally used for simplicity.

A change of 1 unit of pH is the same as changing the concentration of the solution by a factor of 10. This is because of the logarithmic pH – a change in concentration of H^+ ions in solution by a factor of 10.

- For a solution in which $[H^+] = 0.1$ M (or 10^{-1}), the pH is 1.0.
- For a solution in which $[H^+] = 0.01$ M (or 10^{-2}), the pH is 2.0.

FORMULA AND DATA BOOK

- For a solution in which $[H^+] = 0.000\,0001$ M (or 10^{-7}), the pH is 7.0.
- Notice that $[H^+] = 10^{-pH}$.

It is relatively straightforward to work out the pH when the concentration is 0.1 or 0.01, or any factor of 10. When the concentration is 0.015, which is between 0.1 and 0.01, you need a calculator. For $[H^+] = 0.015$ M, the pH $= -\log_{10}(0.015) = 1.82$.

Syllabus link
Chapter 18 of *Nelson QCE Chemistry Units 1 & 2* introduces the pH scale.

WORKED EXAMPLE 4.4.1

a Calculate the pH, given $[H^+] = 1.4 \times 10^{-5}$ M.
b Calculate $[H^+]$ when pH = 8.5.

ANSWERS

a **1** **Determine the formula.**
$pH = -\log_{10}[H^+]$
2 **Substitute the known values.**
$pH = -\log_{10}(1.4 \times 10^{-5})$
3 **Calculate the answer.**
pH = 4.9

b **1** **Determine the formula.**
Since $[H^+] = 10^{-pH}$
2 **Substitute the known values.**
$[H^+] = 10^{-8.5}$
3 **Calculate the answer.**
$[H^+] = 3.2 \times 10^{-9}$ M

pH of polyprotic acids

The pH of a 0.1 M solution of sulfuric acid (H_2SO_4) is about 0.69, not 1.0, which means it is a more acidic solution. The pH indicates that there are more hydronium ions than 0.1 M. The pH value can be used to calculate the concentration of hydronium ions $[H_3O^+]$ as almost 0.2 M. This is because sulfuric acid reacts with water, as shown:

$$H_2SO_4(l) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H_3O^+(aq)$$

Recall from section 4.1 that the complete ionisation of sulfuric acid occurs in two steps. The second step involves HSO_4^-. This is a weaker acid than sulfuric acid and not all the molecules will react with water and ionise. So, the concentration of hydronium ions is not quite twice the concentration of the acid. However, in neutralisation reactions, both protons will be donated. Effectively, the diprotic acid requires twice the number of moles of base.

For each molecule of a diprotic acid, the number of protons that may be donated is two. The concentration of the acid may be 0.1 M, but as two protons can be donated when reacting with strong bases, this must be taken into account. The hydronium ion concentration of strong diprotic acids is greater than that of a monoprotic acid of the same acid concentration.

Calculating the pH of alkaline solutions

If an alkaline solution has a known concentration of hydroxide ion, $[OH^-]$, we can calculate the pH from the relationship:

$$K_w = [OH^-][H^+] = 1.00 \times 10^{-14}$$

Once the hydrogen (or hydronium) ion concentration, $[H^+]$, is known, we can calculate the pH.

In a 0.01 M solution of NaOH, $[OH^-] = 0.01$.

$$K_w = 1.00 \times 10^{-14} = [H^+] \times 0.01$$

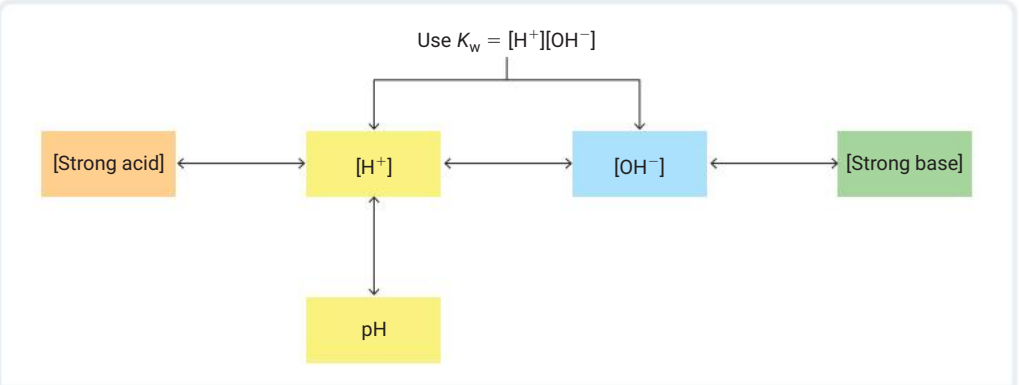


FIGURE 4.4.1 The pathway for performing pH calculations for strong acids and strong bases

$$\text{So, } [H^+] = \frac{1.00 \times 10^{-14}}{0.01} = 1.00 \times 10^{-12}$$

$$\text{So, pH} = -\log_{10}[H^+] = -\log_{10}(1.00 \times 10^{-12}) = 12$$

Figure 4.4.1 shows the pathway for performing pH calculations for strong acids and bases. **Table 4.4.1** lists the pH values for solutions and corresponding $[H^+]$ and $[OH^-]$. Notice that the pH scale 0–14 corresponds to these values. This range is due to the K_w of water, which is equal to 1.00×10^{-14} at 25°C. However, lower and higher pH values are possible for concentrated solutions of strong acids and bases; for example, 10 M KOH has a pH of just less than 15. **Figure 4.4.2** shows the pH scale.

TABLE 4.4.1 pH values for solutions and the corresponding hydrogen and hydroxide ion concentrations

pH	1.0	3.0	5.0	7.0	9.0	11.0	13.0
$[H^+]$	10^{-1}	10^{-3}	10^{-5}	10^{-7}	10^{-9}	10^{-11}	10^{-13}
$[OH^-]$	10^{-13}	10^{-11}	10^{-9}	10^{-7}	10^{-5}	10^{-3}	10^{-1}

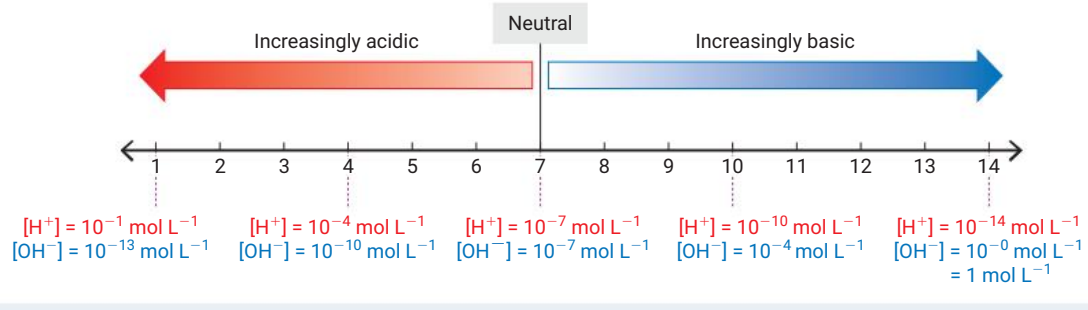


FIGURE 4.4.2 The pH scale

WORKED EXAMPLE 4.4.2

Calculate the pH of a 0.02 M solution of sodium hydroxide.

ANSWER

1 Write the dissociation equation.

NaOH is a strong base and dissociates 100% in solution.

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

2 Determine $[OH^-]$.
The relationship between NaOH and OH^- is 1:1.
$[OH^-]$ = original [NaOH] = 0.02 M

3 Determine the formula.
$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$

4 Substitute the known values.
$[H^+][0.02] = 1.00 \times 10^{-14}$

$$\text{Hence, } [H^+] = \frac{1.00 \times 10^{-14}}{0.02}$$
$$= 5 \times 10^{-13}\ \text{M}$$

5 Calculate the pH of the solution.
$pH = -\log[H^+]$
$= -\log(5 \times 10^{-13}) = 12.3$

Weblink
pH and pOH calculations

Worksheet
The pH scale

The pOH scale

The pH scale is a measure of the concentration of hydrogen ions, H^+ and is determined by using $pH = -\log_{10}[H^+]$

In the same way, it is possible to produce a scale that is a measure of the concentration of hydroxide ions, OH^-. This is called the pOH scale and is determined using:

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

So, if a strong acid has a low pH, then a strong base has a low pOH.
For $[OH^-] = 0.02$ M, the $pOH = -\log_{10}(0.02) = 1.7$.

KEY FORMULA

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

FORMULA AND DATA BOOK

WORKED EXAMPLE 4.4.3

a Calculate the pOH, given $[OH^-] = 1.25 \times 10^{-5}$ M

b Calculate $[OH^-]$ when the pOH = 9.2

ANSWERS

a 1 Determine the formula.
$pOH = -\log_{10}[OH^-]$

2 Substitute the known values.
$pOH = -\log_{10}(1.25 \times 10^{-5})$

3 Calculate the answer.
pOH = 4.9

b 1 Determine the formula.
$[OH^-] = 10^{-pOH}$

2 Substitute the known values.
$[OH^-] = 10^{-9.2}$

3 Calculate the answer.
$[OH^-] = 6.3 \times 10^{-10}$ M

You may be noticing another relationship between pH and pOH in these examples. If we add pH to pOH, the answer is 14. So, if we know the pH of a solution, we can easily work out the pOH and vice versa. For example, the pOH of a solution with a pH of 5.3 would be equal to:

$$pOH = 14 - pH = 14 - 5.3 = 8.7$$

Figure 4.4.3 shows all the interrelationships between $[H^+]$, $[OH^-]$, pH and pOH.

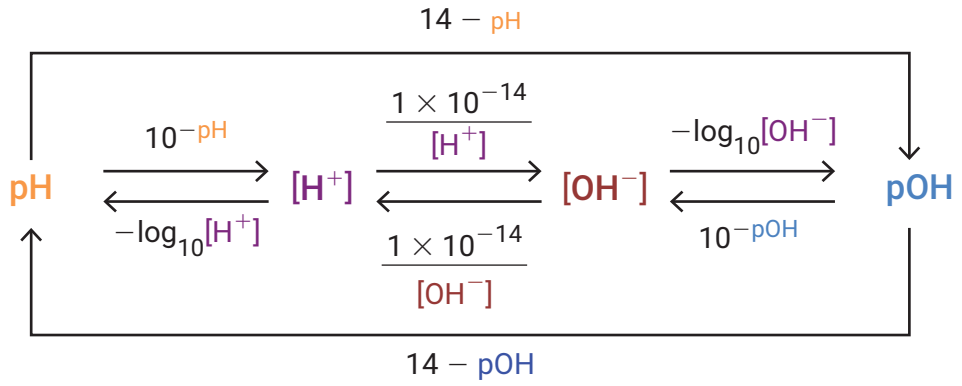


FIGURE 4.4.3 Interrelationships between $[H^+]$, $[OH^-]$, pH and pOH

Syllabus link
Chapter 17 of *Nelson QCE Chemistry Units 1 & 2* described neutralisation reactions.

neutral neither acidic nor basic; has a pH of 7

pH of acid–base reactions

Neutralisation is the reaction of an acid and a base to form a salt and water. According to this definition, if we mix the correct amounts of acid and base, then the resultant solution is **neutral** – neither acidic nor basic. If the solution is not neutral – that is, it does not have a pH of 7 – it is because one reactant was in excess. However, this is only true when strong acids are reacted with strong bases.

WORKED EXAMPLE 4.4.4

If 25 mL of a 0.50 mol L^{-1} solution of NaOH was added to 75 mL of a 0.3 mol L^{-1} solution of H_2SO_4, calculate the final pH of the solution.

ANSWER

1 Write a balanced equation.

$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

2 Calculate the number of moles of each substance.

$c(NaOH) = 0.50$ mol L^{-1}, $V = 25$ mL $= 0.025$ L, $n = ?$

$$0.50 = \frac{n}{0.025}$$

$n(NaOH) = 0.50 \times 0.025 = 0.0125$ mol

$c(H_2SO_4) = 0.30$ mol L^{-1}, $V = 75$ mL $= 0.075$ L, $n = ?$

$$0.30 = \frac{n}{0.075}$$

$n(H_2SO_4) = 0.30 \times 0.075 = 0.0225$ mol

3 Determine which reactant is in excess.

To determine the theoretical value of H_2SO_4 required to react with all 0.0125 mol of NaOH:

$$n(H_2SO_4) = n(NaOH) \times \frac{1}{2}$$

$= 0.006\,25$ mol

Since there is 0.0225 mol of H_2SO_4 available, it is in excess.

H_2SO_4 is in excess by $0.0225 - 0.006\,25 = 0.016\,25$ mol

4 Calculate [H^+].

Since it is a diprotic acid, the relationship between $n(H_2SO_4)$ and $n(H^+)$ is 1:2.

Therefore, $n(H^+) = 0.01625 \times 2 = 0.0325$

Using $c = \frac{n}{V}$, where $V = 25\,mL + 75\,mL = 0.100\,L$

$[H^+] = \frac{0.0325}{0.100} = 0.325\,mol\,L^{-1}$, H^+ is in excess.

5 Calculate the pH of the final solution.

$pH = -\log[H^+]$

$= -\log(0.325) = 0.488$

LEARNING CHECK 4.4

APPLYING

1 **Calculate** the pH of a solution, given:

a $[H^+] = 0.001$ M **b** $[H^+] = 1.2 \times 10^{-5}$ M.

2 Barium hydroxide is a strong base. **Calculate** the pH of a 0.02 M barium hydroxide solution.

3 If the pH of the NaOH solution was 9.5, **calculate** the concentration of the solution.

4 **Determine** the pOH of a solution, given:

a $[OH^-] = 0.0001$ M **b** $[OH^-] = 6.5 \times 10^{-5}$ M.

5 **Determine** the concentrations of H^+ and OH^- in an aqueous solution of:

a black coffee, pH 5.0
b oven cleaner, pH 14.0
c cola drink, pH 2.5
d toothpaste, pH 5.8.

6 **Calculate** the pH of the solutions formed with the addition of:

a 100 cm^3 of water to 25 cm^3 of 0.100 mol dm^{-3} NaOH
b 25 cm^3 of water to 100 cm^3 of 0.100 mol dm^{-3} $Ba(OH)_2$.

7 **Calculate** the resultant pH when:

a 50 mL of 0.1 M NaOH is added to 100 mL of 0.1 M HCl
b 50 mL of 0.2 M HCl is added to 100 mL of 0.1 M NaOH
c 100 mL of a solution of pH 6 is diluted with 100 mL of water.

8 **Determine** how many grams of barium hydroxide is required to neutralise 500 mL of 0.2 M nitric acid. (Recall that $n = \frac{m}{M}$.)

9 **Determine** how much 0.1 M NaOH is required to neutralise 100 mL of 0.277 M hydrochloric acid solution.

10 **Calculate** the pH of a solution produced by mixing 38.95 mL of 0.108 M barium hydroxide ($Ba(OH)_2$) and 44.86 mL of 0.116 M nitric acid (HNO_3).

11 25 mL of a 1.087 M solution of hydrochloric acid is placed into a 250.00 mL volumetric flask. Enough distilled water is added to the flask to make up the volume to 250.00 mL. 20.00 mL of this solution was transferred to a 100.00 mL volumetric flask and made up to the mark with distilled water. **Determine** the pOH of this solution.

12 **Determine** the volume of water that would need to be added to 500 mL of HCl to change the pH from 1.00 to 2.00. **Explain** your reasoning.

CHAPTER SUMMARY

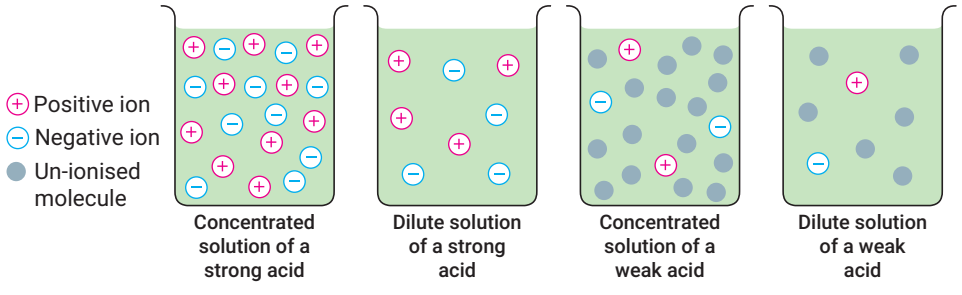
Properties of acids and bases

Acids		Bases	
Examples	**Properties**	**Examples**	**Properties**
Monoprotic • Hydrochloric acid (HCl) • Nitric acid (HNO_3) • Ethanoic acid (CH_3COOH) **Diprotic** • Sulfuric acid (H_2SO_4) **Triprotic** • Phosphoric acid (H_3PO_4)	• Taste sour • pH < 7 • Turn blue litmus red • Neutralise bases to produce a salt and water • Proton donors (proton = H^+) • Increase $[H^+]$ in solution • Are electrolytes • React with carbonates to produce a salt, water and CO_2 • React with active metals to produce a salt and H_2	• Sodium hydroxide (NaOH) • Potassium hydroxide (KOH) • Barium hydroxide ($Ba(OH)_2$) • Ammonia (NH_3) • Methylamine (CH_3NH_2)	• Taste bitter • pH > 7 • Bases turn red litmus blue • Neutralise acids to produce salt and water • Increase $[OH^-]$ in solution • Are electrolytes • Feel slippery

Acid and base strength

Property	Strong acids/bases	Weak acids/bases
Extent of dissociation	Complete ionisation/ dissociation Examples: $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$ $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$ The products have a higher concentration.	Only some particles ionise/dissociate Examples: $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$ $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ The reactants have a higher concentration.
Rate of reaction	Fast	Slow
pH	Extreme (low for acids, high for bases)	Moderate (closer to neutral)
Electrical conductivity	High	Low

Concentration vs strength



Self-ionisation of water

- Water can self-ionise according to the equation:

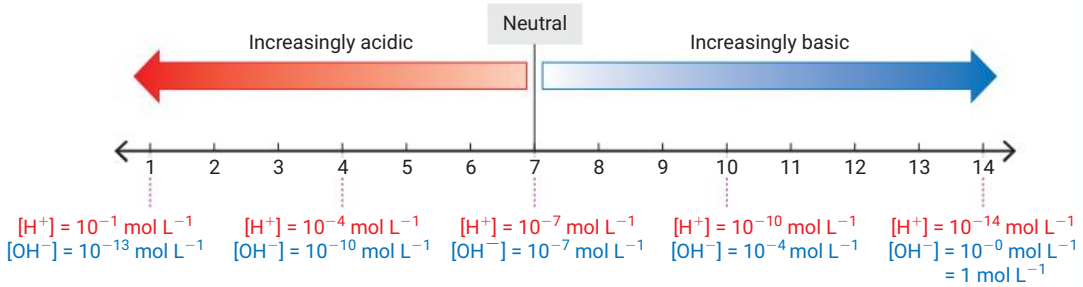
$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

- Water is a weak electrolyte.
- Self-ionisation constant, K_w, the ionic product constant for water.

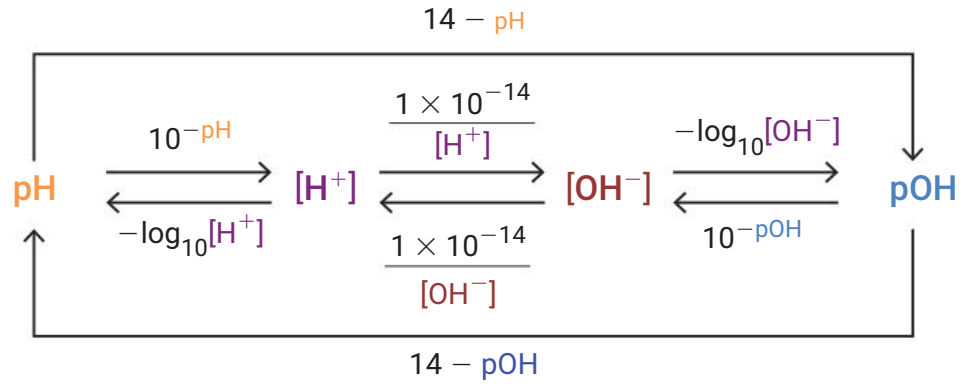
$$K_w = [H^+][OH^-], \text{ where } K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 25°C \text{ (or } 298 \text{ K)}$$

- In pure water, the concentration of H^+ equals the concentration of OH^-: $[H^+] = [OH^-]$.
  At 25°C, when water is neutral, $[H^+] = [OH^-] = 10^{-7}$ M.

pH scale



Relationship between pH, pOH, [H⁺] and [OH⁻]



CHAPTER EXAM

MULTIPLE CHOICE

1. Identify which of the following could be categorised as a strong diprotic acid.

A H_2S

B H_2SO_3

C H_2SO_4

D $H_2C_2O_4$

2. Identify which of the following bases would have the highest electrical conductivity.

A NH_3

B PH_3

C RbOH

D CH_3NH_2

3. Identify which of the following shows the correct ionisation products in the correct order for arsenic acid (H_3AsO_4).

A $AsO_4^{3-} \rightarrow HAsO_4^{2-} \rightarrow H_2AsO_4^-$

B $AsO_4^{3-} \rightarrow H_2AsO_4^- \rightarrow HAsO_4^{2-}$

C $HAsO_4^{2-} \rightarrow AsO_4^{3-} \rightarrow HAsO_4^{2-}$

D $H_2AsO_4^- \rightarrow HAsO_4^{2-} \rightarrow AsO_4^{3-}$

4. Which of the following is true about weak acids?

I They are poor conductors of electricity.

II They have a low pH.

III They react slowly with carbonates to produce carbon dioxide.

A I and II only

B I and III only

C II and III only

D I, II and III

 SCSA 2023 MCQ Q19

5. What can be concluded from the statement $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C?

A Pure water has a pH of 14.

B Pure water does not react with acids or bases.

C The concentration of hydrogen and hydroxide ions is not equal.

D The concentration of hydrogen ions is 1.0×10^{-7} mol L^{-1}.

6. In an aqueous solution of 0.0034 M H_2SO_4, what is $[H_3O^+(aq)]$?

A 1.7×10^{-3} M

B 3.4×10^{-3} M

C 6.8×10^{-3} M

D 0.034 M

7. Calculate the pH of a solution if the concentration of RbOH is 2.45×10^{-3} M.

A 2.6

B 11.34

C 11.39

D 13

8. A solution containing nitric acid (HNO_3) has a pH of 2.3. Calculate $[OH^-]$.

A 5.0×10^{-3} M
B 2.3×10^{-7} M
C 1.0×10^{-12} M
D 2.0×10^{-12} M

9. Which of the following is possible for an acid?

	Acid strength	Concentration (M)	pH
A	Strong	0.01	2.0
B	Weak	0.01	1.0
C	Strong	3	5.5
D	Weak	3	–0.5

10. Two flasks contain two different acids labelled as HA and HB. A student measures the pH of each flask as pH 1 and pH 3, respectively. Which of the following statements is true?

A HA is stronger that HB.
B HB is stronger than HA.
C $[H^+]$ in the solution of HB is three times greater than $[H^+]$ in the solution of HA.
D $[H^+]$ in the solution of HA is 100 times greater than $[H^+]$ in the solution of HB.

SHORT RESPONSE

11. Two solutions, X and Y, are 100% ionised and are known to be acidic. Solution Y has an electrical conductivity approximately twice that of solution X. If both solutions have the same concentration, **deduce** an identity for solution X.

12. **Calculate** $[OH^-]$ when the pOH of a solution is:

a 6
b 11.7.

13. **Determine** the pH of each of the following strong electrolytes.

a 0.01 M HNO_3
b 0.005 M $Ca(OH)_2$
c 0.1 M NaOH
d 0.005 M H_2SO_4

CROSS-CHAPTER QUESTION

14. Pure water undergoes self-ionisation according to the equation:
$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

The self-ionisation of water, K_w, is $[H^+][OH^-] = 1.00 \times 10^{-14}$ at 25°C.

The following data was collected during an experiment.

Temperature (°C)	K_w
0	1.5×10^{-15}
10	3.0×10^{-15}
20	6.8×10^{-15}
30	1.5×10^{-14}
40	3.0×10^{-14}

a **Calculate** $[H^+]$ and the pH of water at:
- **i** 10°C
- **ii** 40°C.

b Using Le Châtelier's principle, **determine** whether the self-ionisation of water is an endothermic or exothermic process.

c **Identify** what changes would occur to $[H^+]$ and the pH when NaOH is added to the pure water.

d **Identify** what changes would occur to $[OH^-]$ and the pOH when $AgNO_3$ is added to the pure water.

e **Evaluate** the following statement. 'Pure water is still neutral no matter what temperature the water is.' **Explain** your reasoning.

DATA ANALYSIS

15. Apply understanding and analyse data

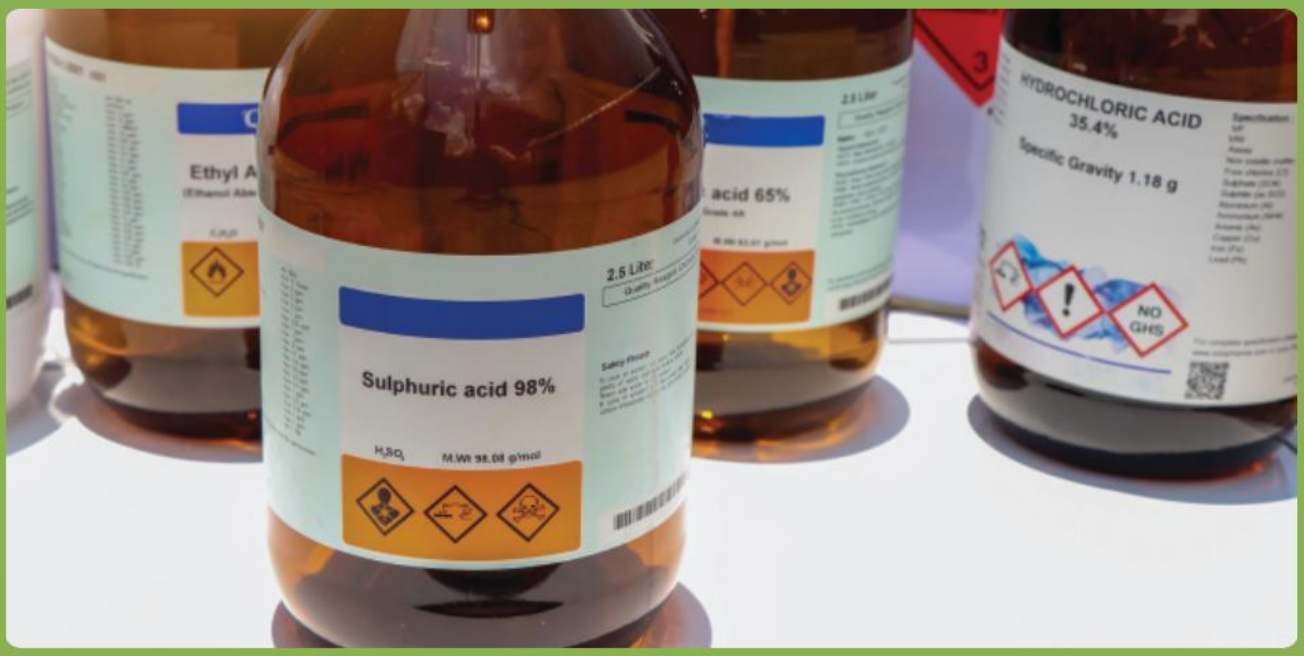
Four monoprotic acids of the same concentration are labelled as follows.

Solution	Label
A	$[OH^-] = 5.0 \times 10^{-11}$ M
B	$[H^+] = 0.20$ M
C	pOH = 11.30
D	pH = 1.20

Sequence the four solutions in order of decreasing acidity. Use calculations to support your answer.

CHAPTER 5

Brønsted–Lowry model



chemical industry/Shutterstock.com

SYLLABUS DOT POINTS

SCIENCE UNDERSTANDING

- 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).
- 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.

Introduction

Work carried out independently by Danish chemist Johannes Nicolaus Brønsted (1879–1947) and English chemist Thomas Martin Lowry (1874–1936) in 1923 led to some important insights in acid–base chemistry, including recognising the reversibility of acid and base reactions and quantifying the strength of acids and bases.

An appreciation of this theory enables a clearer understanding of the role of buffer solutions in many important biological systems.

Practical

- Simple buffer systems (online-only resource)

Worksheets

- The Brønsted–Lowry model
- Buffers and Le Châtelier's principle

Nelson MindTap

To access resources above, visit **cengage.com.au/nelsonmindtap**

ASSUMED KNOWLEDGE

- ✓ Acids donate protons.
- ✓ pH is a quantitative value that indicates how acidic or basic a substance is.
- ✓ The concept of strong and weak for acids and bases is based on the proportion/percentage of particles of acid or base that ionises or dissociates in water.
- ✓ At equilibrium, the forward and reverse reactions occur simultaneously.
- ✓ When the rates of the forward and reverse reactions are the same, equilibrium has been reached.
- ✓ Le Châtelier's principle is used to predict shifts in equilibrium as a result of a change.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ describe acids and bases using the Brønsted–Lowry model
- ✓ explain the Brønsted–Lowry model using chemical equations
- ✓ identify the acid and its conjugate base in a reaction
- ✓ Identify the base and its conjugate acid in a reaction
- ✓ determine the formula of the conjugate acid (or base) from any Brønsted–Lowry base (or acid)
- ✓ identify that amphiprotic species can act as Brønsted–Lowry acids or bases
- ✓ identify the nature of buffers and how they work
- ✓ apply Le Châtelier's principle to explain how buffer systems respond to addition of hydrogen ions and hydroxide ions.

5.1 Brønsted–Lowry model

The ammonia dilemma

Weblink
Reaction of ammonia with hydrogen chloride

Ammonia, a weak base, challenged early chemists' definition of a base. The dilemma facing chemists was that either ammonia was not a base or that their definition was inaccurate or incomplete. Some chemists argued that the definition was acceptable because when ammonia reacts with water, the following reaction occurs:

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

But ammonia gas reacts with hydrochloric acid fumes to form ammonium chloride. There is no water and no OH^- or O^{2-} ions are involved:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

This reaction showed that the original definition of an acid and a base needed to be redefined.

Redefining acids: Brønsted–Lowry acids

In the Brønsted–Lowry model, acids and bases are defined by their ability to donate or accept protons (H^+ ions). This model extends beyond the limitations of earlier definitions, such as the Arrhenius model, and applies to a broader range of chemical reactions, particularly those that occur in non-aqueous systems. This has resulted in new definitions for acids and bases.

- A Brønsted–Lowry acid is a substance that donates a proton (H^+) to another substance.
- A Brønsted–Lowry base is a substance that accepts a proton from another substance.

Therefore, an acid–base reaction is one in which the acid donates a proton (H^+) and the base accepts it.

In equilibrium systems, the Brønsted–Lowry model describes the dynamic process in which protons are transferred between acids and bases, leading to the formation of conjugate acid–base pairs. Members of a conjugate acid–base pair differ from each other by the presence or absence of the transferable H^+ (hydrogen ion). Conjugate acid–base pairs differ from each other by one (or sometimes more) proton.

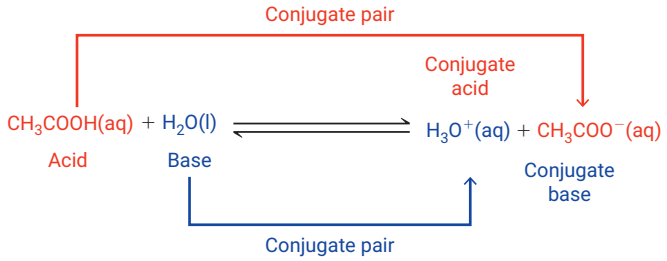


FIGURE 5.1.1 Forming a conjugate base and a conjugate acid

Consider the reaction of ethanoic acid (acetic acid) in water **(Figure 5.1.1)**:

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

In this reaction:

- CH_3COOH acts as a Brønsted–Lowry acid because it donates a proton (H^+) to water.
- H_2O acts as a Brønsted–Lowry base because it accepts the proton, forming the hydronium ion (H_3O^+).
- After donating a proton, CH_3COOH becomes its **conjugate base** (CH_3COO^-), while H_2O, after accepting a proton, becomes its **conjugate acid** (H_3O^+).

conjugate base the base that is formed when an acid donates one or more protons to a base

conjugate acid the acid that is formed when a base accepts one or more protons from an acid

In an equilibrium system, the forward and reverse reactions occur simultaneously, leading to the formation of conjugate acid–base pairs. The equilibrium can be simply expressed as:

$$HA + B \rightleftharpoons A^- + HB^+$$

- HA is the Brønsted–Lowry acid.
- B is the Brønsted–Lowry base.
- A^- is the conjugate base of the acid HA.
- HB^+ is the conjugate acid of the base B.

This continuous exchange of protons forms an equilibrium in which acids and bases coexist, and the system adjusts according to the conditions (e.g. changes in concentration or pressure) to maintain equilibrium. The Brønsted–Lowry model provides a framework for describing acid–base behaviour, emphasising the transfer of protons between conjugate pairs in equilibrium systems.

Sodium hydroxide (NaOH) can still be classified as a strong base using this definition. According to the Brønsted–Lowry definition of acids and bases, it is more correct to say that NaOH is an ionic compound that is the source of the strong base, OH^-.

In the reaction of ammonia with water:

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

ammonia is acting as a base and water is acting as an acid. Ammonium (NH_4^+) is the conjugate acid and hydroxide ions are the conjugate base **(Figure 5.1.2)**.

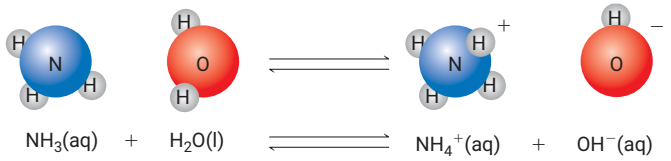
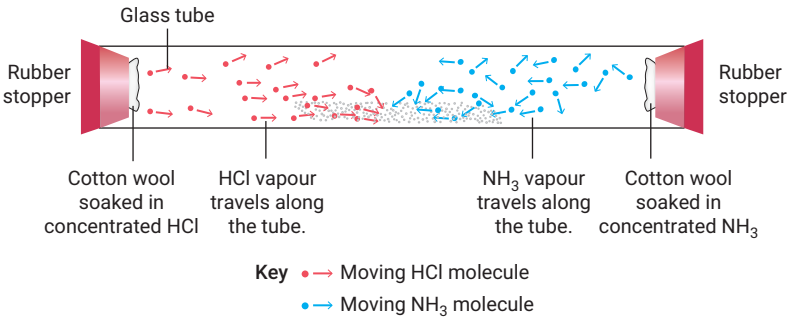


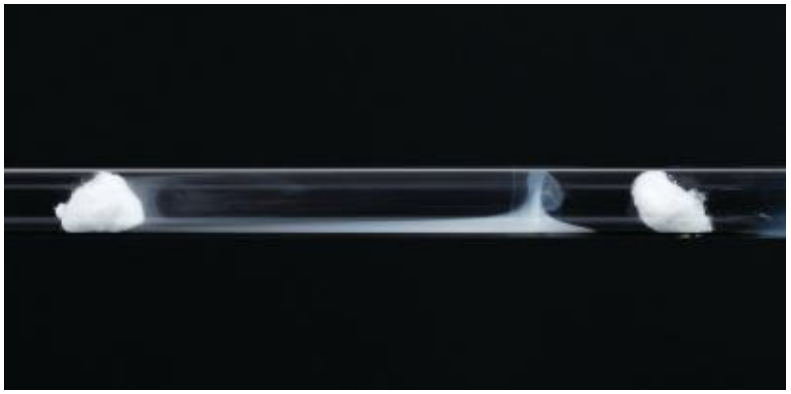
FIGURE 5.1.2 The ammonia molecule reacts with water to form an ammonium ion (conjugate acid) and a hydroxide ion (conjugate base).

In the reaction between ammonia gas and fumes of hydrochloric acid:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

ammonia accepts a proton, acting as a base, to form an ammonium ion (NH_4^+), the conjugate acid **(Figure 5.1.3)**. HCl is acting as an acid because it donates a proton to form a chloride ion (Cl^-), the conjugate base. This solves the ammonia dilemma.





Turtle Rock Scientific/Science Photo Library

FIGURE 5.1.3 The reaction between ammonia gas and hydrogen chloride gas produces a fine white powder of ammonium chloride.

WORKED EXAMPLE 5.1.1

Consider the reaction between bicarbonate ions (HCO_3^-) and ammonia (NH_3) in aqueous solutions. Identify the conjugate acid–base pairs in this reaction.

ANSWER

1 Write the equation for the reaction.

$HCO_3^-(aq) + NH_3(aq) \rightleftharpoons CO_3^{2-}(aq) + NH_4^+(aq)$

2 **Identify the proton transfer.**
In this reaction, HCO_3^- donates a proton to NH_3.

3 **Determine the Brønsted–Lowry acid and base.**
Acid: the substance that donated a proton; in this reaction, HCO_3^-.
Base: the substance that accepts a proton; in the reaction, NH_3.

4 **Identify the conjugate acid–base pairs.**
Conjugate acid: the species formed when a base accepts a proton; in this reaction, NH_4^+.
Conjugate base: the species formed when an acid donates a proton; in this reaction, CO_3^{2-}.

5 **Summarise the conjugate acid–base pairs.**
HCO_3^- (acid) and CO_3^{2-} (conjugate base)
NH_3 (base) and NH_4^+ (conjugate acid)

There is a relationship between the strength of an acid (or base) and the strength of its conjugate base (or conjugate acid):

- The stronger the acid, the weaker its conjugate base.
- The weaker the acid, the stronger its conjugate base.
- The stronger the base, the weaker its conjugate acid.
- The weaker the base, the stronger its conjugate acid.

Table 5.1.1 lists some conjugate acids and bases and their relative strengths.

TABLE 5.1.1 Relative strengths of acids and their conjugate bases

Strength of acid ↑

Acid	Conjugate base
HCl	Cl^-
H_2SO_4	HSO_4^-
HNO_3	NO_3^-
H_3O^+	H_2O
HSO_4^-	SO_4^{2-}
H_3PO_4	$H_2PO_4^-$
HF	F^-
CH_3COOH	CH_3COO^-
H_2CO_3	HCO_3^-
$H_2PO_4^-$	HPO_4^{2-}
NH_4^+	NH_3
HCO_3^-	CO_3^{2-}
HPO_4^{2-}	PO_4^{3-}
H_2O	OH^-

↓ Strength of conjugate base

Weblink
Brønsted–Lowry acid and bases

Worksheet
The Brønsted–Lowry model

LEARNING CHECK 5.1

DESCRIBING

1 State the earliest definition of acids and bases.

2 **Define**:

- **a** Brønsted–Lowry acid
- **b** Brønsted–Lowry base
- **c** conjugate acid–base pair
- **d** conjugate acid
- **e** conjugate base.

3 Carbonates are bases. The earlier definitions could not account for the behaviour of carbonates but the Brønsted–Lowry definition can. **Explain** why.

APPLYING

4 **Identify** the two conjugate acid–base pairs in each equation.

- **a** $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
- **b** $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$
- **c** $HSO_4^-(aq) + O^{2-}(aq) \rightleftharpoons SO_4^{2-}(aq) + OH^-(aq)$
- **d** $H_2PO_4^-(aq) + CO_3^{2-}(aq) \rightleftharpoons HPO_4^{2-}(aq) + HCO_3^-(aq)$
- **e** $HC_2H_3O_2(aq) + HS^-(aq) \rightleftharpoons C_2H_3O_2^-(aq) + H_2S(aq)$

5 Write the formula of the conjugate acids for each of the following bases.

- **a** HCO_3^-
- **b** OH^-
- **c** HPO_4^{2-}
- **d** $(CH_3)_2NH$
- **e** H_2O

6 Write the formula of the conjugate bases for each of the following acids.

- **a** HF
- **b** H_2SO_4
- **c** H_3PO_4
- **d** CH_3COOH
- **e** H_2O

7 **Identify** whether each set contains an acid–base conjugate pair.

- **a** HNO_2, NO_2^-
- **b** H_2CO_3, CO_3^{2-}
- **c** HCl, ClO_4^-
- **d** HS^-, H_2S
- **e** NH_3, NH_4^+

5.2 Amphiprotism

amphiprotic a substance or species that can gain or lose a hydrogen ion to act as an acid or a base

Many substances can act as an acid or a base; that is, they can donate a proton to a base or they can accept a proton from an acid. Such substances are called **amphiprotic** substances or species.

Water (H_2O) is a good example of an amphiprotic substance **(Figure 5.2.1)**. Consider the self-ionisation of water:

$$\underset{\text{Acid}}{H_2O(l)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons \underset{\text{Conjugate acid}}{H_3O^+(aq)} + \underset{\text{Conjugate base}}{OH^-(aq)}$$

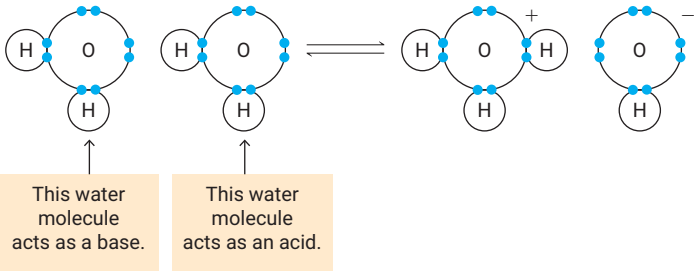


FIGURE 5.2.1 The amphiprotic nature of water: water can act as an acid or a base, depending on what species are present.

Consider the dihydrogen phosphate ion ($H_2PO_4^-$). This acts as an acid by donating one of its protons:

$$\underset{\text{Acid}}{H_2PO_4^-(aq)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons \underset{\text{Conjugate base}}{HPO_4^{2-}(aq)} + \underset{\text{Conjugate acid}}{H_3O^+(aq)}$$

The $H_2PO_4^-$ ion can also act as a base by accepting a proton:

$$\underset{\text{Base}}{H_2PO_4^-(aq)} + \underset{\text{Acid}}{H_2O(l)} \rightleftharpoons \underset{\text{Conjugate acid}}{H_3PO_4(aq)} + \underset{\text{Conjugate base}}{OH^-(aq)}$$

How the amphiprotic substance behaves depends on the other reactant.

LEARNING CHECK 5.2

DESCRIBING

1 **Describe** how can you identify an amphiprotic substance.

APPLYING

2 **Explain**, with the aid of equations, why the hydrogencarbonate ion (HCO_3^-) is amphiprotic.

3 **Explain**, with the aid of equations, why the hydrogen sulfate ion (HSO_4^-) is amphiprotic.

5.3 Buffers

Buffers are solutions that can maintain a pH within a certain range, despite a small amount of acid or base being added. These chemicals play an important role in maintaining the pH of the body within a narrow range. Buffers enable enzymes to continue to function effectively by protecting them from being denatured because of changes in acidity.

buffer a solution that maintains a constant pH when small amounts of acid and base are added

Buffers are solutions in which a weak acid and its conjugate base are both present, or in which a weak base and its conjugate acid are both present. An example is a solution of carbonic acid and sodium hydrogencarbonate (H_2CO_3/HCO_3^-).

The pH of a buffer is determined by the:

- degree to which the acid dissociates (how weak it is)
- ratio of weak base [A^-] to weak acid [HA] in solution.

If a buffer has more acid than base, more H^+ ions are present, and the pH is lower.

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

Syllabus link
Chapter 2 describes Le Châtelier's principle.

If a strong acid is added, the overall pH decreases. According to Le Châtelier's principle, the extra H_3O^+ shifts the equilibrium reaction to the left to partially reduce the concentration of H_3O^+. The pH then increases, but is still slightly lower than the original value. Adding a strong base (OH^-) results in the added OH^- reacting with the H_3O^+. The system will try to oppose this change and move to produce more H_3O^+, shifting to the right. The pH is decreased to near the original value **(Figure 5.3.1)**.

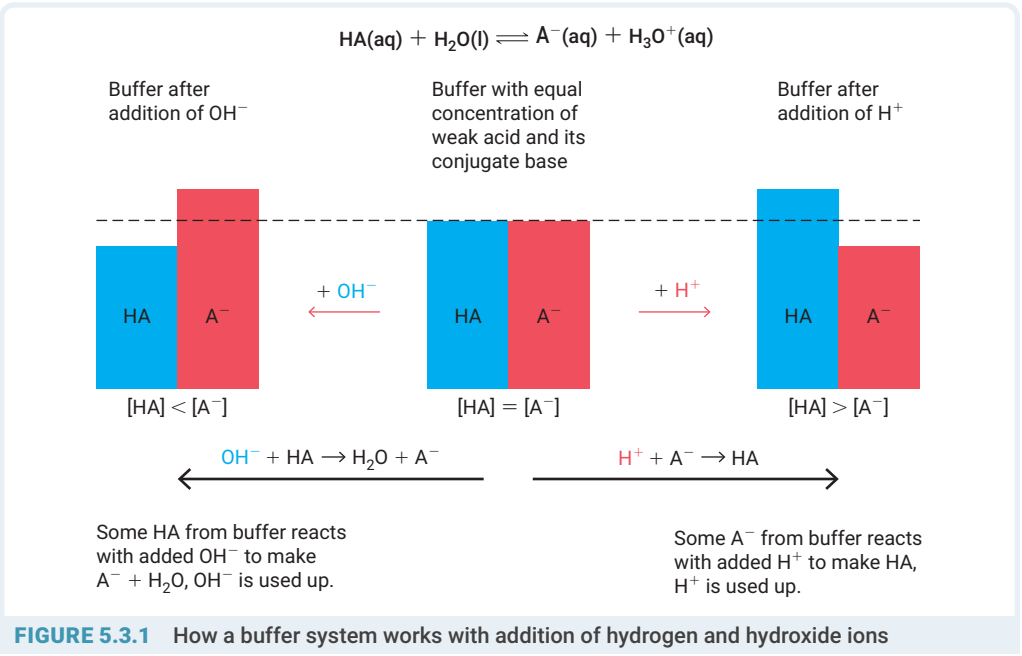


FIGURE 5.3.1 How a buffer system works with addition of hydrogen and hydroxide ions

Practical
Simple buffer systems

The pH is maintained by manipulating the proportion of weak base (A^-) and weak acid (HA) in solution. As long as $\frac{[A^-]}{[HA]}$ is between $\frac{1}{10}$ and 10, the pH is within 1 unit and the solution is therefore buffered. If the buffer's capacity is overwhelmed, a significant change in pH will occur despite the buffer's resistance. A buffer can only neutralise a limited amount of added acid or base. For example, if you add a large amount of HCl to an acetate buffer:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

the buffer will no longer be able to neutralise the H^+ ions, leading to a sharp drop in pH.

Acidic buffer solutions

$$\underset{\text{Weak acid}}{HA(aq) + H_2O(l)} \rightleftharpoons \underset{\text{Conjugate base}}{A^-(aq) + H_3O^+(aq)}$$

For example, the H_2CO_3/HCO_3^- buffer:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

If a small amount of acid (H_3O^+) is added:

- initially the pH decreases slightly because of the increased number of H_3O^+ ions
- then, the HCO_3^- ions react with the excess H_3O^+; the equilibrium is restored, and the pH increases to close to but just lower than its original value.

If a small amount of base (OH^-) is added:

- initially the pH increases slightly because of the increased number of OH^- ions
- but, according to Le Châtelier's principle, the forward reaction is favoured and H_2CO_3 dissociates, producing more H_3O^+ ions that neutralise the excess OH^- ions; the equilibrium is restored, and the pH decreases to close to but just slightly higher than its original value.

Weblinks
How buffers work
Buffer capacity

Worksheet
Buffers and Le Châtelier's principle

Basic buffer solutions

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

Weak base Conjugate acid

For example, the NH_3/NH_4^+ buffer:

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

If a small amount of acid (H_3O^+) is added:

- initially the pH decreases because of the increased number of H_3O^+ ions
- then, more $NH_3(aq)$ reacts, producing more OH^- ions that neutralise the excess H_3O^+ ions; the equilibrium is restored, and the pH increases to close to but just less than its original value.

If a small amount of base (OH^-) is added:

- initially the pH increases slightly because of the increased number of OH^- ions
- then, the conjugate acid (NH_4^+) reacts with the excess OH^- ions; the equilibrium is restored, and the pH decreases to close to but just above its original value.

LEARNING CHECK 5.3

DESCRIBING

1 **Define** 'buffer'.

2 State an example of a buffer.

APPLYING

3 **Identify** whether each of the following could be used to make an acidic buffer solution.
   - **a** HCl and NaCl
   - **b** CH_3COOH and CH_3COONa
   - **c** NH_3 and NH_4Cl
   - **d** HCl and CH_3COONa

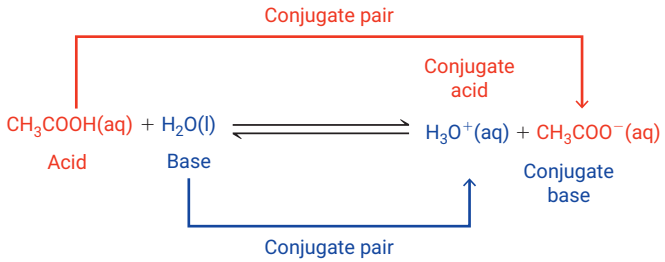
4 **Identify** a suitable substance to mix with methanoic acid (HCOOH) to make a buffer.

5 A buffer solution has been prepared by mixing ethylamine ($CH_3CH_2NH_2$) and ethyl ammonium chloride ($CH_3CH_2NH_3Cl$).
   - **a** Suggest an approximate pH value for this system.
   - **b** Write the equation for the buffer system.
   - **c** With the aid of an equation, **explain** what would happen if a small amount of hydrochloric acid was added to this system.

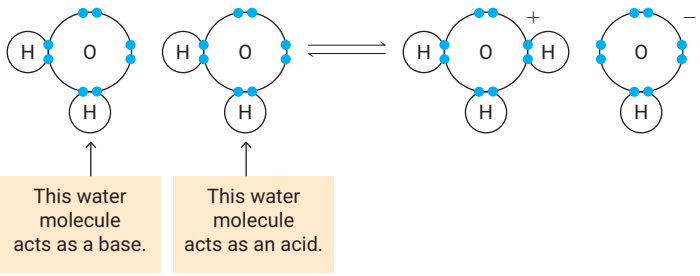
CHAPTER SUMMARY

Brønsted–Lowry theory

- A Brønsted–Lowry acid is a substance that donates one or more protons or hydrogen ions (H^+).
- A Brønsted–Lowry base is a substance that accepts one or more protons.
- A conjugate acid–base pair are two substances in a reaction that differ from each other by one proton.
- A conjugate acid is the acid that is formed when a base accepts a proton from an acid.
- A conjugate base is the base that is formed when an acid donates a proton to a base.

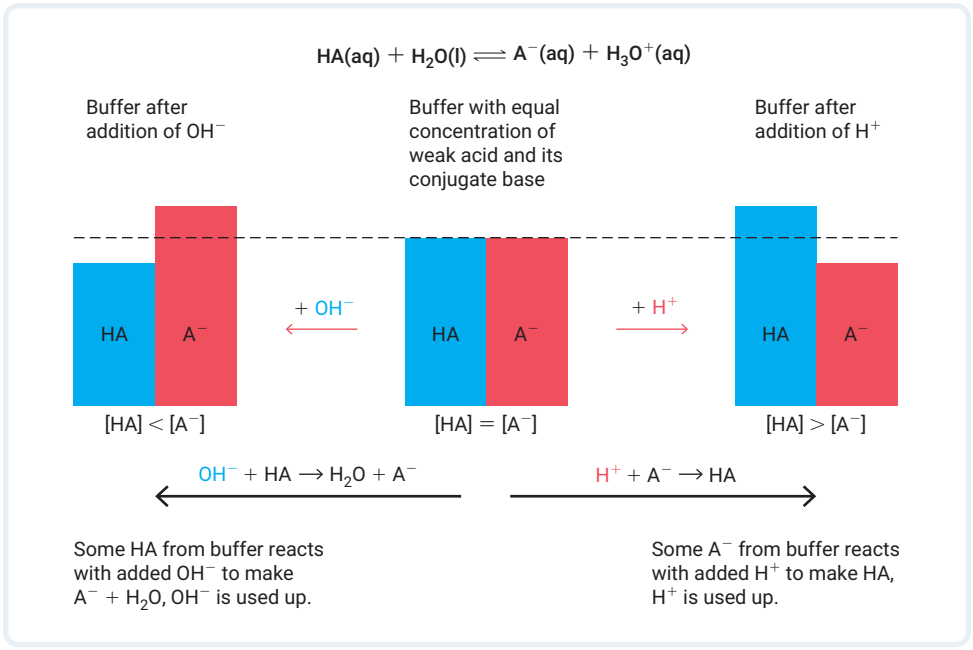


- An amphiprotic substance can gain or lose a proton to act as an acid or a base. Water is an amphiprotic substance.



Buffers

- Buffers are solutions that can maintain a pH within a certain range despite an acid or a base being added.
- Buffers are solutions of a weak acid and its conjugate base or a weak base and its conjugate acid.
- When an acid is added, the pH decreases. According to Le Châtelier's principle, the system will favour the reaction that reduces the concentration of H^+, thereby increasing the pH. However, since it only partially reduces the concentration of H^+, the pH is still slightly lower than the original pH.
- When a base is added, the pH increases. According to Le Châtelier's principle, the system will favour the reaction that reduces the concentration of OH^- ions, producing more H^+ ions, thereby decreasing the pH. However, since it only partially reduces the concentration of OH^-, the pH is still slightly higher than the original pH.



CHAPTER EXAM

MULTIPLE CHOICE

1. According to the Brønsted–Lowry model, a base is:

A a hydrogen ion (proton) acceptor.
B an electrolyte.
C a hydrogen ion (proton) donor.
D a substance that increases the hydrogen ion concentration.

2. Identify the conjugate base of $H_2PO_3^-(aq)$.

A $H_3PO_3(aq)$
B $H_2PO_4^{2-}(aq)$
C $HPO_3^{2-}(aq)$
D $PO_3^{3-}(aq)$

3. In the reaction shown below, identify the Brønsted–Lowry acid for the forward reaction.
$CH_3CH_2CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2NH_3^+(aq) + OH^-(aq)$

A H_2O
B $CH_3CH_2CH_2NH_2(aq)$
C $CH_3CH_2CH_2NH_3^+(aq)$
D None of these

4. Identify the two Brønsted–Lowry bases in the following equation.
$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_2SO_3(aq) + OH^-(aq)$

A $H_2O(l)$ and $H_2SO_3(aq)$
B $HSO_3^-(aq)$ and $H_2O(l)$
C $HSO_3^-(aq)$ and $OH^-(aq)$
D $H_2SO_3(aq)$ and $OH^-(aq)$

5. Identify the conjugate acid–base pair in the following reaction.
$HSO_4^-(aq) + CH_3NH_2(aq) \rightleftharpoons SO_4^{2-}(aq) + CH_3NH_3^+(aq)$

A $CH_3NH_3^+$ and CH_3NH_2
B HSO_4^- and CH_3NH_2
C CH_3NH_2 and SO_4^{2-}
D HSO_4^- and SO_4^{2-}

6. Water can act as an acid or a base. Identify which equation represents water reacting as an acid.

A $H_2O(l) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$
B $H_2O(l) + C(s) \rightleftharpoons CO(g) + H_2(g)$
C $H_2O(l) + HCl(aq) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$
D $H_2O(l) + NH_3(g) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$

7. A buffer solution is most effective when the:

A pH of the solution is 14.
B concentration of the weak acid and its conjugate base are equal.
C concentration of the weak acid is much higher than its conjugate base.
D concentration of the conjugate base is much higher than the weak acid.

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8. Which of the following pairs, in equimolar amounts, would result in an acidic buffer solution?

I CH_3COOH/CH_3COO^-

II H_2CO_3/HCO_3^-

III NH_3/NH_4^+

IV H_2SO_4/HSO_4^-

V $CH_3NH_2/CH_3NH_3^+$

A I, II and IV
B III and V
C II, III and V
D I and II

9. Why does the addition of a small volume of dilute HCl(aq) to a mixture of aqueous solutions of CH_3COOH and CH_3COONa have little effect on the pH?

A H_3O^+ ions in the buffer solution inhibit the ionisation of the HCl.
B The volume of the solution is not increased to a significant extent.
C The CH_3COO^- ions in the buffer solution react with the H_3O^+ ions from the HCl.
D The quantity of H_3O^+ ions produced by CH_3COOH approximately equals the H_3O^+ ions produced by the HCl.

10. Which of the following best describes why a buffer solution has a limited capacity to resist pH changes?

A The buffer components will eventually be used up if too much acid or base is added.
B The buffer solution only resists changes in pH when no ions are present.
C The buffer can only neutralise strong acids and bases.
D The buffer solution only works at a pH of 7.

SHORT RESPONSE

11. When iron(II) sulfate is used for killing weeds in lawns, it is often mixed with the fertiliser ammonium sulfate. Ammonium sulfate also makes the soil acidic. Write an equation to show how the ammonium ion behaves as a Brønsted–Lowry acid in water.

12. The hydrogen citrate ion can undergo the following reactions:

$C_6H_7O_7^-(aq) + H_2O(l) \rightleftharpoons C_6H_6O_7^{2-}(aq) + H_3O^+(aq)$

$C_6H_7O_7^-(aq) + H_2O(l) \rightleftharpoons C_6H_8O_7(aq) + OH^-(aq)$

Identify the type of substance the hydrogen citrate ion is.

13. **Explain** why a solution made with methanoic acid (HCOOH) and sodium methanoate (HCOONa) can act as a buffer. Include relevant equations in your answer.

CROSS-CHAPTER QUESTION

14. The ideal pH of human blood is 7.4. If the pH of a person's blood varies too much from this value, a serious condition can develop. One buffer system for maintaining acid–base balance in blood is the carbonic acid–hydrogencarbonate buffer:

$H_3O^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + H_2O(l)$ (1)

a **Identify** the two conjugate acid–base pairs in equation 1, indicating clearly which is the acid and which is the base in each.

b Write the equilibrium constant expression for equation 1.

Carbonic acid further reacts to form water and carbon dioxide:

$H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(aq)$ (2)

c Combine equations 1 and 2 to create an overall equation that shows the relationship between $HCO_3^-(aq)$ and $CO_2(aq)$.

d **Identify** the effect on the blood's pH when each of the following components are removed.

i Carbon dioxide

ii Hydrogencarbonate ions

e **Calculate** the hydrogen ion concentration of the blood if the pH is 7.4.

DATA ANALYSIS

15. A student prepared two different aqueous solutions, each with a total concentration of 0.10 M, and measured the pH before and after adding small amounts of strong acid (HCl) or strong base (NaOH). The data is shown below.

Solution	Initial pH	After adding 1.0 mL of 0.10 M HCl	After adding 1.0 mL of 0.10 M NaOH
A: 0.050 M CH_3COOH + 0.050 M CH_3COO^-	4.76	4.68	4.83
B: 0.10 M CH_3COOH only	2.87	1.92	5.27

a **Identify** the Brønsted–Lowry acid and the Brønsted–Lowry base in Solution A.

b **Calculate** the pOH of each solution at its initial pH.

c Draw a conclusion as to why the pH changed for each solution after 1.0 mL of 0.10 M HCl was added.

d Using the data, **describe** the pH change for each solution after 1.0 mL of 0.10 M NaOH was added.

e **Identify** which solution is a buffer and justify your choice using only the data provided.

CHAPTER 6

Dissociation constants

Giphotostock/Science Photo Library

SYLLABUS DOT POINTS

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.

Introduction

The qualitative information about the relative strengths of acids and bases available from a pH scale can be useful, but many important situations require a more quantitative approach. Understanding the role of dissociation constants is useful when attempting to determine the extent to which acids and bases dissociate and, hence, the strength of these acids and bases.

Practical

- Acid dissociation constant, K_a (online-only resource)

Worksheets

- Dissociation constants
- Using K_a and K_b to solve problems
- Interpreting data and diagrams

Nelson MindTap

To access resources above, visit **cengage.com.au/nelsonmindtap**

ASSUMED KNOWLEDGE

- ✓ pH is a measure of hydrogen ion concentration.
- ✓ The equilibrium constant (K_c) shows the relative relationship between the concentration of product and reactant at equilibrium and the extent of reaction in either direction.
- ✓ The equilibrium constant can be calculated using $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ for the reaction: $aA + bB \rightleftharpoons cC + dD$. (Solids and pure liquids are not included in the equilibrium constant expression)
- ✓ According Le Châtelier's principle, when a system at equilibrium is disturbed, it will work to partially oppose the change.
- ✓ The equilibrium expression can also be used to calculate unknown concentrations.
- ✓ pH is calculated from hydrogen ion concentration and pOH from hydroxide ion concentration.
- ✓ pH + pOH = 14.
- ✓ The concentration of solutions (in molarity) can be calculated using $c = \frac{n}{V}$.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ write dissociation reactions for acids and bases in water
- ✓ write the equilibrium expression (K_a and K_b) for weak acids and bases
- ✓ use K_a and K_b to calculate pK_a and pK_b for weak acids and bases
- ✓ use K_a, K_b, pK_a and pK_b to compare the relative strengths of weak acids
- ✓ calculate K_b for the conjugate base of an acid and vice versa, using K_w
- ✓ calculate the dissociation constant (K_a and K_b) for weak acids and bases from a given pH
- ✓ calculate the percentage ionisation of weak acids and bases to compare relative strengths
- ✓ calculate pH from a dissociation constant
- ✓ identify dissociation reactions for polyprotic acids.

6.1 K_a and K_b

Practical
Acid dissociation constant, K_a

Acid dissociation constant, K_a

In a weak acid, only some of the acid molecules dissociate. This means that there is equilibrium between the acid and the conjugate base. For example, the weak acid hydrofluoric acid (HF):

$$HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$$

The equilibrium expression for this reaction is:

$$K = \frac{[H_3O^+][F^-]}{[HF][H_2O]}$$

Rearranging the formula gives:

$$K[H_2O] = \frac{[H_3O^+][F^-]}{[HF]}$$

acid dissociation equilibrium constant (K_a) the equilibrium expression of a weak acid

Water is the solvent, and the concentration of water does not alter significantly; it is effectively constant at 55.5 mol L^{-1}. This means that it can be incorporated into K. This now forms the **acid dissociation equilibrium constant (K_a)**.

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

When the weak acid hydrofluoric acid dissolves in water, only a small percentage of the molecules ionise. The extent of the forward reaction is very small. K_a of hydrofluoric acid is very small.

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.8 \times 10^{-4}$$

FORMULA AND DATA BOOK

Generally, for the dissociation of a weak acid

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

KEY FORMULA

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

When a strong acid such as hydrochloric acid dissolves in water, almost 100 per cent of the acid reacts to form hydronium and chloride ions:

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

K_a of a strong acid is very large (e.g $K_a(HCl) = 1.3 \times 10^6$). The reverse reaction only occurs to a very small extent. The conjugate base Cl^- is very weak and does not readily react in the reverse reaction. It is not necessary to use the equilibrium arrows for the reactions of strong acids because they effectively go to completion. The K_a values are not normally given because they are very large.

KEY CONCEPT

Acid dissociation equilibrium constant

K_a is a measure of the strength of acids. In strong acids, all molecules ionise in water; therefore, K_a is very large.

In weak acids, only a fraction of the molecules ionise in water; therefore, K_a is small.

An advantage of the Brønsted–Lowry model is that it shows how the strength of a conjugate acid or base can be related to the strength of the original acid or base.

For example, the following reaction proceeds virtually to completion:

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

This means that HNO_3 is a strong acid and so the equilibrium lies well to the right. Therefore, the conjugate base of HNO_3, the nitrate ion (NO_3^-) is a very weak base.

The reverse of this equilibrium system can be written as:

$$NO_3^-(aq) + H_3O^+(aq) \rightleftharpoons HNO_3(aq) + H_2O(l)$$

The K_a expression for this is:

$$K_a = \frac{[HNO_3]}{[H_3O^+][NO_3^-]}$$

NO_3^- is a very weak base, so the concentration of HNO_3 will be very low and K_a will also be very small.

In contrast, ethanoic acid (CH_3COOH) is quite weak and only dissociates to a small extent:

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

Therefore, the conjugate base (CH_3COO^-) is relatively strong. Table 6.1.1 lists some weak acids and their K_a values.

TABLE 6.1.1 Some weak acids and their K_a values

Acid	Formula	K_a
Ammonium ion	NH_4^+	5.6×10^{-10}
Ethanoic	CH_3COOH	1.7×10^{-5}
Hydrocyanic	HCN	6.3×10^{-10}
Hydrofluoric	HF	6.8×10^{-4}
Lactic	$HC_3H_5O_3$	1.4×10^{-4}
Methanoic	HCOOH	1.8×10^{-4}

The magnitude of K_a indicates the degree to which an acid will ionise in water. If $K_a > 1$, the equilibrium lies to the right and it is a strong acid. If $K_a < 1$, the equilibrium lies to the left, and it is a weak acid.

Base dissociation constants, K_b

According to the Brønsted–Lowry model of acids and bases, when a base reacts with water, it *accepts* a proton from water:

$$B(aq) + H_2O(l) \rightarrow BH^+(aq) + OH^-(aq)$$

Base Conjugate acid

Generally, for the dissociation of a weak base, B:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

KEY FORMULA

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Because this equilibrium constant refers to the dissociation of a base, it is referred to as the **base dissociation equilibrium constant (K_b)**.

base dissociation equilibrium constant (K_b) the equilibrium expression of a weak base

For a strong base, such as sodium hydroxide, dissociation is complete and the equilibrium constant is very large.

Table 6.1.2 shows some examples of weak bases and their K_b. For a weak base, such as ammonia (NH_3), only some of the NH_3 molecules will dissociate:

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

The equilibrium expression for this reaction becomes:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

FORMULA AND DATA BOOK

TABLE 6.1.2 Some weak bases and their K_b values

Base	Formula	K_b
Ammonia	NH_3	1.8×10^{-5}
Methylamine	CH_3NH_2	4.4×10^{-4}
Ethylamine	$CH_3CH_2NH_2$	5.4×10^{-4}
Phenylamine	$C_6H_5NH_2$	4.2×10^{-10}
Phosphine	PH_3	1.0×10^{-14}
Hydrazine	H_2NNH_2	1.3×10^{-6}

Weblink
Relationship between K_a and K_b

WORKED EXAMPLE 6.1.1

Dimethylamine ($(CH_3)_2NH$) is a weak base. Write the dissociation equation for dimethylamine and the K_b expression.

ANSWER

1 **Write the dissociation equation.**
According to the Brønsted–Lowry model of acids and bases, if dimethylamine is a weak base, then it will accept a proton from water.

$(CH_3)_2NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+(aq) + OH^-(aq)$

2 **Write the equilibrium expression.**

$$K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$$

Strength of weak acids and bases

To determine the relative strength of weak acids and weak bases, you can compare their dissociation constants: K_a for weak acids and K_b for weak bases. The larger the K_a or K_b, the stronger the acid or base.

WORKED EXAMPLE 6.1.2

a Compare the strengths of the weak acids ethanoic acid (CH_3COOH), K_a 1.7×10^{-5}, and methanoic acid ($HCOOH$), K_a 1.8×10^{-4}.
b Compare the strengths of the weak bases ammonia (NH_3), K_b 1.8×10^{-5}, and methylamine (CH_3NH_2), K_b 4.4×10^{-4}.

ANSWERS

a **Compare the K_a values.**
Methanoic acid has K_a 1.8×10^{-4}, which is larger than K_a 1.7×10^{-5} for ethanoic acid. Because methanoic acid has a larger K_a, it is the stronger acid.
b **Compare the K_b values.**
Methylamine has K_b 4.4×10^{-4}, which is larger than K_b 1.8×10^{-5} for ammonia. Because methylamine has a larger K_b, it is the stronger base.

Worksheet
Using K_a and K_b to solve problems

Dissociation constants for conjugate acid–base pairs

We know that K_a is the acid dissociation constant for an acid (HA):

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

and K_b is the base dissociation constant for the conjugate base A^-.

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

Therefore:

$$K_b = \frac{[OH^-][HA]}{[A^-]}$$

Using the equations for the dissociation of weak acids, the relationship between K_a and K_b is given by:

$$K_a \times K_b = \frac{\cancel{[A^-]}[H_3O^+]}{\cancel{[HA]}} \times \frac{[OH^-]\cancel{[HA]}}{\cancel{[A^-]}}$$

FORMULA AND DATA BOOK

This leaves:

$$K_a \times K_b = [H_3O^+][OH^-]$$

Since the self-ionisation of water is given by:

$$K_w = 1.00 \times 10^{-14} = [H_3O^+][OH^-]$$

Therefore:

$$K_w = K_a \times K_b$$

This is a significant relationship, and it enables K_a or K_b of a conjugate acid or base to be determined given K_a or K_b of the acid or base.

WORKED EXAMPLE 6.1.3

If K_a for propanoic acid (CH_3CH_2COOH) is 1.35×10^{-5}, determine K_b for the propanoate ion ($CH_3CH_2COO^-$).

ANSWER

1 Write the equilibrium reaction.

By writing the equilibrium reaction, we can see that propanoic acid and propanoate ions are conjugate acid–base pairs:

$CH_3CH_2COOH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COO^-(aq) + H_3O^+(aq)$

2 Determine the formula.

$K_w = K_a \times K_b$

3 Substitute the known values.

$K_w = 1.00 \times 10^{-14}$

$K_a = 1.35 \times 10^{-5}$

$1.00 \times 10^{-14} = 1.35 \times 10^{-5} \times K_b$

4 Calculate the answer.

$$K_b = \frac{1.0 \times 10^{-14}}{1.35 \times 10^{-5}}$$

$$= 7.4 \times 10^{-10}$$

pK_a and pK_b

pK_a is the measure of the strength of an acid in solution. It is the negative logarithm of the acid dissociation constant, K_a:

$$pK_a = -\log_{10}(K_a)$$

A smaller pK_a means a stronger acid; the acid will ionise more in solution, releasing more H^+ ions. A larger pK_a means a weaker acid; the acid will ionise less, releasing fewer H^+ ions. This is similar to the relationship between pH and H^+ ions; a low pH means more H^+ ions, resulting in a stronger acid, whereas a high pH means fewer H^+ ions, resulting in a weaker acid.

pK_b is the measure of the strength of base in solution. It is the negative logarithm of the base dissociation constant, K_b:

$$pK_b = -\log_{10}(K_b)$$

Just like pK_a, a small pK_b indicates a strong base and a large pK_b indicates a weak base.

These values can also help us to predict pH in acid–base reactions and understand the equilibrium position of acid–base reactions.

For any conjugate acid–base pair in water, the sum of pK_a and pK_b is always equal to 14 at 25°C:

$$pK_a + pK_b = 14$$

This means if you know pK_a of an acid, you can calculate pK_b of its conjugate base, and vice versa.

Just like the relationship between pH and $[H^+]$ and pOH and $[OH^-]$, there is a relationship between pK_a and K_a and pK_b and K_b **(Figure 6.1.1)**. So, if K_a or K_b needs to be calculated, you can use the following formulas:

$$K_a = 10^{-pK_a} \text{ and } K_b = 10^{-pK_b}$$

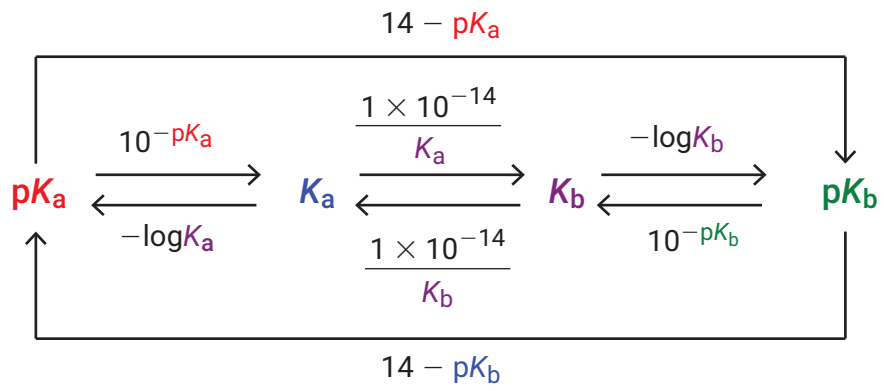


FIGURE 6.1.1 The relationship between K_a, K_b, pK_a and pK_b

Weblink
pK_a and pK_b

Worksheet
Dissociation constants

WORKED EXAMPLE 6.1.4

An ethanoic acid (CH_3COOH) solution has K_a of 1.7×10^{-5}. Calculate:

a pK_a for ethanoic acid
b pK_b for the ethanoate (acetate) ion (CH_3COO^-), the conjugate base of ethanoic acid
c K_b for the ethanoate ion.

ANSWERS

a 1 Determine the formula.

$pK_a = -\log(K_a)$

2 Substitute the known values.

$pK_a = -\log(1.7 \times 10^{-5})$

3 Calculate the answer.

$-\log(1.7 \times 10^{-5}) = 4.77$

b 1 Write a balanced equation.

The dissociation of ethanoic acid:

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

2 Determine the formula.

Because CH_3COOH and CH_3COO^- are a conjugate acid–base pair, the sum of pK_a and pK_b should equal 14. Rearrange this formula to find pK_b.

$pK_b = 14 - pK_a$

3 Calculate the answer.

$pK_b = 14 - 4.77$

$= 9.23$

This shows a conjugate acid–base relationship. Ethanoic acid has a small pK_a, whereas the ethanoate ion has a larger pK_b. This means ethanoic acid is a stronger acid than the ethanoate ion is a base.

c 1 Choose the correct formula and substitute values.

$K_b = 10^{-pK_b}$

$K_b = 10^{-9.23}$

2 Calculate K_b.

$K_b = 5.9 \times 10^{-10}$

LEARNING CHECK 6.1

DESCRIBING

1 Define 'dissociation equilibrium constant'.

APPLYING

2 Write the dissociation equations and K_a or K_b expressions as appropriate for the following acids and bases.

- **a** Carbonic acid (H_2CO_3)
- **b** Hydroxylamine (NH_2OH)
- **c** Hypochlorous acid (HOCl)

3 Organise the acids in Table 6.1.1 in order from strongest to weakest.

4 Organise the bases in Table 6.1.2 in order from weakest to strongest.

5 The ascorbate ion ($C_6H_7O_6^-$) is the conjugate base of ascorbic acid (vitamin C).

- **a** Write the equation showing the ascorbate ion acting as a base when mixed with water.
- **b** Given that K_a for ascorbic acid is 7.9×10^{-5}, **determine** K_b for the ascorbate ion.

6 The pyridinium ion ($C_5H_6N^+$) is the conjugate acid of pyridine.

- **a** Write the equation showing the pyridinium ion acting as an acid when mixed with water.
- **b** Given that K_b for pyridine is 1.7×10^{-9}, **determine** K_a for the pyridine ion.

7 Lactic acid ($CH_3CH(OH)CO_2H$) is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its K_a is 1.38×10^{-4} at 25°C. **Calculate** pK_a for lactic acid and pK_b and K_b for the lactate ion.

8 Hydrazine (NH_2NH_2) is used in the synthesis of various pesticides and as a corrosion inhibitor in boilers. It is a colourless liquid with an ammonia-like odour. Its K_b is 1.3×10^{-6} at 25°C. **Calculate** pK_b for hydrazine and pK_a and K_a for its conjugate acid, the hydrazinium ion ($NH_2NH_3^+$).

6.2 Calculations involving dissociation constants

Calculating a dissociation constant from a given pH

The K_a of an acid can be determined by measuring the pH of the sample. Using HA to represent an acid and A^- to represent the conjugate base, the reaction of a weak acid with water can be represented as:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

And the equilibrium expression is:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

Because $[A^-]$ must equal $[H_3O^+]$, then:

$$K_a = \frac{[H_3O^+]^2}{[HA]}$$

The following assumptions are made:

1. The acid is monoprotic or the expression is showing only the first ionisation of a diprotic/triprotic acid.
2. At equilibrium, [HA] is the same as the initial concentration; the weak acid only ionises to a small degree in water.
3. $[H_3O^+]$ produced by the self-ionisation of water is negligible and has no effect on the calculations.

Recall from Chapter 4, that the key formula to calculate pH of solution, given $[H^+]$, is:

$$pH = -\log[H^+]$$

Therefore, $[H^+]$ can be calculated by rearranging this formula to:

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

Worked example 6.2.1 demonstrates how this can be used to calculate K_a.

WORKED EXAMPLE 6.2.1

A 0.1 M solution of hypobromous acid (HOBr) has a pH of 4.80. Determine K_a for this acid.

ANSWER

1 Write a balanced equation.

$HOBr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OBr^-(aq)$

2 Write the expression for K_a.

$$K_a = \frac{[OBr^-][H_3O^+]}{[HOBr]}$$

3 Determine the formula to calculate $[H_3O^+]$.

$[H_3O^+] = 10^{-pH}$

4 Substitute the known values.

$[H_3O^+] = 10^{-4.80}$

5 Calculate the concentration of $[H_3O^+]$.

$[H_3O^+] = 1.58 \times 10^{-5}$ M.

6 Substitute the known values into the K_a formula.

$$K_a = \frac{[OBr^-][H_3O^+]}{[HOBr]}$$

$$= \frac{[H_3O^+]^2}{0.1}$$

7 Calculate the answer.

$$K_a = \frac{(1.58 \times 10^{-5})^2}{0.1}$$

$$= 2.5 \times 10^{-9}$$

Percentage ionisation

percentage ionisation the percentage of acid that has ionised in water

Weblink
Calculating K_a and K_b

Percentage ionisation is the percentage of acid that has ionised in water. The general reaction for weak acids with water is:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

For each proton that is donated to water, one A^- ion is formed (provided the acid is monoprotic). By measuring the pH, $[H_3O^+]$ can be determined and this is equal to $[A^-]$:

$$[A^-] = [H_3O^+]$$

This can then be used to calculate the percentage of the original acid that has been ionised. Note that [HA] here refers to the initial concentration and not the concentration at equilibrium:

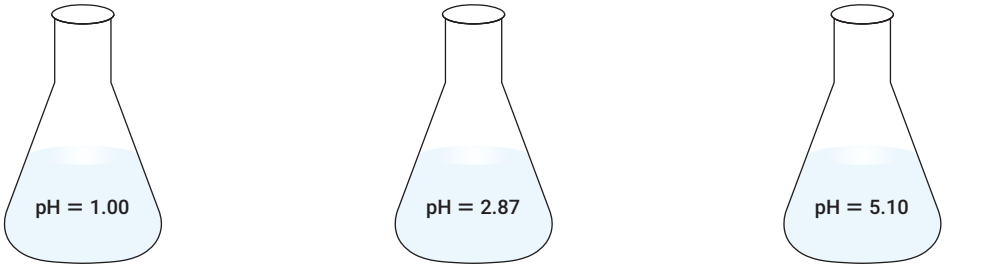
$$\text{Percentage ionisation} = \frac{[A^-]}{[HA]} \times 100\%$$

When calculating the dissociation constant, K_a, for weak acids, it is often assumed that the initial concentration of the acid, $[HA]_{init}$, is approximately equal to the equilibrium concentration of the undissociated acid, $[HA]_{eq}$, because weak acids typically ionise very little. However, for some weak acids with higher percentage ionisation (closer to 100 per cent), this assumption becomes less accurate. In such cases, the difference between $[HA]_{init}$ and $[HA]_{eq}$ can be significant, and using $[HA]_{init}$ instead of $[HA]_{eq}$ might lead to an incorrect calculation of K_a. Once the percentage ionisation is known, you can calculate the equilibrium concentration more precisely.

The percentage ionisation of a weak base tells you how much of the base dissociates in water to form its conjugate acid, BH^+ and hydroxide ions, OH^-. The following formula can be used, where [B] is the initial concentration of the weak base before any dissociation:

$$\text{Percentage ionisation} = \frac{[OH^-]}{[B]} \times 100\%$$

Percentage ionisation can also be used to determine the relative strength of the weak acid or weak base.



0.10 M hydrochloric acid (HCl)
100% ionised
K_a very large (approaching infinity)

0.10 M ethanoic acid (CH_3COOH)
1.3% ionised
$K_a = 1.7 \times 10^{-5}$

0.10 M hydrocyanic acid (HCN)
0.0079% ionised
$K_a = 6.3 \times 10^{-10}$

FIGURE 6.2.2 The strength of acids based on percentage ionisation and K_a. Note that the concentration is the same for each acid.

WORKED EXAMPLE 6.2.2

Hydrofluoric acid reacts with water as shown by:

$HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$

Determine the percentage ionisation of HF(aq) in a 0.1 mol L^{-1} hydrofluoric acid solution that was found to have a pH of 2.1.

ANSWER

1 **Determine the formula.**
The concentration of hydronium ions is:
$[H_3O^+] = 10^{-pH}$

2 **Substitute the known values.**
$[H_3O^+] = 10^{-2.1}$

3 **Calculate the answer.**
$[H_3O^+] = 0.008 \text{ mol } L^{-1}$

4 **Determine $[F^-]$.**
Since the ratio between HF and H_3O^+ is 1:1, the concentration of F^- is also 0.008 mol L^{-1}.

5 **Calculate the percentage ionisation of hydrofluoric acid.**

$$\text{Percentage ionisation} = \frac{[F^-]}{[HF]} \times \frac{100}{1}$$
$$= \frac{0.008}{0.1} \times \frac{100}{1}$$
$$= 8\%$$

Calculating pH from a given dissociation constant

WORKED EXAMPLE 6.2.3

Determine the pH of a 0.01 M solution of hydrofluoric acid ($K_a = 6.8 \times 10^{-4}$).

ANSWER

1 **Determine the formula to calculate $[H_3O^+]$.**

$$K_a = \frac{[F^-][H_3O^+]}{[HF]} = 6.8 \times 10^{-4}$$
$$= \frac{[H_3O^+]^2}{[HF]}, \text{ as } [F^-] = [H_3O^+]$$

2 **Substitute the known values.**
$[H_3O^+]^2 = 6.8 \times 10^{-4} \times [HF]$

3 **Calculate the answer.**
$[H_3O^+] = \sqrt{(6.8 \times 10^{-4} \times 0.01)}$
$= 2.6 \times 10^{-3}$

4 **Determine pH.**
$pH = -\log_{10}[H_3O^+]$
$= -\log_{10}(2.6 \times 10^{-3})$
$= 2.6$

Calculating unknown acid concentrations, given K_a and pH

WORKED EXAMPLE 6.2.4

Calculate the initial concentration of ethanoic acid (CH_3COOH) in an aqueous solution with a pH of 3.86 ($K_a = 1.7 \times 10^{-5}$).

ANSWER

1 Determine the formula to calculate $[H_3O^+]$.

$[H_3O^+] = 10^{-pH}$

2 Substitute the known values.

$[H_3O^+] = 10^{-3.86}$

3 Calculate the answer.

$[H_3O^+] = 1.38 \times 10^{-4}$ M

4 Substitute known values into the K_a expression.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$1.7 \times 10^{-5} = \frac{(1.38 \times 10^{-4})^2}{[CH_3COOH]}$$

5 Calculate $[CH_3COOH]$.

$$[CH_3COOH] = \frac{(1.38 \times 10^{-4})^2}{1.7 \times 10^{-5}}$$

$$= 0.0011\,\text{M}$$

Weblink
Calculating equilibrium concentrations

K_a of polyprotic acids

A separate equation can be written for each step of the ionisation of a polyprotic acid. Each step has its own equilibrium expression and K_a. These are generally labelled K_{a1}, K_{a2} and so on, with the first K_a usually being the largest value. Sulfuric acid is a diprotic acid; it can release two protons, and the first proton is very easily donated to water. Sulfuric acid (H_2SO_4) is a strong acid with a conjugate base, HSO_4^-.

$$H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq) \qquad K_{a1} = 1.0 \times 10^9$$

K_a for the strong acid is very large.
The second reaction is:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq) \qquad K_{a2} = 1.0 \times 10^{-2}$$

The conjugate base HSO_4^- is now donating a proton and acting as a weak acid by reacting with water to form SO_4^{2-}. The weaker the acid, the stronger its conjugate base, so the reverse reaction occurs to a higher degree. The species HSO_4^- is amphiprotic. In a solution of sulfuric acid, the main species present are HSO_4^-, H_3O^+ and water.

Diprotic weak acids such as sulfurous acid (H_2SO_3) have two ionisable protons:

$$H_2SO_3(l) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + H_3O^+(aq) \qquad K_{a1} = 1.4 \times 10^{-2}$$

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq) \qquad K_{a2} = 6.5 \times 10^{-8}$$

Sulfurous acid is a weak acid. In the first reaction, it is in equilibrium with the conjugate base. While K_{a1} is bigger than K_{a2}, all three species H_2SO_3, HSO_3^- and SO_3^{2-} would be present, as well as water in an aqueous solution of sulfurous acid.

LEARNING CHECK 6.2

APPLYING

1 A 0.1 mol L^{-1} solution of methanoic acid (HCOOH) has a pH of 2.37. **Calculate** the:

- **a** concentration of hydronium ions
- **b** concentration of methanoate anions
- **c** K_a for this acid
- **d** percentage ionisation.

2 A 0.1 mol L^{-1} solution of ammonia (NH_3) has a pH of 11.1. **Calculate** the:

- **a** concentration of hydroxide ions
- **b** concentration of ammonium ions
- **c** K_b for this base
- **d** percentage ionisation.

3 Citric acid is the weak acid responsible for the characteristic flavour in lemons and oranges. **Calculate** the percentage of the acid ionised in a 0.30 M solution with a pH 2.96 at 25°C.

4 The pH of a 0.050 M solution of nitrous acid (HNO_2) is measured as 2.22. **Determine** K_a.

5 **Determine** the pH of a 0.2 M ethylamine solution ($K_b = 5.4 \times 10^{-4}$).

6 **Determine** the pH of a 0.2 M ethanoic acid solution ($K_a = 1.7 \times 10^{-5}$).

7 Carbonic acid (H_2CO_3) is a diprotic acid, which means that it dissociates to the carbonate ion (CO_3^{2-}) in two stages.

- **a** Write the equations for both stages of the dissociation.
- **b** Write the K_a expressions for both stages of the dissociation.
- **c** If K_a for the hydrogencarbonate ion (HCO_3^-) is 4.7×10^{-11}, **calculate** K_b for the carbonate ion.

Worksheet
Interpreting data and diagrams

CHAPTER SUMMARY

Strengths of acids and bases

- Strong acids and bases fully dissociate in solution, so calculating their pH or pOH is straightforward, by using the concentration of $[H_3O^+]$ or $[OH^-]$.
- Only a small percentage of molecules of weak acids and bases dissociate, so additional calculations involving K_a or K_b are needed to determine $[H_3O^+]$ or $[OH^-]$, and thus the pH or pOH.
- In the case of weak acids and bases, the dissociation constants K_a and K_b account for partial dissociation, and the relevant pK_a or pK_b values help to quantify their strength.

Calculations with acids and bases

Calculation	Strong acids and bases	Weak acids and bases
pH	$pH = -\log[H^+]$	$pH = -\log[H^+]$ (after calculating $[H^+]$ from K_a)
pOH	$pOH = -\log[OH^-]$	$pOH = -\log[OH^-]$ (after calculating $[OH^-]$ from K_b)
$[H^+]$ from pH	$[H^+] = 10^{-pH}$	$[H^+] = 10^{-pH}$
$[OH^-]$ from pOH	$[OH^-] = 10^{-pOH}$	$[OH^-] = 10^{-pOH}$
pH from pOH	$pH + pOH = 14$	$pH + pOH = 14$
K_w	$K_w = [H^+][OH^-]$	$K_w = [H^+][OH^-]$
Acid dissociation constant, K_a	–	$K_a = \frac{[H^+][A^-]}{[HA]}$
Base dissociation constant, K_b	–	$K_b = \frac{[BH^+][OH^-]}{[B]}$
pK_a	–	$pK_a = -\log(K_a)$
pK_b	–	$pK_b = -\log(K_b)$
K_a from pK_a	–	$K_a = 10^{-pK_a}$
K_b from pK_b	–	$K_b = 10^{-pK_b}$
Relationship K_a and K_b	–	$K_a \times K_b = K_w = 1.00 \times 10^{-14}$
Relationship pK_a and pK_b	–	$pK_a + pK_b = 14$

- Percentage ionisation is the percentage of acid or base that has ionised in water.
- Percentage ionisation (acid) $= \frac{[A^-]}{[HA]} \times 100\%$
- Percentage ionisation (base) $= \frac{[OH^-]}{[B]} \times 100\%$

CHAPTER EXAM

MULTIPLE CHOICE

1. Identify which of the following is the weakest acid.

A Ammonium ion (NH_4^+) $K_a = 5.6 \times 10^{-10}$

B Benzoic acid (C_6H_5COOH) $K_a = 6.5 \times 10^{-5}$

C Hypochlorous acid (HClO) $K_a = 3.0 \times 10^{-8}$

D Nitrous acid (HNO_2) $K_a = 4.6 \times 10^{-4}$

2. The conjugate bases of the acids in Question 1 are given below. Identify which has the lowest K_b.

A Ammonia (NH_3)

B Benzoate ion ($C_6H_5COO^-$)

C Hypochlorite ion (OCl^-)

D Nitrite ion (NO_2^-)

3. Determine the pH of a 0.1 M chloroethanoic acid ($CH_2ClCOOH$) solution ($K_a = 1.4 \times 10^{-3}$).

A 1.5

B 1.9

C 3.1

D 3.8

4. Use the following acid dissociation constants to identify the correct decreasing order of base strengths.

HF	$K_a = 6.8 \times 10^{-4}$
HNO_2	$K_a = 4.5 \times 10^{-4}$
HCN	$K_a = 6.3 \times 10^{-10}$

A $CN^- > NO_2^- > F^-$

B $NO_2^- > F^- > CN^-$

C $F^- > CN^- > NO_2^-$

D $F^- > NO_2^- > CN^-$

5. The first disinfectant used by Joseph Lister was called carbolic acid. This substance is now known as phenol ($pK_a = 10.0$). Determine the pH of a 0.10 M solution of phenol.

A 3.5

B 5.5

C 6.5

D 10.0

6. Boric acid is frequently used as an eyewash to treat eye infections. The pH of a 0.050 M solution of boric acid is 5.28. Calculate the boric acid dissociation constant, K_a.

A 5.79×10^{-4}

B 5.25×10^{-6}

C 5.43×10^{-8}

D 5.51×10^{-10}

7. A 0.100 M solution of a monoprotic weak acid has a pH of 3.00. Determine the pK_a of this acid.

A 0.999

B 3.00

C 5.00

D 9.99

8. Determine the concentration of $[OH^-]$ in a 0.20 M solution of ammonia. K_b for ammonia is 1.8×10^{-5}.

A 0.20 M
B 1.9×10^{-3} M
C 1.8×10^{-4} M
D 3.6×10^{-6} M

9. Calculate the percentage ionisation of a 0.125 M solution of nitrous acid (a weak acid), with a pH of 2.09.

A 1.25%
B 2.5%
C 6.5%
D 12.5%

10. Hydrocyanic acid (HCN) has $K_a = 6.3 \times 10^{-10}$. Determine K_b for the cyanide ion (CN^-).

A 6.2×10^{-6}
B 1.6×10^{-5}
C 7.8×10^{-4}
D 5.6×10^{-3}

SHORT REPSONSE

11. If the K_b value for aniline ($C_6H_5NH_2$) is 4.3×10^{-10}, **determine** K_a for the conjugate acid of aniline.

12. Phosphoric acid (H_3PO_4) is a triprotic acid.

a Write the dissociation equations in water for each stage.
b Given that the K_a values for each dissociation stage are 7.1×10^{-3}, 6.5×10^{-8} and 4.5×10^{-13}, respectively, **determine** K_b for the strongest conjugate base formed when H_3PO_4 has fully dissociated. Show your working.
c **Calculate** the pH of a 0.1 M dihydrogen phosphate solution ($H_2PO_4^-$). Show your working and state any assumptions made.

13. A 0.5 M solution of phenol (C_6H_5OH) has a pH of 5.1. **Determine** its percentage ionisation.

CROSS-CHAPTER QUESTION

 Modified from QCAA paper 2 2023 SA Q5

14. The following table gives the properties of four monoprotic acids.

Acid	Concentration (mol L^{-1})	$[H^+]$ (mol L^{-1})	pH	K_a
A	0.200	9.70×10^{-5}		
B	0.100	1.34×10^{-3}	2.87	1.8×10^{-5}
$C_6H_5COOH(aq)$	0.100			6.3×10^{-5}
$HNO_3(aq)$	0.010	1.00×10^{-2}	2.00	>1

a **Determine** the relative strength of acids A and B by contrasting their K_a values.
b Write a balanced chemical equation for the dissociation of benzoic acid (C_6H_5COOH).

c **Identify** whether the conjugate base of benzoic acid is amphiprotic. **Explain** your reasoning.

d **Calculate** the pH of the aqueous solution of benzoic acid. Show your working.

e **Determine** the volume of water that would need to be added to 100.0 mL of $HNO_3(aq)$ to change the pH from 2.00 to 3.00. **Explain** your reasoning.

DATA ANALYSIS

15. Interpret evidence

An experiment was conducted to determine the K_b of ammonia (NH_3) by measuring the pH of ammonia solutions at different concentrations and temperatures. The following table shows the pH values of ammonia solutions at room temperature (25°C) and an elevated temperature (35°C).

$[NH_3]$ (mol L^{-1})	pH (25°C)	pH (35°C)
0.01	11.08	10.95
0.05	10.75	10.62
0.10	10.60	10.46
0.20	10.44	10.29
0.50	10.22	10.08

a **Calculate** the concentration of hydroxide ions $[OH^-]$ for the 0.20 mol L^{-1} at both temperatures.

b **Determine** the K_b of ammonia for the 0.20 mol L^{-1} for each concentration at both temperatures.

c **Compare** the calculated K_b values at 25°C and 35°C.

d **Discuss** the effect of temperature on the dissociation of ammonia.

e **Identify** potential sources of error in the experiment and **discuss** how these might have affected the accuracy of the results.

f **Evaluate** the accuracy of the experimental K_b values with the theoretical value of 1.8×10^{-5} at 25°C.

CHAPTER 7

Titrations

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SYLLABUS DOT POINTS

SCIENCE UNDERSTANDING

- 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 p$K_a \pm 1$).
- 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.

Introduction

Most acids and bases are colourless solutions. Therefore, it is important to have a way to distinguish between acids and bases, and to determine the strength of the acid or base.

Fortunately, we have acid–base indicators. An indicator is a substance that consists of a weak acid in equilibrium with its conjugate base. What makes indicators so useful is that the weak acid is a different colour from its conjugate base.

Determining whether a chemical reaction has occurred is a form of qualitative analysis; it gives a 'yes' or 'no' answer. However, there are times when chemists not only want to know whether a chemical reaction occurs, but also to quantify the reaction. For this, they need to be able to perform quantitative analyses. Volumetric analysis is one type of quantitative analysis. Volumetric analysis determines the concentration of a sample by measuring the volume of this sample that reacts with a known volume of another substance of known concentration.

ASSUMED KNOWLEDGE

- ✓ Strong and weak acids and bases are defined according to the extent to which they ionise.
- ✓ Conjugate acid–base pairs differ by a H^+.
- ✓ Equilibrium can shift in response to pH changes.
- ✓ Indicators change colour over a specific pH range.
- ✓ Acids and bases undergo neutralisation reactions.
- ✓ The formula $c = \frac{n}{V}$ can be used to calculate unknown concentrations and/or amounts.
- ✓ Buffers work to keep the maintain the pH of a solution.
- ✓ K_{sp} indicates the degree of ionisation/dissociation.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ identify that indicators are weak acids or weak bases where the conjugate acid–base pair have different colours depending on the pK_a of the indicator
- ✓ identify the relationship between pH and colour change of the indicator
- ✓ analyse data to determine an appropriate indicator to use for a titration, given the equivalence point
- ✓ discriminate between the terms 'end point' and 'equivalence point'
- ✓ identify the difference between volumetric and conductometric titrations
- ✓ sketch graphs of volumetric and conductometric titrations
- ✓ interpret volumetric and conductometric graphs to determine the intercept with pH axis or conductivity axis, equivalence point, volume of titrant, buffer region and where pK_a = pH or pK_b = pOH
- ✓ calculate solubility through volumetric analysis
- ✓ analyse graphs to determine number of moles, mass, volume and concentration
- ✓ analyse graphs to calculate the concentration of a solution with reference to a standard solution.

7.1 Acid–base indicators

Syllabus link
Chapter 18 of *Nelson QCE Chemistry Units 1 and 2* introduces indicators.

Indicators are molecular substances that change colour depending on the pH of the solution. An indicator is either a weak acid and its conjugate base pair or a weak base and its conjugate acid pair. The weak acid or base is a different colour from its conjugate base or acid. **Table 7.1.1** lists some common acid–base indicators, the pH ranges over which they change colour and their pK_a values. **Figure 7.1.1** shows the colours of three common indicators in acidic and alkaline solution.

Acid–base indicators can be represented by the following:

Weak acid indicator: $HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$

Colour 1 Colour 2

Weak base indicator: $BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$

Colour 1 Colour 2

In a weak acid indicator, if the solution is acidic, the above equilibrium will be shifted to the left and more HIn will be present; colour 1 will dominate. If the solution is alkaline, the equilibrium will shift to the right and more In^- will be present; colour 2 will dominate.

If the indicator is a weak base, colour 1 will occur in alkaline conditions and colour 2 in acidic conditions. Indicators change colour when pH = pK_a. The colour change for most indicators takes place over a range of pK_a ± 1.

TABLE 7.1.1 Acid–base indicators

Indicator	pH range of colour change	Colour change		pK_a at 298 K
		Acid	Base	
Methyl orange	3.1–4.4	Red	Yellow	3.7
Bromophenol blue	3.0–4.6	Yellow	Blue	4.2
Bromocresol green	3.8–5.4	Yellow	Blue	4.7
Methyl red	4.4–6.2	Pink	Yellow	5.1
Bromothymol blue	6.0–7.6	Yellow	Blue	7.0
Phenol red	6.8–8.4	Yellow	Red	7.9
Phenolphthalein	8.3–10.0	Colourless	Pink	9.6

Andrew Lambert/Science Photo Library

FIGURE 7.1.1 Common indicators in acidic and alkaline solutions

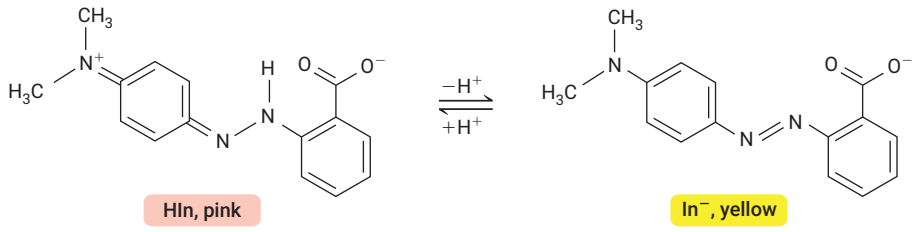


FIGURE 7.1.2 In acidic solution, methyl red exists in the pink form (HIn), and changes to the yellow conjugate base (In^-) in alkaline solution.

Methyl red exists in two forms: the pink acid form (HIn) and the yellow conjugate base form (In^-) **(Figure 7.1.2)**. When [HIn] = [In^-], the concentrations of the pink and yellow forms are equal. This occurs at a specific pH of 5.1 (at 298 K) for methyl red, known as the pK_a of the indicator. At this point, the indicator appears orange, a mixture of pink and yellow. This midpoint is significant because it marks the pH at which methyl red changes colour. Below pH 5.1, the solution is more acidic, favouring the pink acid form (HIn). Above pH 5.1, it is more basic, favouring the yellow conjugate base form (In^-). This is also the point where K_a of methyl red equals [H^+] and the pH equals the pK_a.

$K_a = \frac{[H^+][In^-]}{[HIn]}$, when [HIn] = [$In^-$], the equation simplifies to $K_a = [H^+]$ because the ratio of [In^-] to [HIn] is 1:1. This point reflects the balance of the two forms of methyl red, meaning that the pH of the solution is equal to the pK_a of the indicator. Since p$K_a = -\log(K_a)$ and pH = $-\log[H^+]$, the condition $K_a = [H^+]$ implies pK_a = pH.

Methyl red changes colour in the pH range 4.4–6.2. For example, when methyl red is added to an acidic solution in which the concentration of H_3O^+ is high (pH < 4.4), the pink form predominates because the system attempts to partially oppose the increase in H_3O^+. By favouring the formation of HIn, the amount of hydronium ions is reduced. When methyl red is added to a basic solution in which the concentration of H_3O^+ is low (pH > 6.2), the forward reaction is favoured and the yellow form predominates. The system attempts to partially oppose the decrease in H_3O^+ by shifting the reaction forward to produce more H_3O^+ ions according to Le Châtelier's principle.

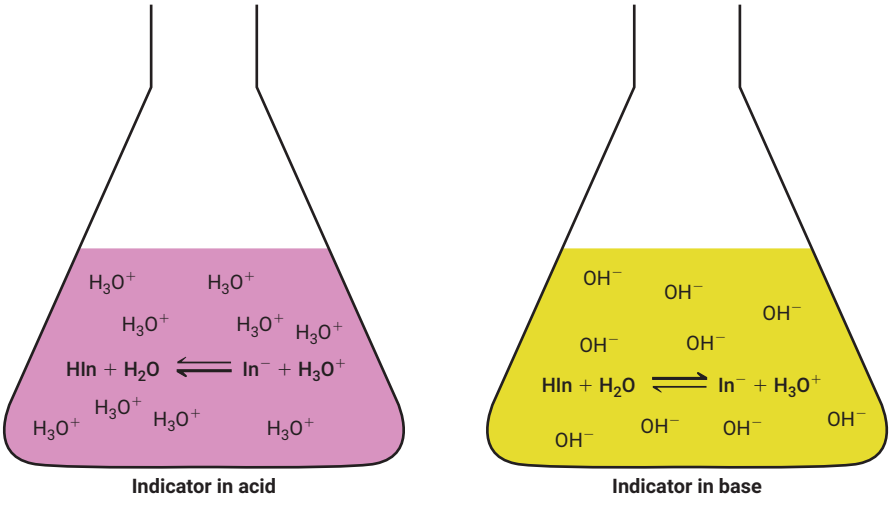


FIGURE 7.1.3 How an acid–base indicator works

Weblink
Acid–base indicators

Worksheet
Acid–base indicators

When the pH of the solution is less than the pK_a of the indicator, [HIn] is much larger than [In^-], and the solution is pink. Most of the indicator is present as HIn(aq) form **(Figure 7.1.3)**.

When the pH of the solution is greater than the pK_a of the indicator, [HIn] is much smaller than [In^-], and the solution is yellow. Most of the indicator is present in the In^- form. This shows the relationship between the pH range of colour change for methyl red and its pK_a.

Note that indicators do not change colour at the precise pH governed by their pK_a. The colour change occurs over a narrow pH range. Generally, an indicator changes colour over a range that is approximately ±1 of their pK_a. For example, methyl orange indicator has a pK_a of 3.7 and its useful range is between pH 3.1 and 4.4; phenolphthalein has a pK_a of 9.6 and has a useful range between pH 8.3 and 10.0.

LEARNING CHECK 7.1

DESCRIBING

1 **Define**:
   - **a** indicator
   - **b** indicator (acid form)
   - **c** indicator (basic form).

2 Write the general equation for an indicator, HIn, reacting with water to give the In^- ion.

3 Write the K_a and K_b expressions for the acid and base forms of an indicator HIn.

APPLYING

4 Chlorophenol red is a common acid–base indicator. The reaction of chlorophenol red with water is:

$HClr(aq) + H_2O(l) \rightleftharpoons Clr^-(aq) + H_3O^+(aq) \qquad pK_a = 6.2$

Estimate the useful pH range of chlorophenol red.

5 Congo red is an acid–base indicator that consists of a weak acid in equilibrium with its conjugate base. K_a for the acid is 7.9×10^{-5}. In an acid solution, the indicator appears blue; in a basic solution it appears red. **Determine** the pH at which the solution will appear violet.

6 Table 7.1.2 shows the colours of three acid–base indicators in solutions containing 10 mL samples of nitric acid at various concentrations.

TABLE 7.1.2 The colours of three acid–base indicators in different concentrations of nitric acid

	Nitric acid concentration (mol L^{-1})						
	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}
Methyl red	Red	Red	Red	Orange	Yellow	Yellow	Yellow
m-Cresol purple	Red	Orange	Yellow	Yellow	Yellow	Yellow	Yellow
Alizarin red s	Yellow	Yellow	Yellow	Yellow	Red	Red	Violet

Solutions of three different weak acids with a concentration of 1.0 mol L^{-1} are prepared. Table 7.1.3 shows the colours of the different indicators in these weak acid solutions.

TABLE 7.1.3 The colours of the different indicators in three weak acid solutions

	Methyl red	*m*-Cresol purple	Alizarin red s
Solution A	Red	Yellow	Yellow
Solution B	Red	Red	Yellow
Solution C	Yellow	Yellow	Red

The three acid solutions, in no particular order, are:

- bromoacetic acid ($BrCH_2COOH$, $K_a = 1.25 \times 10^{-3}$)
- hypochlorous acid ($HOCl$, $K_a = 3.0 \times 10^{-8}$)
- hypoiodous acid (HOI, $K_a = 2.3 \times 10^{-11}$)

Determine the identities of solutions A, B and C. **Justify** your answers with appropriate equations and calculations.

7.2 End point and equivalence point

Acid–base indicators and how they operate are an important part of volumetric analysis. Most acids, bases and their reaction products are colourless, so it can be difficult to assess when an acid–base reaction is complete. Indicators show when neutralisation has occurred because they change colour when the reaction is complete.

Consider the neutralisation of hydrochloric acid by sodium hydroxide:

$$\underbrace{HCl\,(aq) + NaOH(aq)}_{\text{Colourless}} \rightarrow \underbrace{NaCl(aq) + H_2O(l)}_{\text{Colourless}}$$

When this reaction occurs, there is no obvious sign when the hydrochloric acid has been neutralised by the sodium hydroxide.

If a few drops of bromothymol blue indicator are added to the acid:

$$\underbrace{\text{Bromothymol blue} + HCl(aq)}_{\text{Yellow}} + \underbrace{NaOH(aq)}_{\text{Colourless}} \rightarrow \underbrace{NaCl(aq) + H_2O(l)}_{\text{Green}}$$

the acid/bromothymol blue indicator mixture is yellow. As sodium hydroxide is added, it begins to neutralise the hydrochloric acid. Eventually the solution begins to turn green as enough sodium hydroxide is added so that all of the hydrochloric acid has been neutralised. If one more drop of sodium hydroxide is added, the solution turns blue.

For volumetric analysis to be meaningful, we need to know the precise point at which neutralisation occurs; that is, when the number of moles of acid and base reflect the stoichiometric ratio as shown in the balanced equation; in other words, when $n(H_3O^+) = n(OH^-)$. This is called the **equivalence point**.

equivalence point the point at which the reactants are present in the ratio shown by the mole ratio in the balanced chemical equation for the reaction

Indicators change colour over a wide range of pH values, so it is important to choose an indicator that will change colour at, or close to, the expected pH of the equivalence point. The pH when the indicator changes colour is called the **end point**. This method of volumetric analysis is also known as titration and will be discussed further in section 7.3.

end point the physical sign that indicates that the equivalence point has been reached; achieving the correct end point depends on using an appropriate indicator that will undergo a physical change at the appropriate point

When choosing an indicator for an acid–base reaction, it is important to pick one whose end point is as close as possible to the equivalence point of the reaction **(Figure 7.2.1)**.

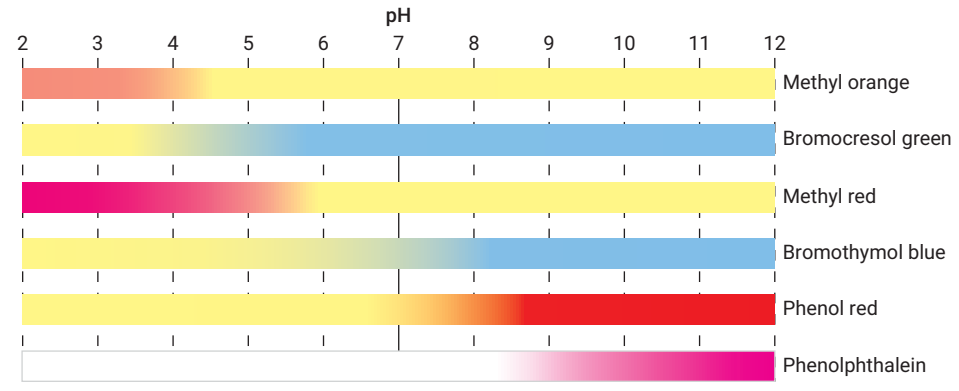


FIGURE 7.2.1 Colours of common indicators over ranges of pH

Weblinks
Choosing acid–base titration indicators
Acid–base reactions

Types of acid–base reactions

The choice of an indicator for an acid–base reaction is complicated by the type of acid–base reaction being studied. The type of reaction is based on the *strength* of the acid and the base involved.

It is important to consider what is left in the flask once the equivalence point has been reached.

Strong acid–strong base

Example: Hydrochloric acid and sodium hydroxide

$$\cancel{HCl(aq)} + \cancel{NaOH(aq)} \rightarrow NaCl(aq) + H_2O(l)$$

At the equivalence point, *just enough* sodium hydroxide has been added to neutralise the hydrochloric acid. All that is left is sodium chloride and water. These must be inspected for acidic or basic properties:

- $Na^+(aq)$ ions have no acidic or basic properties.
- $Cl^-(aq)$ ions are the conjugate base of a strong acid and, although technically a base, have no basic properties.
- $H_2O(l)$ is neutral.

Therefore, the solution remaining after the equivalence point has a pH of 7. From the indicator chart in Figure 7.2.1, it can be seen that the indicator with an end point close to pH 7 is bromothymol blue. Table 7.1.1 backs up the selection of bromothymol blue indicator because it has a pK_a of 7.0.

Strong acid–weak base

Example: Hydrochloric acid and ammonia solution

At the equivalence point: $\cancel{HCl(aq)} + \cancel{NH_3(aq)} \rightarrow NH_4^+(aq) + Cl^-(aq)$

This leaves ammonium ions, $NH_4^+(aq)$, and chloride ions, $Cl^-(aq)$.

- $Cl^-(aq)$ ions have no acidic or basic properties.
- $NH_4^+(aq)$ is the conjugate acid of a weak base and so is a weak acid:

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

Therefore, the solution remaining after the equivalence point has a pH of about 4 or 5. From Figure 7.2.1, the indicator with an end point close to this is methyl orange.

Weak acid–strong base

Worked example 7.2.1 shows an example of a weak acid–strong base: ethanoic acid and sodium hydroxide.

WORKED EXAMPLE 7.2.1

An ethanoic acid solution ($CH_3COOH(aq)$) is titrated with a sodium hydroxide solution. Using Table 7.1.1, suggest a suitable indicator for this titration. Explain the choice of indicator and state the colour change at the end point. The equation for the reaction is:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

ANSWER

1 Determine what occurs at the equivalence point.

Remember, at the equivalence point, there is no CH_3COOH or NaOH. Inspect what remains:

$$\cancel{CH_3COOH(aq)} + \cancel{NaOH(aq)} \rightarrow CH_3COO^-(aq) + Na^+(aq) + H_2O(l)$$

$CH_3COO^-(aq)$

$Na^+(aq)$

$H_2O(l)$

2 Analyse the remaining substances for acid–base properties.
$Na^+(aq)$ has no acid or base properties.
$H_2O(l)$ is neutral.
$CH_3COO^-(aq)$ is the conjugate base of a weak acid.

3 Write the equation for the reaction between ethanoate ion ($CH_3COO^-(aq)$) and water.
$CH_3COO^-(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + OH^-(aq)$
The conjugate base, the ethanoate ion, produces some $OH^-(aq)$ ions. Therefore, it is a weak base.

4 Estimate the pH of the solution.
Since the ethanoate ion ($CH_3COO^-(aq)$) is the conjugate base of a weak acid, it is a weak base. It should have a pH of about 9.

5 Choose the indicator.
From Table 7.1.1, the pK_a closest to a pH of 9 is phenolphthalein, with a pK_a of 9.6. At the end point, phenolphthalein will change colour from colourless to pink.

Weak acid–weak base

Example: Ethanoic acid and ammonia solution

$$CH_3COOH(aq) + NH_3(aq) \rightleftharpoons CH_3COO^-(aq) + NH_4^+(aq)$$

This is a complex system with no clear-cut equivalence point. An acid–base indicator would not be appropriate to monitor this type of reaction. This type of acid–base reaction is not a syllabus requirement.

LEARNING CHECK 7.2

DESCRIBING

1 Define:
a end point
b equivalence point.

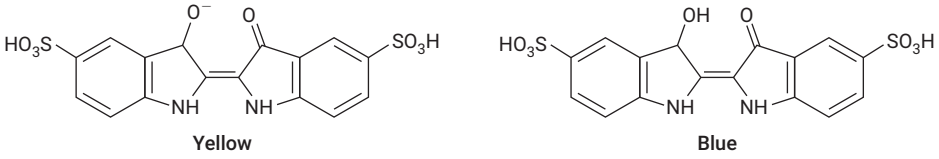
APPLYING

2 Copy and complete the table, using the indicator chart in Figure 7.2.1.

Acid	Base	Products	Equivalence point	Indicator
Propanoic		Sodium propanoate	9	
	Ammonia	Ammonium nitrate		
Hydrochloric		Potassium chloride		
Ethanoic		Ammonium ethanoate	None visible	

3 Identify a suitable indicator from Table 7.1.1 for the titration between:
a nitric acid and phenylamine ($C_6H_5NH_2$)
b hydrocyanic acid (HCN) and potassium hydroxide (KOH).

4 Indigo carmine is an acid–base indicator with a pK_a of 12.2. The two forms of the indicator are shown here.



a During an acid–base titration, what colour change would you expect as the acid is run into the base at the end point? **Explain** your decision.
b **Suggest** an acid–base combination for which this indicator would be most suitable.

7.3 Acid–base titrations

Consider the following reaction:

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$$

The mole ratio indicates that 2 moles of sodium hydroxide react with 1 mole of sulfuric acid. The equivalence point is the point at which there are twice as many moles of sodium hydroxide present as there are moles of sulfuric acid. This is because 1 mole of sulfuric acid produces 2 moles of hydrogen ions (H^+), and 2 moles of sodium hydroxide produce 2 moles of hydroxide ions (OH^-). Therefore, there are equal numbers of moles of hydrogen ions and hydroxide ions. Hence, the equivalence point is when the reactants are present in the mole ratio given in the balanced equation for this reaction.

In the reaction above, both solutions are colourless, as are the products. It is not possible to see when the equivalence point has been reached. An acid–base indicator helps with volumetric analysis, as the end point is shown by a change in colour.

Titrations can be used to detect the end point by a variety of methods, such as the use of acid–base indicators, conductivity and pH probes. Chemists must have an understanding of the chemistry of the specific reaction to determine the most appropriate way to determine the end point.

titration a type of volumetric analysis for determining an end point

Specialised glassware

Since volumetric analysis involves measuring volumes, **accuracy** is very important. Glassware with accurate measuring scales is essential, the most common types being volumetric flasks, burettes and pipettes (Table 7.3.1). To ensure accuracy, **parallax error** must be minimised by keeping the measuring line directly in line with eye level when reading the volume (Figure 7.3.1).

accuracy the degree to which a measurement conforms to the correct value; depends on the measuring instrument being used

parallax error an error in measurement due to the observer's position relative to the meaningful scales; if the reading is taken at an angle to the scale, then an error is introduced

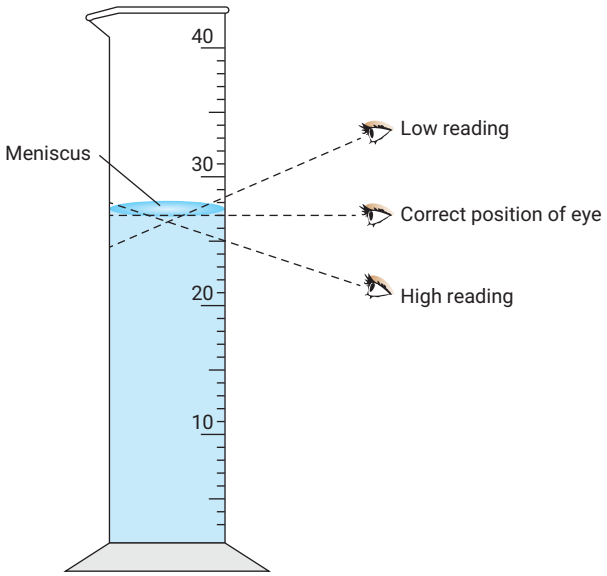


FIGURE 7.3.1 How to read a measuring cylinder and avoid parallax error

TABLE 7.3.1 Some specialised glassware and its uses

Glassware	Description and use
Volumetric flask  Sealstep/Shutterstock.com	• A flat-bottomed flask with a long narrow neck. • Often used for accurately diluting a solution. A line on the flask indicates the volume that can be accurately measured. • The volumetric flask is always rinsed with a solvent, generally distilled water, prior to use.
Burette  i4lcocl2/Shutterstock.com	• A long, narrow glass tube with a tap at the bottom. • The measuring scale on a burette is inverted because it measures the volume of solution that leaves the burette through the tap. • The burette is always rinsed with the solution that will be placed in the burette prior to use. To rinse, close the tap, pour a small volume of solution into the burette. Turn the burette so that all surfaces on the inside of the burette are rinsed with the solution. Open the tap to Empty this solution.
Pipette  Sciencephotos/Alamy Stock Photo	• A thin glass tube that accurately measures a fixed volume of solution. • The pipette is always rinsed with the solution that will be placed in it prior to use. To rinse the pipette, use a pipette filler to draw up a small volume of solution. Hold the pipette horizontally and turn the pipette so that all surfaces are rinsed with the solution. Empty this solution. • When emptying a small volume of solution will remain in the pipette; do not try to evacuate this solution. The pipette has been calibrated to evacuate the specified volume when it empties naturally under gravity.

Primary standard solutions

To accurately determine the concentration of an unknown solution, it is titrated against a solution with an accurately known concentration. Accuracy is the number of significant figures to which a quantity is known. Some mass balances measure to the nearest gram, while others measure to the nearest milligram (0.001 g). Accuracy is determined by the measuring instrument that is used.

A chemical that can be made up into a solution of accurately known concentration is called a **primary standard**. A primary standard must be stable over a long time under common laboratory conditions.

primary standard a solution of accurately known concentration that remains stable under common laboratory conditions for extended periods of time

A primary standard must:

- have a large molar mass so that a reasonable mass is measured; hence, there is a smaller percentage error
- be cheap so that it is affordable for use
- be of high purity so that no side reactions occur
- be stable in the presence of air, so that no reaction with air occurs
- not have any water of hydration, which may change due to atmospheric conditions such as humidity
- dissolve readily in a solvent, generally water, to form a stable solution.

Anhydrous sodium carbonate (Na_2CO_3) and sodium hydrogencarbonate ($NaHCO_3$) are frequently used as primary standards in school laboratories because they meet all of these criteria.

Performing volumetric analysis

The solution in the burette is called the **titrant**. The solution to be analysed usually in a conical flask, which has the unknown concentration, is called the **analyte**.

titrant a solution of known concentration that is added to another solution from a burette

analyte a solution of an unknown concentration that will be analysed

The most common titration conducted in a school science laboratory is the acid–base titration. The following describes the basic technique for performing a titration (Figure 7.3.2). Note that this procedure can only be used if one of the solutions has an accurately known concentration.

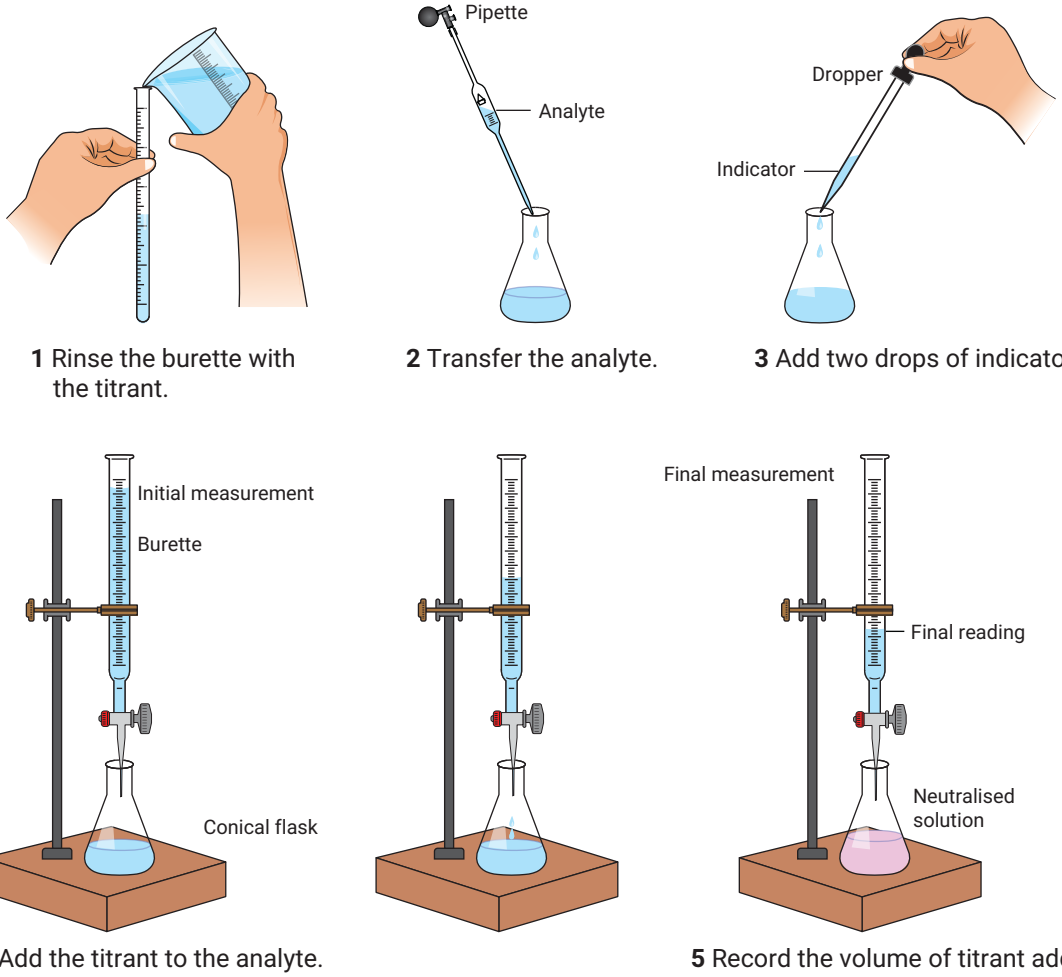
1. Rinse the burette with a small amount of the titrant. This is generally, but not always, the solution whose concentration is known.
2. Use a pipette to transfer a known volume (an **aliquot**) of the analyte into a conical flask that has been rinsed with water.
3. Add two drops of an appropriate acid–base indicator to the analyte.
4. Slowly add the titrant to the analyte. Make sure to swirl the flask as the titrant is added. This ensures that the reactants are adequately mixed. Stop adding the titrant when the indicator shows the first permanent colour change.
5. Record the volume of titrant added.
6. Repeat the experiment several times until the volume of the titrant added from the burette is consistent to within about one-third of a division (0.03 mL). The second and subsequent titrations should involve slowing the rate of flow of the titrant from the burette to dropwise and parts of drops when near the end point. Use the average titre for the most accurately known titrations for your calculations.
7. Write a balanced chemical equation and use mole calculations to determine the concentration of the unknown analyte.

aliquot a sample of specific volume of a larger volume of solution

Weblinks

Titration screen experiment

Back titration



1 Rinse the burette with the titrant.

2 Transfer the analyte.

3 Add two drops of indicator.

4 Add the titrant to the analyte.

5 Record the volume of titrant added.

FIGURE 7.3.2 The steps in a titration

WORKED EXAMPLE 7.3.1

Potassium hydrogen phthalate ($KH(C_8H_4O_4)$) (or KHP) is a good primary standard for standardising alkali solutions. It contains one acidic hydrogen per formula unit.

Potassium hydrogen phthalate (0.917 g) was dissolved in water and titrated with approximately 0.2 mol L^{-1} sodium hydroxide (NaOH) solution; 27.2 mL hydroxide solution was needed to reach the end point. Calculate the accurate molarity of the hydroxide solution.

ANSWER

1 Write a balanced equation for the reaction.

$KH(C_8H_4O_4)(aq) + NaOH(aq) \rightarrow Na^+(aq) + K(C_8H_4O_4)^-(aq) + H_2O(l)$

2 Calculate the number of moles of potassium hydrogen phthalate (known substance) that reacted with the sodium hydroxide (unknown).

$$n(\text{KHP}) = \frac{0.917}{204.23}$$

$$= 0.00449 \text{ mol}$$

3 Calculate the number of moles of sodium hydroxide (unknown substance) that reacted with the potassium hydrogen phthalate (known substance).
From the balanced equation, the relationship between NaOH and KHP is 1:1.
Therefore:

$n(\text{NaOH}) = n(\text{KHP}) = 0.004\,49 \text{ mol}$

4 Calculate the molarity of the sodium hydroxide (unknown) solution.
Remember to convert the volume to the appropriate units: 27.2 mL = 0.0272 L

$$c(\text{NaOH}) = \frac{0.004\,49}{0.0272}$$
$$= 0.165 \text{ mol L}^{-1}$$

Overall, the basic steps for titration calculations involve:

- finding the number of moles of the 'known' substance reacted
- using stoichiometry to determine the number of moles of the 'unknown' substance
- calculating the value (usually concentration) of the unknown substance.

Sometimes the solutions to be titrated are diluted first. This is not a straightforward calculation because the dilution factor needs to be taken into account. Worked example 7.3.2 shows show to handle these types of questions.

Syllabus link
Chapter 14 of *Nelson QCE Chemistry Units 1 & 2* described dilution and their calculations in further detail.

WORKED EXAMPLE 7.3.2

Before analysis, a vinegar (CH_3COOH) solution was diluted by pipetting 50.00 mL into a 250 mL volumetric flask. Distilled water was added to the 250.0 mL mark.

A 20.00 mL aliquot of diluted vinegar required on average 23.65 mL of 7.070×10^{-2} mol L^{-1} sodium carbonate solution to reach the end point. Determine the concentration of ethanoic acid in the undiluted vinegar solution.

ANSWER

1 Write a balanced equation for the reaction.

$2CH_3COOH(aq) + Na_2CO_3(aq) \rightarrow 2NaCH_3COO(aq) + H_2O(l) + CO_2(g)$

2 Calculate the number of moles of sodium carbonate (known substance) used in the titration.

$n(Na_2CO_3) = c \times V$

Remember to convert the volume to the appropriate units:

23.65 mL = 0.023 65 L

$n(Na_2CO_3) = 7.070 \times 10^{-2} \times 0.023\,65$
$= 0.001\,672 \text{ mol}$

3 Calculate the number moles of vinegar (unknown substance) in the 20.00 mL aliquot.

The ratio CH_3COOH to Na_2CO_3 from balanced equation is 2:1.

$n(CH_3COOH) = 2 \times 0.001\,672 = 0.003\,344 \text{ mol}$

4 There are two options to calculate the concentration of the original solution.
Option A: Using number of moles

i Calculate the number of moles of vinegar (CH_3COOH) in the 250.0 mL diluted solution.
Given that there is 0.003 344 mol in a 20.00 mL solution, we have to determine how much more vinegar is 250.0 mL.

$$n(CH_3COOH) = \frac{250.0}{20.00} \times 0.003\,344 = 0.041\,80 \text{ mol}$$

ii Calculate the number of moles of vinegar (CH_3COOH) in the original 50.00 mL solution.

All of the vinegar in the 250.0 mL came from the original 50.00 mL solution.

Therefore:

$n(CH_3COOH) = n(CH_3COOH)$ in 250.0 mL of dilute solution $= 0.041\,80$ mol

$$c(CH_3COOH) = \frac{0.04180}{0.050\,00} = 0.8360 \text{ mol L}^{-1}$$

Option B: Using concentration

i Calculate the concentration of vinegar (CH_3COOH) in the 20.00 mL aliquot.

$$c = \frac{0.003\,344}{0.020\,00}$$

$$= 0.1672 \text{ M}$$

ii Determine the concentration of vinegar in the 250 mL diluted solution.

The concentration of vinegar in the 20.00 mL aliquot is the same as the concentration in the 250.0 mL solution that the aliquot was taken from. Therefore, the concentration of the dilute solution is also 0.1672 M.

iii Calculate the concentration of the undiluted vinegar (CH_3COOH) solution.

For dilution calculations, recall that:

$c_1V_1 = c_2V_2$

Where c_1 and V_1 are the concentration and volume of the 'original' solution.

Substituting the values:

$c_1 \times 0.050\,00 = 0.1672 \times 0.2500$

$c_1 = 0.8360 \text{ mol L}^{-1}$

Recall from Chapter 4 that acids can be monoprotic, diprotic or triprotic depending on the number of hydrogen ions it will dissociate into. Worked example 7.3.3 shows how you would perform calculations with a polyprotic acid in a titration.

WORKED EXAMPLE 7.3.3

The acidity of a particular white wine was determined by titrating 25.0 mL of the wine with 0.0511 mol L^{-1} sodium hydroxide solution; 8.70 mL was required.

Calculate the concentration of hydrogen ions in the wine and the concentration of the tartaric acid in moles per litre. Assume that the hydrogen ions come entirely from diprotic tartaric acid ($H_2C_4H_4O_6$).

ANSWER

1 Write a balanced chemical equation for the reaction.

$H_2C_4H_4O_6(aq) + 2NaOH(aq) \rightarrow 2Na^+(aq) + C_4H_4O_6^{2-}(aq) + 2H_2O(l)$

2 Calculate the number of moles of sodium hydroxide (known substance) that reacts with tartaric acid.

$n(NaOH) = c(NaOH) \times V(NaOH)$

$= 0.0511 \times 0.008\,70$

$= 4.45 \times 10^{-4}$ mol

3 Calculate the number of moles of acid (unknown substance) that react with the sodium hydroxide.
The relationship between sodium hydroxide and tartaric acid is 2:1. Therefore, the number moles of tartaric acid will be half the number of moles of sodium hydroxide.

$$n(H_2C_4H_4O_6) = \frac{4.45 \times 10^{-4}}{2}$$
$$= 2.23 \times 10^{-4} \text{ mol}$$

4 Calculate the concentration of tartaric acid.

$$c(H_2C_4H_4O_6) = \frac{2.23 \times 10^{-4}}{0.0250}$$
$$= 0.008\,92 \text{ mol L}^{-1}$$

5 Calculate the concentration of hydrogen ions in tartaric acid.
Because tartaric acid is diprotic, the relationship between the tartaric acid and H^+ is 1:2. Therefore, the concentration of hydrogen ions will be double the concentration of tartaric acid.
$c(H^+) = 2 \times 0.008\,92$
$= 0.0178 \text{ mol L}^{-1}$

The real-life applications of volumetric analysis with respect to acid–base reactions are extremely important, from quality control of domestic food to maximising efficiency of industrial chemical processes to monitoring the effects of atmospheric pollution.

Volumetric analysis can determine, with precision, the amounts of unknown substances by monitoring acid–base reactions with indicators or pH meters.

In reality, titration experiments require multiple trials to decrease the impact of any random errors. As a result, the volume of titrant used in a calculation is often an average of the three **concordant titres**.

concordant titres titres that differ by 0.1 mL from the highest to the lowest value

WORKED EXAMPLE 7.3.4

Table 7.3.2 was obtained in an experiment to determine the amount of citric acid ($C_6H_8O_7$) in freshly squeezed lime juice. 25.00 mL samples of lime juice were tested in each trial.

TABLE 7.3.2 The results of a lime juice experiment

	Burette reading (mL)			
	Rough	1	2	3
Initial	0.00	23.05	0.10	22.25
Final	22.50	45.20	22.20	44.45
Titre	22.50	22.15	22.10	22.20
Average		22.15 (calculated using concordant titres)		

Mass of 100 mL of freshly squeezed lime juice = 101.48 g
Concentration of sodium hydroxide = 0.984 M

a Which indicator would have been used in this titration?

b Use the data to determine the percentage, by weight, of citric acid in freshly squeezed lime juice.

ANSWERS

a 1 Determine the approximate pH for the equivalence point.

Citric acid is a weak acid, so it is best to titrate it with a strong base such as sodium hydroxide. Typically, a weak acid–strong base titration has an equivalence point around pH 9.

2 Use the pH and pK_a values to determine the most suitable indicator.

Phenolphthalein indicator has a pK_a of 9.6. Therefore, it would be a suitable indicator.

b 1 Write the balanced equation for this reaction.

$C_6H_8O_7(aq) + 3NaOH(aq) \rightarrow Na_3C_6H_5O_7(aq) + 3H_2O(l)$

2 Calculate the number of moles of sodium hydroxide (known substance) delivered from the burette using the average calculated from concordant titres.

$n(NaOH) = 0.984 \times 0.022\,15$

$= 0.0218$ mol

3 Using the mole ratio from the balanced equation, determine the number of moles of citric acid (unknown substance).

According to the equation, the relationship between $C_6H_8O_7$ and NaOH is 1:3.

Therefore:

$$n(C_6H_8O_7) = \frac{n(NaOH)}{3}$$

$$= \frac{0.0218}{3}$$

$= 0.007\,27$ mol

4 Calculate the mass of citric acid.

$m(C_6H_8O_7) = 0.007\,27 \times 192.14$

$= 1.40$ g

5 Calculate the percentage by mass of citric acid in the sample.

$$\% = \frac{\text{mass of citric acid in sample}}{\text{mass of lime juice}} \times 100$$

Since only 25.00 mL samples were used, we would need to calculate the mass of citric acid in 25.00 mL.

$$m(\text{citric acid})_{\text{in 25.00 mL}} = \frac{101.48}{4}$$

$= 25.37$ g

$$\% = \frac{1.40}{25.37} \times 100$$

$= 5.5\%$

PRACTICAL ACTIVITY 7.3.1

ACID–BASE TITRATION TO CALCULATE CONCENTRATION OF A SOLUTION WITH REFERENCE TO THE STANDARD SOLUTION

Introduction

In this titration, you will be using the primary standard sodium carbonate (0.05–0.06 mol L^{-1}) solution to determine the unknown concentration of a solution of hydrochloric acid. Hydrochloric acid is a strong acid and sodium carbonate is a weak base so the equivalence point will be in the acidic region. Methyl orange is a suitable indicator for this titration.

Research question

How can volumetric analysis be used to accurately determine the concentration of an unknown hydrochloric acid (HCl) solution?

Aim

To determine the concentration of a hydrochloric acid solution by volumetric analysis

Materials

- 250 mL of an accurately known concentration of sodium carbonate
- 200 mL of hydrochloric acid of unknown concentration
- dropper bottle containing methyl orange indicator
- wash bottle with distilled water
- 50 mL burette
- retort stand and burette clamp
- 25 mL volumetric pipette and pipette filler
- 2 × 150 mL beakers
- 3 × 250 mL conical flasks
- 2 small labels for the 150 mL beakers
- filter funnel

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Dilute solutions of hydrochloric acid, sodium carbonate and methyl orange indicator may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Glassware could break and cut your hands.	Keep glassware away from the edge of the bench. When the pipette is not in use, leave the pipette filler on the pipette to prevent it rolling off the bench. If glassware does break, inform your teacher immediately.

Copy and complete the risk assessment table in your write-up. Add any more risks you can think of, and ways to manage them. Ask your teacher to check your table before you proceed.

Procedure

1. Rinse one of the 150 mL beakers with a small amount of hydrochloric acid solution, empty it, label it and fill it with about 100 mL of hydrochloric acid solution.
2. Prepare the burette and place the filter funnel in the top of the burette. Fill the burette with hydrochloric acid solution. Be sure to remove the filter funnel before taking any readings.
3. Rinse the other 150 mL beaker with a small amount of the sodium carbonate solution, empty it, label it and fill with about 100 mL of the sodium carbonate solution.
4. Rinse the conical flask with water.
5. Prepare the pipette, then use the pipette to transfer 25 mL of the sodium carbonate solution to the conical flask.
6. Add two drops of methyl orange indicator to the conical flask and swirl to mix.
7. Place the conical flask under the burette and begin the titration.
8. When the first permanent colour change has occurred, record all results.
9. Repeat the titration several more times until the amount of titrant added is within 0.03 mL.

Results

Draw up a suitably formatted table and record the following results.

- Concentration of sodium carbonate solution
- Volume of sodium carbonate used
- Volume of hydrochloric acid used

Analysis of results

1 Calculate the average volume of hydrochloric acid used.
2 Write a balanced chemical equation for the reaction between hydrochloric acid and sodium carbonate.
3 Calculate the number of moles of sodium carbonate placed in the reaction vessel (conical flask).
4 Use the mole ratio from your balanced chemical equation to determine the number of moles of hydrochloric acid that was titrated.
5 Calculate the concentration of hydrochloric acid that was titrated.

Evaluation

6 Compare your value for the concentration of the hydrochloric acid with that of other students and with the value provided by your teacher.
7 Discuss any variations in the value and suggest how to improve the accuracy of your results.
8 Justify why the conical flask was rinsed with water and not with the solutions that were placed in it.

Worksheet
Titrations

Practical activity 7.3.1 is the simplest type of titration, where an acid and a base are titrated directly against each other using an appropriate acid–base indicator. The issues to be considered are:

- identifying the correct indicator to use
- making sure that the chemical equation is correctly balanced to ensure that the correct mole ratio is used in the calculations.

Titration and solubility equilibria

As explained in Chapter 3, many substances are only partially soluble in water. This includes many covalently bonded compounds that contain acidic hydrogens atoms, such as organic acids. Examples include citric acid, acetylsalicylic acid and tartaric acid.

Tartaric acid ($H_2C_4H_4O_6$) is a diprotic acid, meaning each molecule can donate two protons. It forms a slightly soluble salt called potassium hydrogen tartrate (KHT, $KHC_4H_4O_6$) which is also weakly acidic. Its limited solubility in water establishes an equilibrium:

$$KHC_4H_4O_6(s) \rightleftharpoons K^+(aq) + HC_4H_4O_6^-(aq)$$

When the system is at equilibrium, it is said to be saturated. The solubility of this salt is described by the solubility product constant (K_{sp}), with the expression:

$$K_{sp} = [K^+][HC_4H_4O_6^-]$$

A solubility titration can be used to measure the concentration of these ions and calculate K_{sp}. Since $HC_4H_4O_6^-$ is a weak acid, a strong base such as sodium hydroxide is used to titrate it. The acid–base reaction is:

$$NaOH(aq) + HC_4H_4O_6^-(aq) \rightarrow H_2O(l) + C_4H_4O_6^{2-}(aq)$$

This is a 1:1 molar ratio reaction. So, if we add just enough base to neutralise the acid, the number of moles of NaOH used equals the number of moles of $HC_4H_4O_6^-$ present. From this, we can calculate its concentration.

This titration can be performed using phenolphthalein as the indicator. The concentration is calculated using the same approach as in Worked example 7.3.5.

WORKED EXAMPLE 7.3.5

A saturated solution of the slightly solubility acid KHT ($KHC_4H_4O_6$) was prepared by mixing excess solid with distilled water and leaving it to stand overnight. A 25.00 mL sample of the clear solution was taken. It was titrated with 0.01025 mol L^{-1} NaOH, starting at an initial volume of 0.15 mL and ending at 34.65 mL. Calculate the solubility and solubility product, K_{sp}.

ANSWER

1 Write a balanced chemical equation for the reaction.

$NaOH(aq) + HC_4H_4O_6^-(aq) \rightarrow H_2O(l) + C_4H_4O_6^{2-}(aq)$

2 Calculate the volume of NaOH used.

$V(NaOH)$ = final volume – initial volume

= 34.65 – 0.15 = 34.50 mL = 0.034 50 L

3 Calculation the number moles of NaOH added.

$n(NaOH) = c \times V$

$= 0.010\,25 \times 0.034\,50 = 0.000\,3536$ mol

4 Calculate the number of moles of $HC_4H_4O_6^-$ neutralised.

The relationship between $HC_4H_4O_6^-$ and NaOH is 1:1:

$n(NaOH) = n(HC_4H_4O_6^-) = 0.000\,3536$ mol

5 Calculate the concentration of $HC_4H_4O_6^-$ in solution.

$$c(HC_4H_4O_6^-) = \frac{n}{V}$$

$$= \frac{0.000\,3536}{0.025\,00}$$

$= 0.014\,14$ mol L^{-1}

Since each KHT unit produces one K^+ and one $HC_4H_4O_6^-$:

$c(K^+) = c(HC_4H_4O_6^-) = 0.014\,14$ mol L^{-1}

6 Calculate the solubility of $KHC_4H_4O_6$ (concentration × molar mass).

Solubility = $0.014\,14 \times 188.19 = 2.661$ g L^{-1}

7 Calculate the solubility product, K_{sp}.

$K_{sp} = [K^+][HC_4H_4O_6^-]$

$= 0.014\,14^2$

$= 2.00 \times 10^{-4}$

Conductometric titrations

Conductometric titrations are very useful in analytical chemistry. In this type of titration, electrical conductivity of the solution is measured throughout the titration process owing to the ions in the solution carrying electric current. As the titrant is added, the concentration of these ions changes, causing the conductivity to increase or decrease. **Figure 7.3.3** shows an example of the apparatus used. A conductivity probe can also be used if your school has one. Note that a beaker is used instead of a conical flask.

The equivalence point (the point where the acid and base completely neutralise each other) is identified by plotting conductivity against the volume of titrant added. The conductivity depends on the concentration and strength of the acid and base. Greater concentration leads to greater conductivity and stronger acids/bases means there is more ionisation, which leads to a higher concentration of ions. Some ions are also more mobile in solution than others. Hydrogen

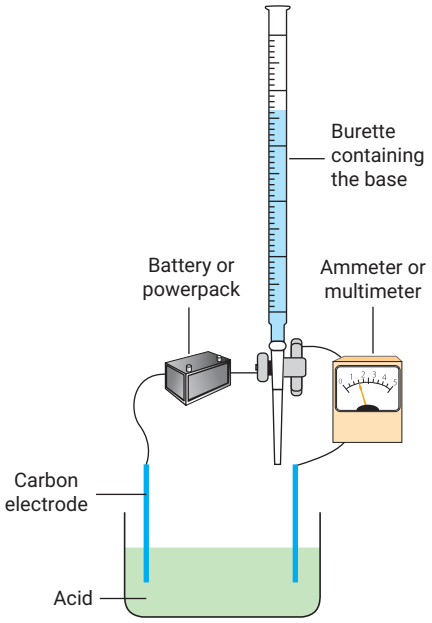


FIGURE 7.3.3 The apparatus used in a conductometric titration

ions from the acid are more mobile than other cations and hydroxide ions are more mobile than other anions because of their smaller sizes.

Some advantages of the conductometric process are that it:

- is useful in titrations of very dilute solutions and weak acids
- can be used for solutions that are coloured or turbid, and for which the end point of the titration with normal indicators cannot be easily observed by the human eye
- gives a very sharp and accurate end point compared to other titration processes
- can be used in acid–base titrations, redox titrations, precipitation titrations and complex titrations.

A disadvantage of the conductometric process has to do with the accuracy of conductometric titration. It is low when the concentrations of the electrolyte are high. A relatively high concentration of hydrogen ions can mask the conductivity of the solution. Conductometric titration graphs will be analysed further in section 7.4.

LEARNING CHECK 7.3

ANALYSING

1 Oxalic acid dihydrate ($(COOH)_2.2H_2O$) can be used as a primary standard for standardising alkali solutions. 0.291 g diprotic oxalic acid required 18.2 mL of a potassium hydroxide solution for exact neutralisation. **Calculate** the molarity of the hydroxide solution.

2 5.267 g anhydrous sodium carbonate was dissolved in water in a volumetric flask and the volume made up to 250 mL. Using a pipette, 10 mL of this solution was transferred into a conical flask and titrated with hydrochloric acid. 21.3 mL was needed to reach the equivalence point. This solution was then used to determine the concentration of an unknown barium hydroxide solution. 25 mL of the barium hydroxide solution required 27.1 mL hydrochloric acid solution for exact neutralisation. **Calculate** the:

a molarity of the hydrochloric acid solution
b molarity of the barium hydroxide solution
c concentration of the barium hydroxide solution in grams per litre.

3 Calcium hydroxide ($Ca(OH)_2$) has a low solubility in water. The OH^- can be titrated with a standardised HCl solution.

a Write the reaction for the dissolution of $Ca(OH)_2(s)$ in water.

b Write the K_{sp} expression for the reaction.

A saturated solution of $Ca(OH)_2$ was prepared and then filtered to remove the solid material. 25.00 mL of the supernatant liquid was then titrated three times with 0.015 14 mol L^{-1} HCl. The average titration volume was 38.83 mL.

c **Calculate** the concentration of OH^- in the 25.00 mL aliquot sample.

d **Calculate** the concentration of calcium ions in the 25.00 mL aliquot sample.

e Using your K_{sp} expression, **calculate** the value for the solubility product constant.

7.4 Graphs

Volumetric analysis

If the solution being analysed is not colourless, then it will interfere with the colour change of the indicator. Some solutions, such as malt vinegar and red wine, are so dark that the indicator colour cannot be seen at all. In this case, a pH meter would be used rather than an indicator, and the pH of the solution would be measured as the solution from the burette is added to the conical flask. The titration can be analysed by plotting a graph of pH against volume of acid or base added. This kind of graph is called a **titration curve** (or pH curve).

titration curve a graphical representation of a titration; the *x*-axis shows the volume of titrant added, and the *y*-axis shows the pH of the solution

Weblink
Acid–base titration curves

During an acid–base titration, the pH of the solution in the reaction vessel changes. If the base is pipetted into the conical flask, then the acid is added from the burette, and the pH will change from basic to acidic. The shape of the graph depends on the strength of the acid and base used; however, it is not a linear change. The pH of the final solution at equivalence point depends on the type of salt produced from neutralisation. The type of salt formed depends on the relative strengths of acids and bases used in titration. A neutral salt has a pH of 7, an acidic salt has a pH below 7 and a basic salt has a pH above 7.

Strong base–strong acid

The graph for a titration of a strong base and a strong acid shows that the pH starts at a very high value in the basic region (Figure 7.4.1). It remains fairly constant until close to the equivalence point, when it suddenly decreases. The pH drops from 12–13 to 1–2. When acid is in excess, the pH stays reasonably constant, again at a very low pH. The equivalence point is the midpoint of the sudden change in the pH.

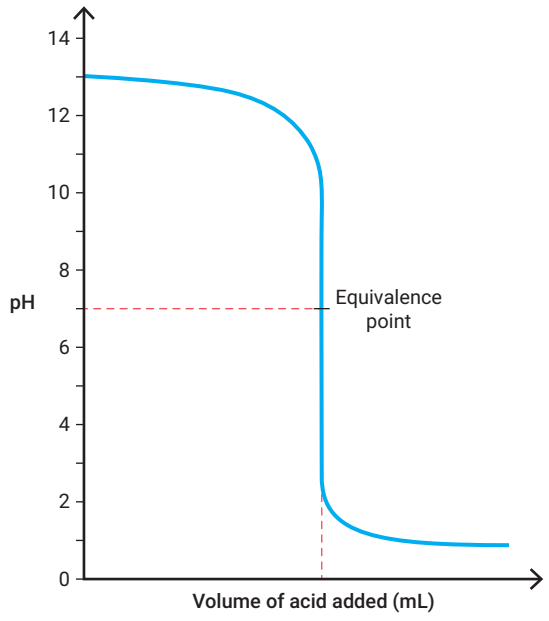


FIGURE 7.4.1 A titration curve for a strong base–strong acid titration

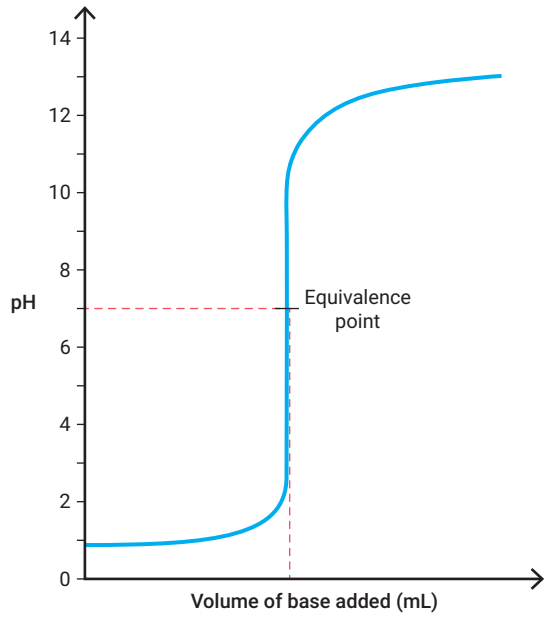


FIGURE 7.4.2 A titration curve for a strong acid–strong base titration

The graph for a titration of a strong acid and a strong base shows the pH starting at a very low value; it is in the acidic region **(Figure 7.4.2)**. It remains fairly constant until close to the equivalence point, when it suddenly increases. The pH rises from 1–2 to 12–13. When the base is in excess, the pH stays reasonably constant, again at a very high pH.

In both of these cases, a neutral salt is formed and the equivalence point is equal to pH 7. An appropriate indicator for these types of titration is bromothymol blue.

Strong base–weak acid

The graph for a titration of a strong base and a weak acid also begins with a very high basic pH **(Figure 7.4.3)**. It remains fairly constant until close to the equivalence point, when it suddenly decreases, although not as much as for the strong base–strong acid titration. The pH drops from 12–13 to about 4.

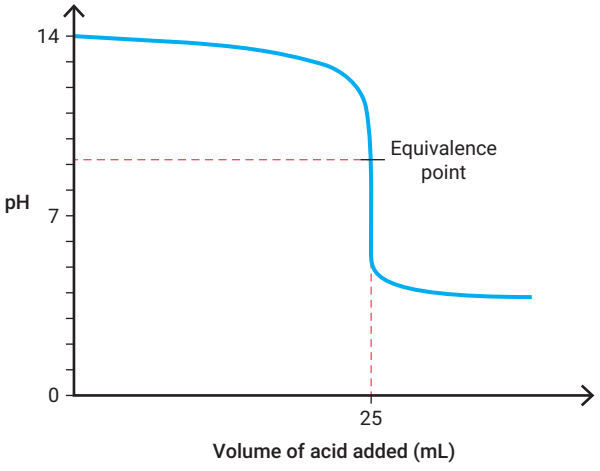


FIGURE 7.4.3 A titration curve for a strong base–weak acid titration

When acid is in excess, the slope of the pH graph changes and eventually stays reasonably constant at a low pH. The equivalence point is the midpoint of the sudden change in the pH. A basic salt is produced at neutralisation and results in an equivalence point above pH 7. Phenolphthalein is an appropriate indicator for this type of titration.

Weak base–strong acid

The graph for the titration of a weak base and a strong acid shows that the pH starts at a high basic value, although it is not as high as for the strong base **(Figure 7.4.4)**. It decreases slightly and then close to the equivalence point it suddenly decreases, although not as much as for the strong base–strong acid titration. The pH drops from 8–9 to 1–2. When acid is in excess, the pH stays reasonably constant again at a very low pH. The equivalence point is the midpoint of the sudden change in the pH. An acidic salt is produced at neutralisation and results in an equivalence point below pH 7. Methyl orange is an appropriate indicator for this type of titration.

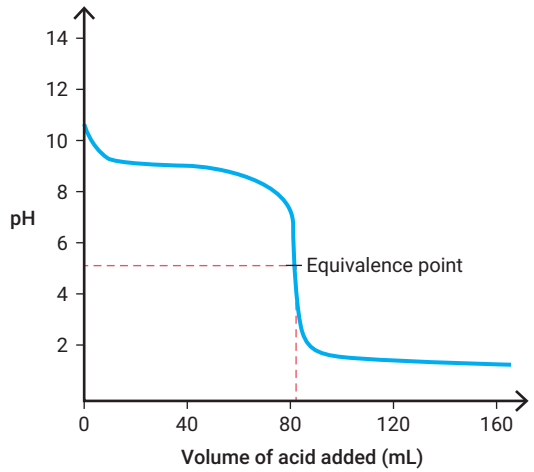


FIGURE 7.4.4 A titration curve for a weak base–strong acid titration.

Worked example 7.4.1 shows how a titration curve can be used in real-life situations.

WORKED EXAMPLE 7.4.1

Balsamic vinegar is a common ingredient in salad dressings, risotto and pasta dishes. A major problem when determining the ethanoic acid content of balsamic vinegar is that it is a very dark, almost black solution. This makes it hard to use an indicator to determine the equivalence point.

An experiment is conducted in which 20 mL of balsamic vinegar is transferred to a 250 mL volumetric flask. Distilled water is added up to the 250 mL mark. A 25 mL sample of this solution is transferred to a conical flask by pipette. A 0.118 M sodium hydroxide solution is added to the flask from a burette. A pH probe in the solution in the conical flask monitors the pH changes throughout the experiment. A graph is plotted of pH against volume of sodium hydroxide added. Using this information and the titration curve in **Figure 7.4.5**, calculate the percentage of ethanoic acid in the balsamic vinegar.

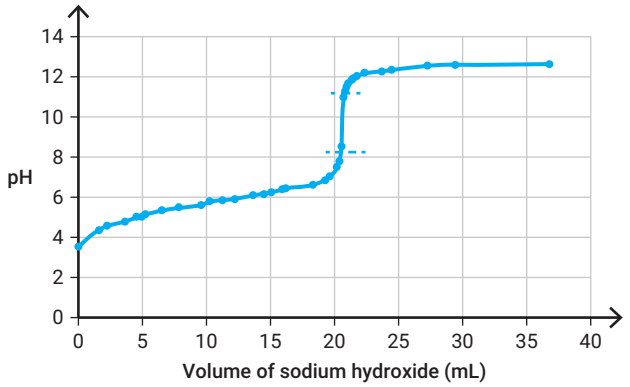


FIGURE 7.4.5 The titration curve for the reaction between balsamic vinegar and sodium hydroxide

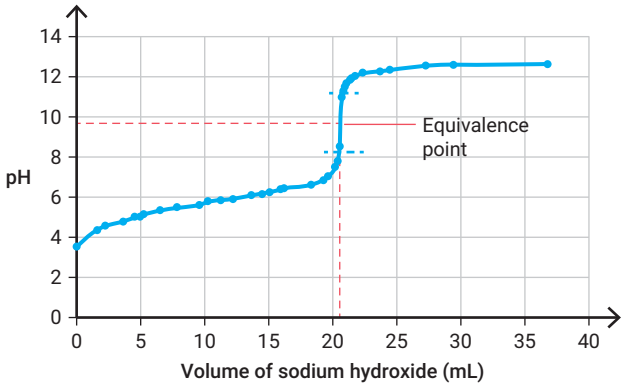
ANSWER

1 Write the balanced equation for this reaction.

$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$

2 Determine the equivalence point of the titration from the titration curve.

Using the blue dotted lines (which show the lower and upper limits of the near vertical part of the graph), measure half of this distance to find the equivalence point. Draw dotted lines from this point to the pH axis and the NaOH volume axis. This gives a volume of 20.6 mL.



3 Calculate the number of moles of sodium hydroxide added from the burette.

$n(NaOH) = c \times V$

$= 0.118 \times 0.0206$

$= 0.002\,43$ mol

4 Determine the number of moles of ethanoic acid in 25 mL vinegar solution in the conical flask.

Based on the mole ratio from the balanced equation, the relationship between CH_3COOH and NaOH is 1:1:

$n(CH_3COOH) = n(NaOH)$

$= 0.002\,43$ mol

5 Determine the number of moles of ethanoic acid in the 250 mL volumetric flask.

25 mL vinegar solution = 0.002 43 mol

$\therefore$ 250 mL vinegar solution = $0.002\,43 \times 10 = 0.0243$ mol

6 Calculate the mass of ethanoic acid in the original 20.0 mL vinegar solution.

Since the 0.0243 mol of ethanoic acid came from the original 20.0mL sample of vinegar (before dilution), the mass of ethanoic acid in that original sample is:

$$m(CH_3COOH) = n \times M$$
$$= 0.0243 \times 60.06$$
$$= 1.46 \text{ g}$$

7 Calculate the percentage, by mass of the ethanoic acid.

The 1.46 g of ethanoic acid came from the 20 mL sample of balsamic vinegar solution. Assuming that the density of the balsamic vinegar sample is 1 g mL^{-1}:

$$\therefore \% \text{ ethanoic acid} = \frac{\text{mass of ethanoic acid in sample}}{\text{mass of balsamic vinegar}} \times 100$$
$$= \frac{1.46}{20.0} \times 100$$
$$= 7.30\%$$

Features of a titration curve

Figure 7.4.6 shows a titration curve for the reaction between sodium hydroxide, in the conical flask, and ethanoic acid, in the burette. The equation for this reaction is:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

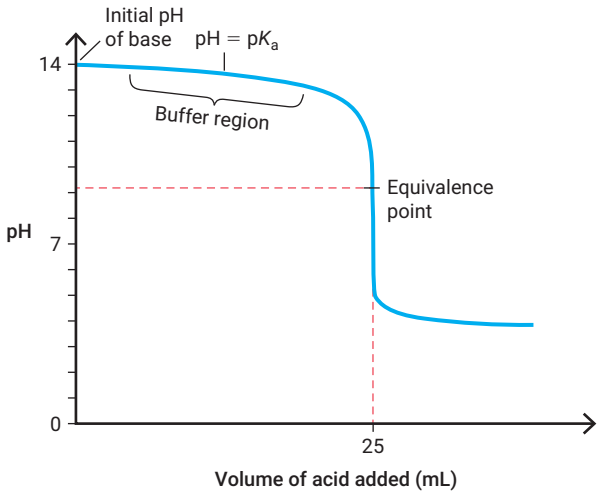


FIGURE 7.4.6 A titration curve for a strong base–weak acid titration

Initially, the pH of the solution in the flask is 14, because it only contains sodium hydroxide, a strong base. As ethanoic acid is added, the pH of the solution decreases slowly. This almost horizontal part of the graph is known as the **buffer region**. It can be seen from the equation above that as ethanoic acid is added, its conjugate base, the ethanoate (acetate) ion, is produced. This forms a buffer solution of a weak acid and its conjugate base.

The conjugate base reacts with water to produce $OH^-(aq)$ ions:

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

buffer region the part of a titration curve during which the pH changes little as titrant is added; occurs when one of the reagents is a weak acid or a weak base and is the result of a buffer solution being set up

In this region, it is reasonable to assume:

$$[\text{base}] = [\text{salt}]$$

Therefore:

$$\text{pH} = \text{p}K_a$$

In this situation, the pH is just over 13. The $\text{p}K_a$ of sodium hydroxide is 13.8. This point is also known as the **half-equivalence point**, the point at which exactly half of the acid has reacted with the base. In this case, 12.5 mL of acid has been added.

half-equivalence point the point at which exactly half of the acid in the buffer solution has reacted with the titrant

Sodium hydroxide is a base; therefore, the procedure above can be repeated with respect to bases:

$$\text{p}K_a + \text{p}K_b = 14$$

$$\text{p}K_b = 14 - 13.8$$

$$= 0.2$$

The $\text{p}K_b$ for sodium hydroxide is 0.2.

Weblink
pH curves

Conductometric titration graphs

The electrical conductivity of a solution is proportional to the concentration of ions in the solution. The conductivity of a solution of a strong acid or base, which ionise completely, is higher than the conductivity of a solution of a weak acid or base. Similarly, a concentrated solution will have higher conductivity than a dilute solution of the same substance. Other factors that affect conductivity are the size of the ions (as ion size increases, conductivity decreases because larger ions are less mobile) and temperature (as temperature increases, conductivity increases because the mobility of the ions has increased).

Changes in conductivity during a conductometric titration are because during the titration one of the ions is replaced by another of different conductivity. The equivalence point is determined graphically by plotting change in conductance against the volume of titrant added. Just as for titration curves, the shape of the graph depends on the strength of the acid and base used.

Conductivity of ions

Some ions are better conductors or charge carriers than others. Hydrogen and hydroxide ions are the most conductive due to their smaller sizes. Table 7.4.1 shows conductivities of some cations and anions at 298 K.

TABLE 7.4.1 Molar conductivities of selected ions in solution

Cation	Molar conductivity (S L mol^{-1} cm^{-1})*	Anion	Molar conductivity (S L mol^{-1} cm^{-1})
H^+	0.3498	OH^-	0.1986
K^+	0.0735	Br^-	0.0781
NH_4^+	0.0735	Cl^-	0.0764
Na^+	0.0501	CH_3COO^-	0.0409

*S = siemens, the SI unit of conductance

Strong acid and strong base

In this titration, hydrochloric acid (HCl) is added from the burette into a beaker containing sodium hydroxide (NaOH). The reaction can be written as:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Or, to better observe the ions in the solution, it is written as full ionic equations:

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$$

Table 7.4.2 and **Figure 7.4.7a** (p. 160) summarise this type of titration.

TABLE 7.4.2 Conductivity during the titration of a strong acid and a strong base

Stage of conductivity titration	Observations of conductivity
Initial conductivity	Sodium hydroxide is a strong base that completely dissociates in water to produce sodium and hydroxide ions. The initial conductivity of the solution is high because OH^- ions are good conductors of current.
Adding HCl	As HCl is added, the highly mobile OH^- ions react with the H^+ ions to form weakly ionised water molecule, which is not a conductor. This replacement of OH^- with Cl^- leads to a drop in conductivity. Chloride ions are less conductive than hydroxide ions, so the overall conductivity steadily decreases.
Approaching the equivalence point	As more HCl is added, the conductivity reaches a minimum value when the titration reaches the equivalence point. All of the hydroxide ions have been neutralised by the hydrogen ions, leaving only the less conductive Na^+ and Cl^- in solution at this point.
After the equivalence point	Once the equivalence point is passed, any additional HCl added will add excess hydrogen ions, which are highly conductive. This causes the conductivity to increase sharply after the equivalence point.

Weak acid and strong base

For the reaction between a weak acid and a strong base, there is low conductance before titration. This is because of the small degree of ionisation of the weak acid. When the strong base is added, the H^+ ion reacts with OH^- ions to form weakly ionised water, resulting in a slight decrease in conductivity. This is also due to the presence of the weak acid anion that supresses the ionisation of the weak acid. This is called the common ion affect. For example, consider:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

According to Le Châtelier, increasing concentration of the $CH_3COO^-(aq)$ will drive the reaction in the reverse direction, preventing ionisation. However, with further addition of the strong base, the conductivity increases as the strong base reacts with the un-ionised weak acid molecules and produces a salt, which is basic. Near the equivalence point, the graph is curved because of the hydrolysis of the salt produced. Continued addition of the strong base leads to a rapid increase in conductivity.

In this titration, we are adding sodium hydroxide (NaOH) from the burette into a beaker containing ethanoic acid (CH_3COOH). The reaction can be written as:

$$NaOH(aq) + CH_3COOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$$

Table 7.4.3 and **Figure 7.4.7b** summarise this type of titration.

TABLE 7.4.3 Conductivity during the titration of a weak acid and a strong base

Stage of conductivity titration	Observations of conductivity
Initial conductivity	Ethanoic acid is a weak acid that partially ionises; this results in a low conductivity because there are only a small number of free ions (mainly H^+ and CH_3COO^-) to carry the current.
Adding NaOH	The added hydroxide ions start neutralising the small number of highly conductive hydrogen ions, reducing the number of H^+ and replacing them with less conductive Na^+. This causes a slight decrease in conductivity.
Shifting equilibrium	After some hydrogen ions are neutralised, the equilibrium of the ethanoic acid ionisation shifts to the right to produce more H^+ and CH_3COO^-. The newly formed H^+ ions are again neutralised by the added OH^-, but more ethanoate ions and sodium ions are present, which increases the conductivity.
Approaching the equivalence point	As more NaOH is added, the shift in equilibrium continues to increase until the equivalence point. At this point, there is mainly sodium ethanoate and water in the solution.
After the equivalence point	Once the equivalence point is reached, additional NaOH will add excess OH^-. These ions are very conductive, so the conductivity increases sharply at this point. The solution now contains sodium ions, acetate ion and hydroxide ions, which all contribute to the increased conductivity.

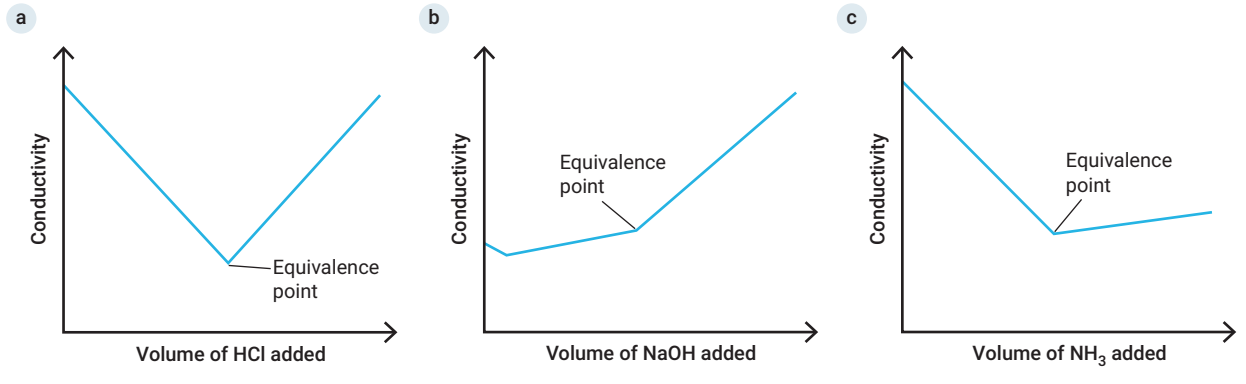
Strong acid and weak base

For strong acids and weak bases, conductance begins at a high value because of the highly mobile H^+. When a weak base is added, the OH^- reacts with the H^+, forming water. The decrease in H^+ causes the conductivity to decrease until the equivalence point. Unlike the strong base situation, continued addition of the weak base does not lead to an increase in conductivity. The graph becomes almost horizontal because the weak base is not appreciably ionised. The equivalence point is the minimum of the curve

In this type of titration, ammonia solution is added from the burette into a beaker containing hydrochloric acid. The reaction can be written as follows:

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$

Table 7.4.4 and **Figure 7.4.7c** summarise this type of titration.



Adapted from HSC Chemistry – Conductometric Titration, Science Ready.

FIGURE 7.4.7 Conductometric titration graphs: (**a**) a strong acid and a strong base; (**b**) a weak acid and a strong base; (**c**) a strong acid and a weak base

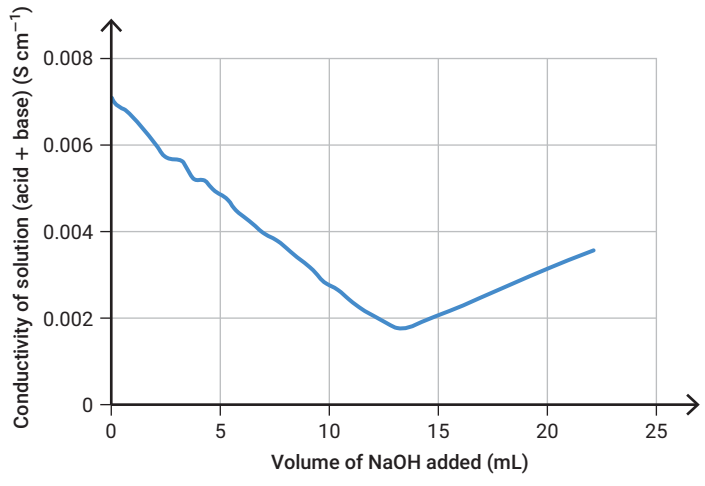
TABLE 7.4.4 Conductivity during the titration of a strong acid and a weak base

Stage of conductivity titration	Observations of conductivity
Initial conductivity	HCl is a strong acid that completely ionises to produce hydrogen and chloride ions. Since the H^+ are very conductive, the initial conductivity of the solution is high.
Adding NH_3	As the weak base ammonia is added, it reacts with the H^+ to form ammonium ions. This reaction reduces the concentration of hydrogen ions, and the conductivity decreases. Ammonium ions are less conductive than hydrogen ions, so the overall conductivity continues to fall.
Approaching the equivalence point	The equivalence point is reached when all the hydrogen ions have been neutralised by the ammonia. At this point, the solution consists mostly of ammonium ions and chloride ions, both of which are weakly conductive. The conductivity reaches its lowest value at the equivalence point.
After the equivalence point	When additional ammonia is added, it does not have any hydrogen ions left to neutralise, and excess ammonia is present in the solution. The increase in conductivity after the equivalence point is minimal.

WORKED EXAMPLE 7.4.2

25 mL of an unknown concentration of hydrochloric acid solution was titrated with a 0.10 M solution of sodium hydroxide. Interpret the conductometric titration curve in Figure 7.4.8 to determine the:

a intercept with the conductivity axis
b equivalence point
c volume of titrant
d concentration of the unknown hydrochloric acid solution.



Adapted from ramesh.ammanamanchi/Plotly. https://chart-studio.plotly.com/~ramesh.ammanamanchi/25/conductometric-titration-curve/#plot

FIGURE 7.4.8 The conductometric titration of hydrochloric acid titrated with 0.1 M sodium hydroxide

ANSWERS

a **Determine the intercept with the conductivity axis.**
The intercept with the conductivity axis is the initial conductivity before any sodium hydroxide is added.
The intercept with the conductivity axis is 0.007 S cm^{-1}.

b Determine the equivalence point.
The equivalence point is where the amount of sodium hydroxide added completely neutralises the hydrochloric acid. This is typically observed as the lowest point on the conductivity curve, followed by an increase in conductivity as excess sodium hydroxide is added.
The lowest conductivity recorded is 0.0018 S cm^{-1} at 13 mL of NaOH; this is the equivalence point.

c Determine the volume of titrant added at the equivalence point.
From the curve, volume of titrant is 13 mL.

d 1 Write a balanced equation for the reaction.
$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

2 Calculate the amount in moles of sodium hydroxide.
$n(NaOH) = c \times V$
$= 0.1 \times 0.013$
$= 0.0013$ mol

3 Calculate the number of moles of hydrochloric acid.
Since the mole ratio is 1:1, the number of moles of HCl is also 0.0013 mol.

4 Calculate the concentration of hydrochloric acid.

$$c(HCl) = \frac{n}{V}$$
$$= \frac{0.0013}{0.025}$$
$$= 0.052 \text{ mol } L^{-1}$$

PRACTICAL ACTIVITY 7.4.1

CONDUCTOMETRIC ACID–BASE NEUTRALISATION

Research question

How can conductometric titration be used to determine the equivalence point of hydrochloric acid solution when titrated with a sodium hydroxide solution?

Aim

- To conduct a titration between hydrochloric acid and sodium hydroxide while measuring the change in conductivity
- To determine the equivalence point of the titration based on the conductivity data

Materials

- 1.0 M hydrochloric acid
- 2.0 M sodium hydroxide
- bromothymol blue
- conductivity apparatus (or conductivity probe)
- 250 mL beaker
- 150 mL beaker
- 25 mL volumetric pipette
- pipette filler
- filter funnel
- magnetic stirrer
- magnetic stir bar
- wash bottle with distilled water
- 50 mL burette
- burette clamp
- boss head and clamp
- retort stand
- 50 mL measuring cylinder
- wash beaker

RISK ASSESSMENT

What are the risks in doing this experiment?	How can you manage these risks to stay safe?

Copy and complete the risk assessment table in your write-up. Add any risks you can think of, and ways to manage them. Ask your teacher to check your table before you proceed.

Procedure

1. Set up the conductivity apparatus.
2. Rinse the burette as per previous practical activities.
3. Set up a burette in a retort stand using a burette clamp.
4. Position the magnetic stirring plate on the base of the retort stand.
5. Position the burette over the magnetic stirring plate.
6. Place the conductivity apparatus in another clamp.
7. Transfer 25.0 mL of 1.0 M HCl solution to a clean, dry 150 mL beaker. Record the molarity and volume used.
8. Add 50.0 mL of distilled water to the beaker.
9. Put 3 drops of bromothymol blue indicator into the beaker with the HCl solution.
10. Place the 150 mL beaker with the hydrochloric acid solution under the burette. Carefully place the magnetic stirring rod in the bottom of the beaker. The conductivity apparatus electrodes should be immersed in the solution. Turn on the magnetic stirrer at a slow and steady rate.
11. Open the stopcock on the burette and add 1 mL of the 2.0 M NaOH into the HCl solution.
12. Record the conductivity in the results table.
13. Keep adding the NaOH 1 mL at a time. Continue to record the conductivity and record the volume of titrant used when the bromothymol blue indicator changes colour.
14. Continue until approximately 20 mL of extra NaOH solution has been added to the beaker.
15. Dispose of the used solutions according to your teacher's instructions.

Results

Draw up a table like the one below. You will need a lot of rows to record all of this information.
Concentration of HCl: _____ M
Volume of HCl: _____ mL

Conductivity	Burette reading (mL)

Analysis of results

1. Calculate the number of moles of hydrochloric acid added to the beaker in step 7.
2. Calculate the molarity of the hydrochloric acid after 50.0 mL of distilled water was added in step 8.
3. Calculate the number of moles of hydrochloric acid after 50.0 mL of distilled water was added in step 8.
4. The point where the solution changes colour is called the 'end point'. What was the volume of 2.0 M NaOH required to reach the end point of the reaction? Label this point on the graph.
5. In this procedure the colour change end point is also the equivalence point. What is equal at the equivalence point?

6 The neutralisation reaction between HCl and NaOH occurs in stoichiometric proportions. Describe the region of the graph where NaOH is the limiting reactant in the reaction. Describe the region of the graph where HCl is the limiting reactant in the reaction.

7 Explain why there is a change in the conductivity curve around the equivalence point.

Evaluation

8 During the neutralisation experiment with HCl and NaOH, the bromothymol blue colour-change end point did not occur at the same volume of NaOH as the change in the conductivity graph. Provide some reasons for the discrepancy.

9 Identify at least two limitations of this experiment.

LEARNING CHECK 7.4

DESCRIBING

1 **Define**:
   - **a** titration curve
   - **b** buffer region
   - **c** half-equivalence point.

2 **Sketch** a pH curve for a titration between potassium hydroxide and ethanoic acid. The potassium hydroxide is in the burette. On the graph, identify the equivalence point and the buffer region. Estimate the value of pK_a for ethanoic acid and mark it on your curve.

APPLYING

3 A student was asked to determine the concentration of a propanoic acid solution using 20.00 mL of 0.1 mol L^{-1} potassium hydroxide solution.

Use the information given in the titration curve in Figure 7.4.9 to **determine** the concentration of the propanoic acid:

$CH_3CH_2COOH(aq) + KOH(aq) \rightarrow CH_3CH_2COOK(aq) + H_2O(l)$

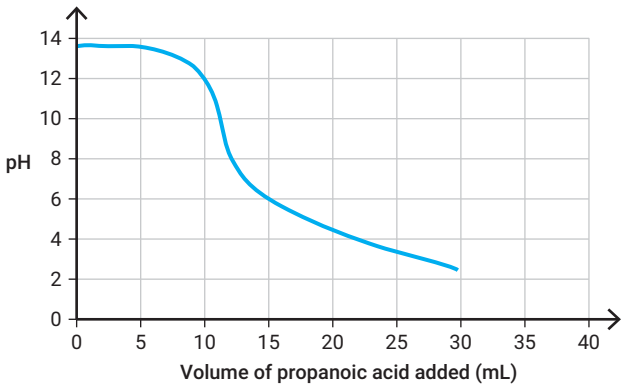
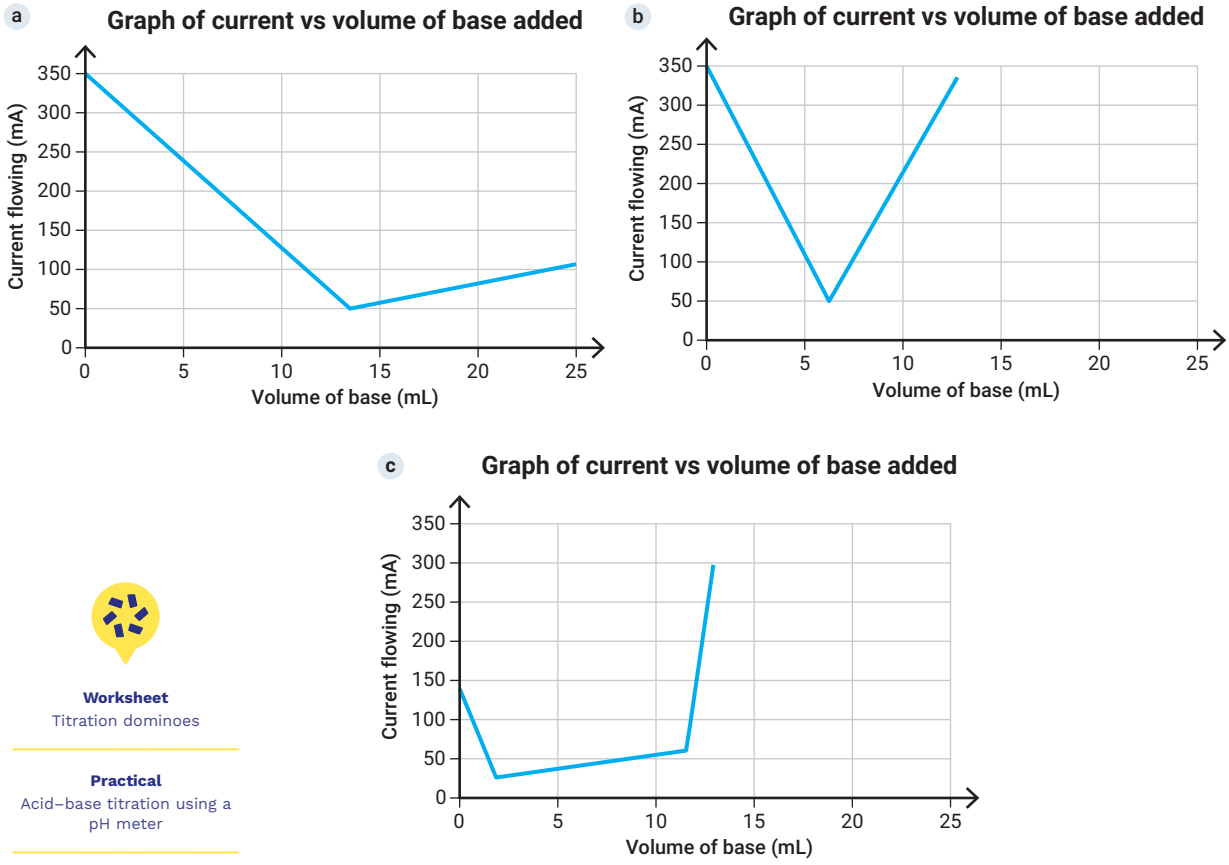


FIGURE 7.4.9 A titration curve

4 When a titration is carried out, a graph of current against volume of base added is produced. The graphs in Figure 7.4.10 were produced from titrations using various acids and bases.

The solutions used in these titrations were ammonia (NH_3), potassium hydroxide (KOH), hydrochloric acid (HCl) and ethanoic acid (CH_3COOH).

For each titration a–c, **identify** an acid and a base from the above list that best matches the shape of the graph. **Explain** your choice in each case.



Worksheet
Titration dominoes

Practical
Acid–base titration using a pH meter

FIGURE 7.4.10 Three titration curves

CHAPTER SUMMARY

Acid–base indicators

- Indicators change colour when pH = pK_a.

Indicator	pH range of colour change	Colour change		pK_a at 298 K
		Acid	Base	
Methyl orange	3.1–4.4	Red	Yellow	3.7
Bromophenol blue	3.0–4.6	Yellow	Blue	4.2
Bromocresol green	3.8–5.4	Yellow	Blue	4.7
Methyl red	4.4–6.2	Pink	Yellow	5.1
Bromothymol blue	6.0–7.6	Yellow	Blue	7.0
Phenol red	6.8–8.4	Yellow	Red	7.9
Phenolphthalein	8.3–10.0	Colourless	Pink	9.6

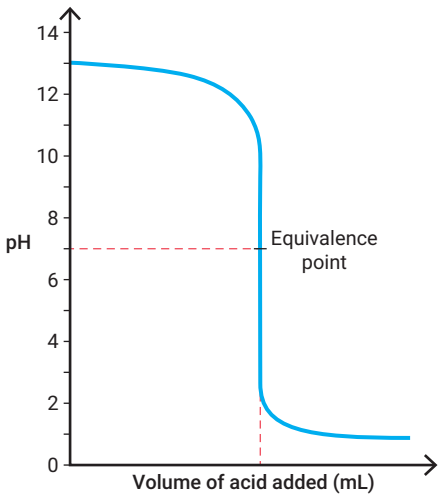
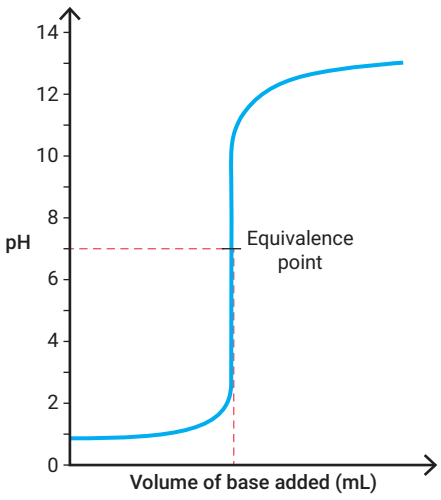
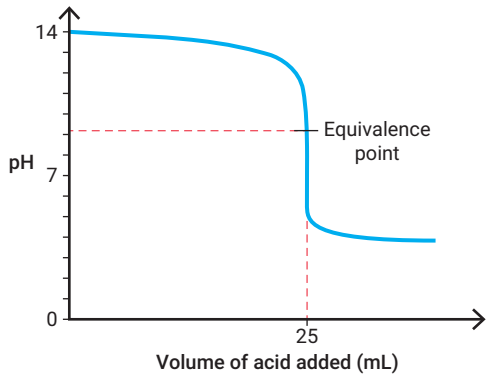
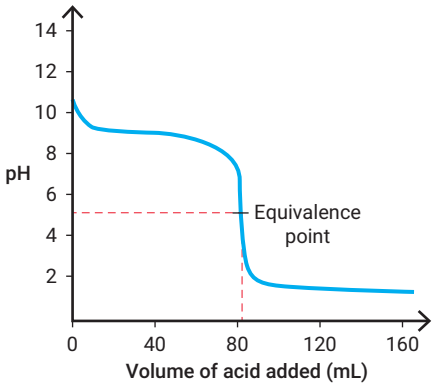
Indicators for titrations

- Acid–base indicators are a conjugate pair with at least one of the pair being intensely coloured. In titrations, the end point is when the colour changes. Indicators are chosen so that the colour change occurs near the equivalence point of the reaction. Therefore, the end point (colour change) is equal or close to the equivalence point and errors are reduced.

Type of acid	Type of base	pH range at equivalence point	Suitable indicators
Strong	Strong	Approximately 7	Bromothymol blue
Weak	Strong	7–11	Phenol red (6.8–8.4) Phenolphthalein (8.2–10.0)
Strong	Weak	3–7	Methyl orange (3.1–4.4) Methyl red (4.4–6.2)

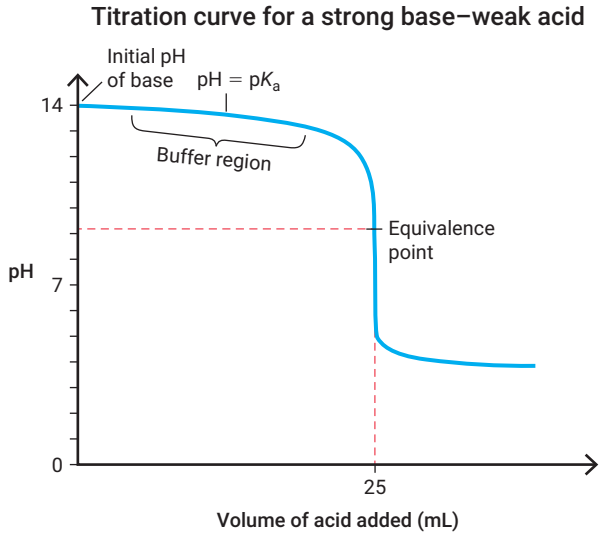
Acid–base titration curves

- The shape of the titration curves can indicate the strength of the acids and bases involved in the titration.
- The volume of titrant used in the titration can be used to calculate unknown values for the analyte such as concentration and mass.

Strong base–strong acid	Strong acid–strong base
	
Initial pH: 13–14 Equivalence point: pH 7 Final pH: 1–2	Initial pH: 1–2 Equivalence point: pH 7 Final pH: 13–14
Strong base–weak acid	**Weak base–strong acid**
	
Initial pH: 13–14 Buffer region with half-equivalence point Equivalence point: above pH 7 Final pH: 3–4	Initial pH: 10–11 Buffer region with half-equivalence point Equivalence point: below pH 7 Final pH: 1–2

Features of a titration curve

- In a titration curve, the equivalence point is the midpoint of the sudden change in the pH.
- The starting pH indicates the nature of the analyte. A high pH indicates that the analyte is a base, whereas a low starting pH indicates the analyte is an acid.
- The buffer region is the region before the equivalence point (approximately at the half-equivalence point) and is where pH = pK_a.

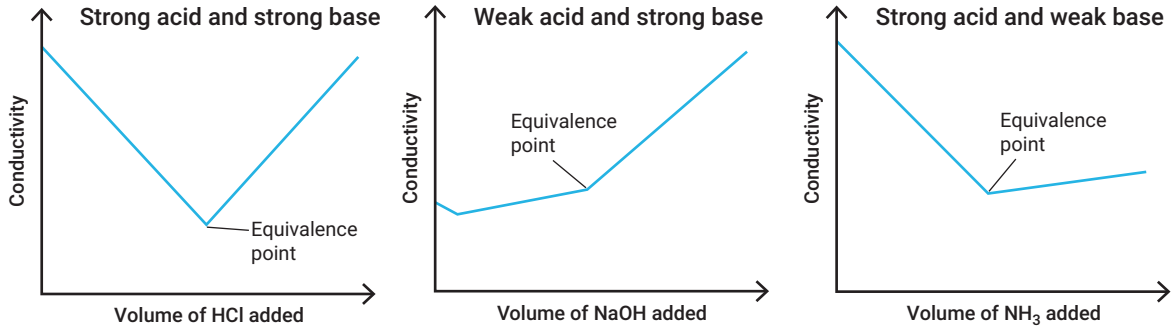


Solubility titrations

- A solubility titration is a type of acid–base titration used to determine the concentration of ions in a saturated solution of a sparingly soluble salt. This allows chemists to calculate the solubility of the salt and, if required, its K_{sp} (solubility product constant).

Conductometric titrations

- The electrical conductivity of a solution is proportional to the concentration of ions in the solution.
- The conductivity of strong acids and bases is greater than the conductivity of weak acids and bases.
- A concentrated solution will have higher conductivity than a dilute solution of the same substance.



Adapted from HSC Chemistry – Conductometric Titration, Science Ready.

CHAPTER EXAM

MULTIPLE CHOICE

1. An indicator changes colour in the pH range between 9 and 11. Identify K_a for the indicator.

A 1×10^{-7}
B 1×10^{-9}
C 1×10^{-10}
D 1×10^{-13}

2. Identify which of the following always applies at the end point (colour change) for the indicator HIn.

A $[HIn] = [H_3O^+]$
B $[HIn] = [In^-]$
C $[In^-] = [OH^-]$
D $[In^-] = [H_3O^+]$

3. Determine the pH at the equivalence point for an indicator with $K_a = 1.26 \times 10^{-3}$.

A 11.1
B 4.1
C 2.9
D 1.26×10^{-3}

4. The indicator bromothymol blue can be represented by the general equation:

$$\underset{\text{Yellow}}{HIn\,(aq)} + H_2O(l) \rightleftharpoons \underset{\text{Blue}}{In^-(aq)} + H_3O^+(aq)$$

At a pH 6.9, it is a greenish colour.

If sodium hydroxide is added to this indicator solution, identify the equilibrium change and resulting indicator colour change.

A Change: Decrease in $[H_3O^+]$ Indicator colour change: blue → yellow
B Change: Increase in $[H_3O^+]$ Indicator colour change: yellow → blue
C Change: Increase in $[H_3O^+]$ Indicator colour change: blue → yellow
D Change: Decrease in $[H_3O^+]$ Indicator colour change: yellow → blue

5. Which of the following is not a desirable property of a substance that is to be used as a primary standard?

A Is of high purity so that no side reactions occur
B Has a low molar mass to ensure its solubility
C Is stable in the presence of air
D Has no water of hydration

6. Which piece of laboratory equipment is most suitable for transferring an accurately known volume of liquid?

A Burette
B Conical flask
C Volumetric pipette
D Measuring cylinder

7. If a 20 mL sample of nitric acid requires 28.95 mL of 0.098 M sodium hydroxide to reach the equivalence point, what is the concentration of the nitric acid?

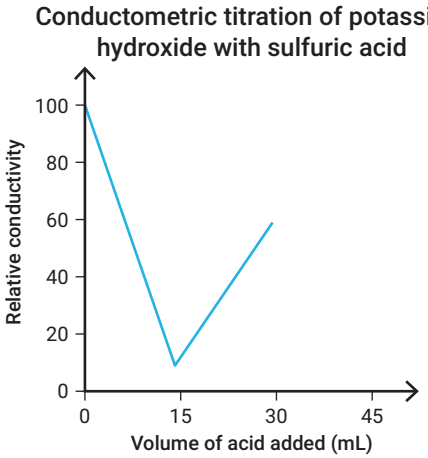
A 0.49 M
B 0.284 M
C 0.071 M
D 0.142 M

8. Anhydrous sodium carbonate (Na_2CO_3) is dissolved in 50 mL of distilled water. This is transferred to a 250 mL volumetric flask. Distilled water is added until the solution reaches the 250 mL mark. A pipette is used to transfer 20 mL of this solution to another 250 mL flask and made up to the mark with distilled water.

If the concentration of this solution was found to be 0.098 M, what mass of sodium carbonate must have been used in the beginning?

A 3.246 g
B 32.46 g
C 87.52 g
D 2.597 g

9. 20.00 mL of potassium hydroxide (KOH) solution was titrated with 0.20 mol L^{-1} of sulfuric acid (H_2SO_4) solution in a conductometric titration. The data obtained was plotted to give the graph shown.



Adapted from https://www.ausetute.com.au/conductab.html

What was the concentration of KOH?

A 0.30 mol L^{-1}
B 0.15 mol L^{-1}
C 0.12 mol L^{-1}
D 0.075 mol L^{-1}

10. In a titration of a strong acid and a weak base, in what pH range should the ideal indicator change colour?

A pH 2–4
B pH 4–6
C pH 6–8
D pH 7–9

SHORT RESPONSE

11. In a titration, what is the general term for the solution of unknown concentration?

12. A student is investigating the solubility of calcium hydroxide, $Ca(OH)_2$, in water.

A saturated solution is prepared by adding excess $Ca(OH)_2$ to distilled water, stirring, and filtering. A 25.00 mL aliquot of the filtrate is titrated with 0.100 M HCl. It takes 38.50 mL of the acid to reach the end point.

a Calculate the solubility of $Ca(OH)_2$ in mol L^{-1}.

b Calculate the solubility product (K_{sp}) of $Ca(OH)_2$.

13. You are given a white crystalline solid and told that it could be citric acid or tartaric acid. To determine which acid it is, you decide to titrate the solid with sodium hydroxide.

$$H_3C_6H_5O_7(s) + 3NaOH(aq) \rightarrow Na_3C_6H_5O_7(aq) + 3H_2O(l)$$

Citric acid

$$H_2C_4H_4O_6(s) + 2NaOH(aq) \rightarrow Na_2C_4H_4O_6(aq) + 2H_2O(l)$$

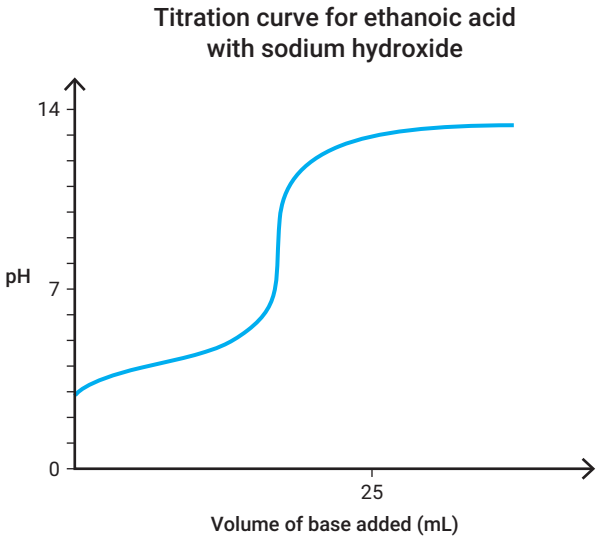
Tartaric acid

A 0.956 g sample of the solid requires 29.10 mL of 0.513 M NaOH for titration to the end point. **Identify** the unknown acid.

14. To determine the ammonia (NH_3) concentration in a cleaning product, a chemist diluted 20 mL of the product to 500 mL. 25 mL of this solution was titrated with 0.151 M nitric acid. The end point occurred at 26.2 mL. **Calculate** the concentration of ammonia in the cleaning fluid.

CROSS-CHAPTER QUESTION

15. The graph shows a pH curve for the titration of ethanoic acid with sodium hydroxide.



a Copy the graph and label the buffer region and the equivalence point.

b With the aid of equations, **explain** what is meant by 'buffer region'.

c With the aid of equations, **explain** the value of the pH at the equivalence point.

d **Explain** the significance of the intercept of the graph with the *y*-axis.

e Write the expression for the equilibrium constant (K_a) for this reaction.

f Estimate K_a for ethanoic acid.

g **Explain** how the addition of sodium ethanoate (CH_3COONa) to the solution would affect the position of equilibrium.

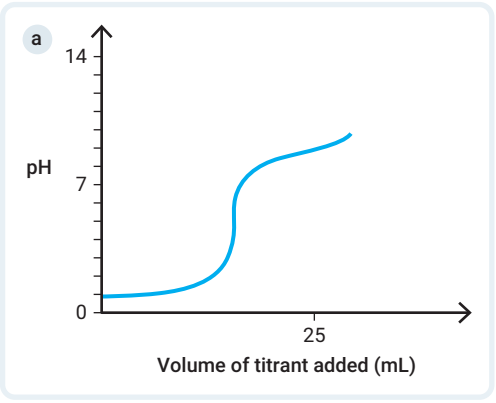
h If a strong acid is added to the solution, **predict** and **explain** the change in pH and the shift in equilibrium.

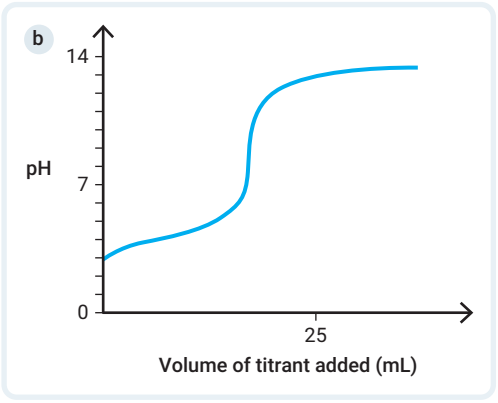
DATA ANALYSIS

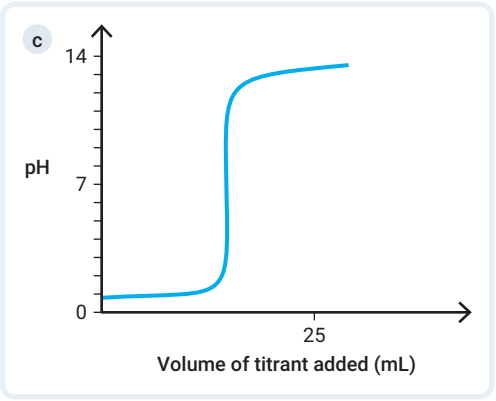
16. Analyse data

Use the information in the table to **deduce** suitable indicators for the reactions represented by the titration curves shown.

Indicator	pK_a	Colour change
Congo red	4.1	Blue → yellow/orange
Thymolphthalein	9.9	Colourless → blue
Bromocresol green	4.7	Yellow → blue
Methyl orange	3.7	Red → yellow/orange
Bromothymol blue	7.0	Yellow → blue
Phenolphthalein	9.6	Colourless → red/violet
Alizarin yellow	11.2	Yellow → red
Congo red	4.1	Blue → yellow/orange







SCIENCE AS A HUMAN ENDEAVOUR

Syllabus dot point

- 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.

From water to wine

You probably know that wine is made from grapes and a series of complex chemical reactions are involved in its production **(Figure 1)**. The main reaction is the fermentation of sugars in the grapes into ethanol and carbon dioxide:

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

Arcangela/Shutterstock.com

FIGURE 1 Wine is produced from grapes in a series of complex reactions.

Almost 98 per cent of wine is water and ethanol; however, it is the other 2 per cent that gives each wine its unique colours and flavours. It has been estimated that there are more than 800 different chemical compounds in wine, including organic acids, phenolics and aromatic compounds. Organic acids help to give wines their acidity and tartness and regulate the pH, phenolics contribute to the colour and flavour of the wine, and the aromatic compounds give wines their 'smell'. **Figure 2** shows examples of these types of compounds.

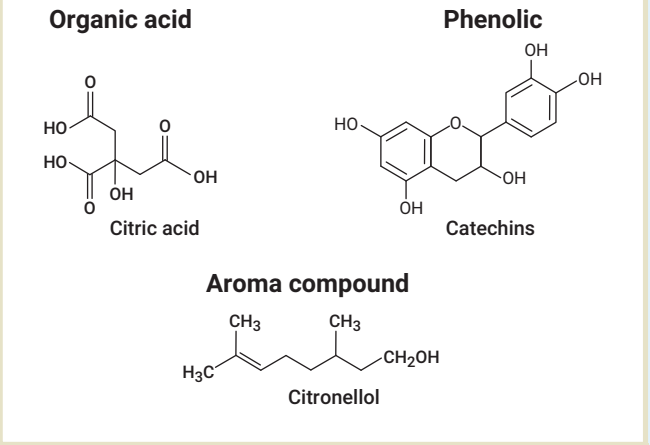


FIGURE 2 Some organic acid, phenolic and aroma compounds in wines

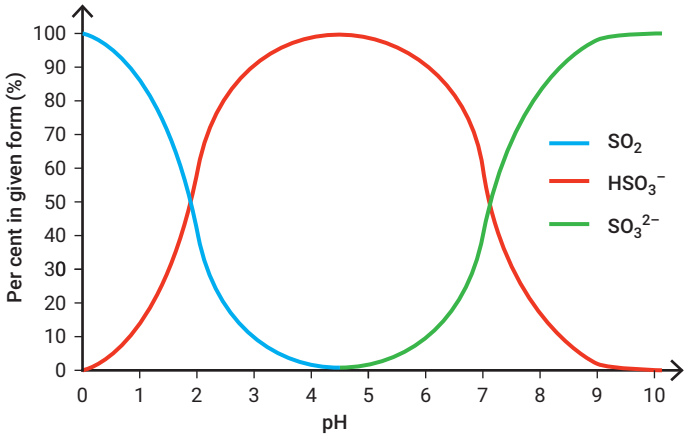
Stopping the spoil

When wine is left in the open for too long, oxygen in the air leads to the oxidation of ethanol, phenols and other compounds. The oxidation of ethanol to ethanal results in a distinct 'green apple' odour that affects the integrity of the wine. The oxidation of phenols and acids discolours the wine and produces hydrogen peroxide, respectively. This further affects the flavour of the wine.

Sulfur dioxide is added to wines to manage the growth of microbes and to reduce the impact of oxidation. When sulfur dioxide dissolves in water, it forms sulfites. Depending on the pH of the water (or wine), this can take the form of bisulfite (HSO_3^-) or sulfite (SO_3^{2-}) ions:

$$H_2O(l) + SO_2(g) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \rightleftharpoons 2H^+(aq) + SO_3^{2-}(aq)$$

Since the pH of wine is approximately between 3 and 4, the bulk of sulfur exists as either sulfur dioxide or bisulfite ions (Figure 3).



Sulphur Dioxide, http://www.brsquared.org/wine/Articles/SO2/SO2.htm

FIGURE 3 The percentage of the different forms of sulfur dioxide at different pH levels

In wine, oxygen is reduced to hydrogen peroxide (H_2O_2), which is a strong oxidising agent. In the presence of iron ions, hydrogen peroxide can oxidise ethanol to ethanal. However, bisulfite ions can interact with hydrogen peroxide, reducing the amount available to oxidise ethanol. Bisulfite ions can also interact with compounds called quinones and reverse the polyphenol-to-quinone reaction, which causes browning.

Maintaining the integrity of wine requires careful timing of when to add sulfur dioxide. Too late and the wine could spoil; too early and it may interrupt the colouring of the wine. The wine industry is continuing to conduct research to identify how chemical reactions can be used to maintain and even improve the quality of wine.

CHAPTER 8

Redox reactions

Paul Seftel/Shutterstock.com

SYLLABUS DOT POINTS

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 (acidic 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 INQUIRY

- Investigate displacement reactions.

Introduction

Oxidation–reduction reactions, or redox reactions, are one of the largest groups of reactions. They include reactions that underpin the operation of batteries, reactions that are used to extract important metals and reactions that provide energy to power our cars, airplanes and power stations. Redox chemistry is used in our water supplies and swimming pools to kill harmful bacteria and algae. The food we eat is oxidised by our bodies to provide the energy we need to live. The detection and analysis of a huge array of useful and harmful chemicals relies on redox chemistry. An understanding of redox principles relating to the corrosion of metals is vital in civil, structural and mechanical engineering.

ASSUMED KNOWLEDGE

- ✓ Reactions can be classified as single displacement, double displacement, combination, decomposition or combustion.
- ✓ Equations for reactions can be written as neutral species (full chemical) equations, full ionic equations and net ionic equations.
- ✓ Groups 1, 2 and 13 metals lose electrons to form cations with a charge of 1+, 2+ and 3+, respectively.
- ✓ Groups 15, 16 and 17 non-metals gain electrons to form anions with a charge of 3–, 2– and 1– respectively.
- ✓ Compounds can be ionic, covalent molecular and covalent network.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ identify displacement reactions of metals, combustion and corrosion reactions
- ✓ determine whether reactions are redox reactions
- ✓ identify oxidation and reduction in terms of loss and gain of electrons
- ✓ write half-equations, net ionic equations and overall balanced equations for redox reactions
- ✓ identify the element being oxidised and the element being reduced
- ✓ identify the oxidising agent and the reducing agent
- ✓ determine the oxidation states of elements in compounds
- ✓ use oxidation states to identify redox reactions
- ✓ apply correct notation to name transition metal compounds
- ✓ write and balance redox reactions using oxidation states and half-equations.

Syllabus link
Chapters 9 and 11 describe the application of spontaneous and non-spontaneous redox reactions.

8.1 The range of redox reactions

redox reaction a reaction that involves the oxidation of one atom and the reduction of another atom

oxidation the loss of electrons from an atom, which is said to be oxidised

reduction the gain of electrons by an atom, which is said to be reduced

As you learnt in Chapter 8 of *Nelson QCE Chemistry Units 1 & 2*, chemical reactions can be classified in many ways, including:

- single-displacement reactions
- double-displacement reactions
- combination reactions
- decomposition reactions
- combustion reactions.

These classifications represent broad categories of reactions, and it is sometimes useful to consider reactions using other classifications including acid–base and oxidation–reduction (redox), which were also mentioned in Year 11. Displacement reactions of metals, combustion reactions and corrosion reactions are all examples of redox reactions. Electrochemical processes are ones that either cause or are caused by the movement of an electric current. These processes may be spontaneous or non-spontaneous. Chapters 9 and 11 describe spontaneous and non-spontaneous electrochemical processes.

FIGURE 8.1.1 Unpacking redox

Redox reactions are **oxidation** and **reduction** reactions (oxidation–reduction reactions) **(Figure 8.1.1)** and involve the transfer of electrons. They form new substances when one species loses electrons and another species gains these electrons. Oxidation involves an atom losing electrons, whereas reduction involves an atom gaining electrons. One cannot occur without the

other. An atom cannot lose electrons unless there is another atom to accept them. The atom that loses one or more electrons is said to be oxidised and the atom that gains one or more electrons is said to be reduced.

The mnemonic OIL RIG, in Figure 8.1.2, may help you to remember which process is oxidation and which is reduction.

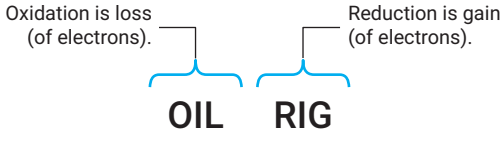


FIGURE 8.1.2 A mnemonic for oxidation and reduction

Metal-displacement reactions

Metal-displacement reactions (also called single-displacement reactions) are examples of redox reactions. A metal-displacement reaction may occur when a solid metal is added to a solution containing the ion of another metal. In this process, the solid metal loses one or more electrons to become a positive ion while the positive ion of the other metal gains the electron(s) to become solid metal. The anion in the solution is a spectator ion because it does not take part in the chemical reaction.

KEY FORMULA

General equation for a metal-displacement reaction

$A(s) + BC(aq) \rightarrow B(s) + AC(aq)$

Syllabus link
Chapter 8 of *Nelson QCE Chemistry Units 1 & 2* discussed metal-displacement reactions.

Weblink
Redox reactions

For example, if a piece of zinc metal is added to a test tube containing copper(II) sulfate solution, the zinc reacts, the solution turns from blue to colourless, and red-brown copper metal is deposited on the bottom of the test tube. This is an example of a metal-displacement reaction. The neutral species equation for the reaction is:

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

The complete ionic equation for this reaction is:

$$Zn(s) + Cu^{2+}(aq) + SO_4^{2-}(aq) \rightarrow Zn^{2+}(aq) + SO_4^{2-}(aq) + Cu(s)$$

The sulfate ion ($SO_4^{2-}(aq)$) is a spectator ion in this reaction because it appears on both the reactant and product sides of the equation.

It is useful to track the chemical changes of each of the metals, zinc and copper, separately from their states as reactants to products.

Considering zinc:

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

Although this is balanced in terms of the zinc atoms, it also must be balanced in terms of charge. This is done by adding electrons so both sides of the equation have the same overall charge.

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

KEY CONCEPT

Charge is balanced by adding the appropriate number of electrons to the more positive side of the equation so the overall charge on both sides of the equation is the same.

In this case, zinc has lost two electrons. This is an example of oxidation.

Considering copper:

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

Balancing for charge gives:

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

In this case, Cu^{2+} has gained two electrons to form solid copper. This is an example of reduction.

half-equation the oxidation reaction or the reduction reaction of a redox reaction

When these **half-equations** are combined, the net ionic equation for the reaction is produced:

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

The electrons don't appear in the net ionic equation because they are the same on each side and, like spectator ions, cancel out.

PRACTICAL ACTIVITY 8.1.1

METAL-DISPLACEMENT REACTIONS

Introduction

You will use combinations of metals and ionic solutions of these metals to rank the metals from most reactive to least reactive; that is, most easily oxidised (most likely to lose electrons) to least likely to be oxidised (least likely to lose electrons).

Research question

Which metals are most easily oxidised, and which are less likely to be oxidised?

Aim

To rank metals from most easily oxidised to least likely to be oxidised

Materials

- 20 mL of 1 mol L^{-1} $AgNO_3$
- 20 mL of 1 mol L^{-1} $CuSO_4$
- 20 mL of 1 mol L^{-1} $MgSO_4$
- 20 mL of 1 mol L^{-1} acidified $FeSO_4$
- 20 mL of 1 mol L^{-1} $ZnSO_4$
- 20 mL of 1 mol L^{-1} NaCl
- 5 strips of copper metal
- 5 strips of magnesium ribbon
- 5 ungalvanised iron nails
- 5 strips of zinc metal
- 6 × 10 mL measuring cylinders
- 20 test tubes
- test-tube racks
- waste bottles for heavy metals
- 7 cm × 7 cm piece of sandpaper

RISK ASSESSMENT

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Silver nitrate can stain skin.	Be careful when pouring from the bottle to the beaker. Wipe up drips with paper towelling or a sponge.
Silver ions and copper ions are harmful to the environment.	Dispose of solutions containing these as directed by your teacher. Do not pour them down the drain.

Copy and complete the risk assessment table in your write-up. Add any more risks you can think of, and ways to manage them. Ask your teacher to check your table before you proceed.

Procedure

1. Use the sandpaper to clean all the pieces of metal.
2. Pour 5 mL of 1 mol L^{-1} $AgNO_3$ into four separate test tubes.
3. Place one piece of each metal into each of these test tubes.

4 Record your observations. If there is no apparent reaction, allow the mixture to stand for at least 10 minutes before finalising your decision.
5 Repeat steps 2–4 for all the other combinations of metals and solutions. You do not need to place metals with their corresponding solution; for example, you do not need to place magnesium into the $MgSO_4$ solution.
6 Record your observations for all combinations.
7 Dispose of copper(II) sulfate and silver nitrate as directed by your teacher.

Results

1 Draw up a table where the metals are across the top and the solutions are down the side.
2 Record your results in the table, using either words or photos. Remember that no reaction is also a result.

Analysis of results

3 Identify the combinations of metals and solutions where chemical reactions occurred.

Interpretation

4 Deduce which metal was most reactive.
5 Deduce which metal was least reactive.
6 Explain why $AgNO_3$ and NaCl were included in the experiment. Compare the ability of silver ions and sodium ions to react with metals, with reference to your observations.
7 Arrange the metals in order from most reactive to least reactive.

WORKED EXAMPLE 8.1.1

If a piece of iron metal is placed into a solution of silver nitrate, eventually the iron disappears and small, needle-like pieces of solid silver appear.

a Write the overall balanced equation for the reaction.
b Write the half-equations associated with the iron and silver.
c Identify each half-equation as oxidation or reduction.
d Write the net ionic equation for the reaction.

ANSWERS

a **1** **Determine the products of the reaction.**

The products are $Fe(NO_3)_2(aq)$ and $Ag(s)$.

2 **Write a balanced equation.**

$Fe(s) + 2AgNO_3(aq) \rightarrow Fe(NO_3)_2(aq) + 2Ag(s)$

3 **Write the complete ionic equation and check it is balanced.**

$Fe(s) + 2Ag^+(aq) + 2NO_3^-(aq) \rightarrow Fe^{2+}(aq) + 2NO_3^-(aq) + 2Ag(s)$

b **1** **Identify the change for each metal or metal ion.**

$Fe(s)$ has become $Fe^{2+}(aq)$.
$Ag^+(aq)$ has become $Ag(s)$.

2 **Write each of these changes as a half-equation.**

$Fe(s) \rightarrow Fe^{2+}(aq)$
$Ag^+(aq) \rightarrow Ag(s)$

3 **Balance charge by adding electrons to the more positive side of the equation.**

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

c 1 Identify which half-equation shows the loss of electrons (oxidation) and which shows the gain of electrons (reduction).

According to the half-equations, Fe solid has lost 2 electrons while silver ions has gained an electron.

2 Label the two half-equations.

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ oxidation
$Ag^+(aq) + e^- \rightarrow Ag(s)$ reduction

d 1 Determine if the number of electrons lost and gained are the same.

In the oxidation reaction, two electrons are lost by the iron, but in the reduction reaction only one electron is gained by the silver.

2 Multiply each equation by an appropriate factor to equalise the loss and gain of electrons.

The reduction half-equation must be multiplied by two so there are two electrons gained.

$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$

3 Add the two half-equations together to produce the net ionic equation for the reaction.

Note: electrons do not appear in the net ionic equation because they cancel out.

$Fe(s) + 2Ag^+(aq) \rightarrow Fe^{2+}(aq) + 2Ag(s)$

KEY CONCEPT

If the number of electrons in a half-equation is multiplied by a number, then *everything* in the half-equation must be multiplied by the same number.

Sodium and potassium metals react violently with water and acids, so they are not used in schools. Both metals are normally stored in kerosene (to prevent them from reacting with air and water). They oxidise readily in water; hence, they are more reactive than calcium. Potassium is more reactive than sodium and its reactions are more violent. Potassium metal is banned in many educational jurisdictions across Australia, while sodium metal can be used only in teacher demonstrations.

reactivity series of metals a list of metals in order of decreasing ease of reactivity (i.e. most easily oxidised to least easily oxidised)

Based on the different reactivities of metals, chemists have developed a **reactivity series of metals** that lists metals in order of reactivity. The activity series shown lists metals in order (from left to right) of decreasing reactivity. This means the metals are listed in order from most easily oxidised to least easily oxidised:

K > Na > Li > Ba > Ca > Mg > Al > Zn > Fe > Sn > Pb > (H) > Cu > Ag > Pt > Au

REACTIVITY SERIES OF METALS

K > Na > Li > Ba > Ca > Mg > Al > Zn > Fe > Sn > Pb > (H) > Cu > Ag > Pt > Au

A more comprehensive list is provided in the *Formula and Data Book*.

The reactivity series of metals can be used to identify whether a reaction will occur when a metal is placed in a solution containing the ions of a different metal. Using the series to predict reactions is relatively straightforward. Any metal will react with ions of any less reactive metal. That means any metal will be oxidised by the ions of any other metal that follows it in the reactivity series. (Note: The metal should be cleaned to remove any oxide coating before reacting because the oxide coating may prevent a reaction occurring.)

FORMULA AND DATA BOOK

Once it has been identified that a reaction will occur, the oxidation and reduction half-equations can then be determined with the metal being oxidised and ions being reduced.

WORKED EXAMPLE 8.1.2

a Use the reactivity series of metals to justify whether a chemical reaction will occur when a piece of cleaned aluminium metal is placed in an aqueous solution containing Pb^{2+} ions.

b Use the reactivity series of metals to justify whether a chemical reaction will occur when a piece of cleaned aluminium metal is placed in a solution of Ca^{2+} ions.

c For any reaction identified as occurring in parts a and b:

i identify the species being oxidised and the one being reduced

ii write the oxidation and reduction half-equations.

ANSWERS

a 1 Identify the relative positions of the metal and metal ions in the reactivity series.
Aluminium is listed before lead in the reactivity series.

2 Determine if a reaction will occur.
A reaction will occur because aluminium is more reactive than lead.

b 1 Identify the relative positions of the metal and metal ions in the reactivity series.
Aluminium is listed after calcium in the reactivity series.

2 Determine if a reaction will occur.
A reaction will not occur because aluminium is less reactive than calcium.

c i 1 Identify the metal being oxidised.
Aluminium metal will be oxidised to Al^{3+} ions.

2 Identify the ions being reduced.
Pb^{2+} ions will be reduced to Pb metal.

ii 1 Write the oxidation half-equation.
$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

2 Write the reduction half-equation.
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

Combustion

At first glance, combustion reactions do not appear to be redox reactions; however, if we look at an earlier definition of oxidation and reduction, it becomes clear that combustion reactions are redox.

As you learnt when studying acids and bases, definitions change over time as scientists learn more about chemical processes. Originally 'oxidation' was defined as 'gain of oxygen' (hence, oxidation) and 'reduction' as 'loss of oxygen'. For many years, chemists used the following definitions:

- Oxidation is gain of oxygen or loss of hydrogen.
- Reduction is loss of oxygen or gain of hydrogen.

These definitions are consistent with our modern definitions of electron loss and gain; however, sometimes it is easier to consider oxidation and reduction in terms of loss or gain of oxygen or hydrogen, especially when the substances involved in the reactions are covalent molecular compounds.

For example, consider the complete combustion of methane gas:

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

The carbon has lost hydrogen and gained oxygen, so it has been oxidised. The oxygen has gained hydrogen, so it has been reduced. In this case, there is no obvious gain and loss of electrons, so the original definitions are more helpful.

Weblink
What is combustion?

Corrosion

In its simplest form, corrosion is the reaction is between a metal and oxygen in the air. The metal undergoes oxidation while the oxygen is reduced and the product is a metal oxide. The water vapour also present in air acts as the conductor for the transfer of the electrons from the metal to the oxygen. This is why in very dry environments, such as deserts, metals undergo very little corrosion.

$$\text{Metal} + \text{oxygen} \rightarrow \text{metal oxide}$$

This is a spontaneous chemical reaction. However, it is also a very slow reaction. Corrosion takes time. For example, magnesium reacts with oxygen to form magnesium oxide:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

A strip of magnesium metal that is exposed to the air for a period of time will lose some of its lustre. This is because it oxidises to form magnesium oxide. This happens to many metals and explains why sandpaper is used to clean metals before they are used in experiments: to remove the outer oxide layer and ensure that the metal is taking part in the reaction.

Weblink
Corrosion

The most common example of corrosion is rust. Rust is hydrated iron(III) oxide, which is produced when iron corrodes. Overall, the simplified reaction is:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

The chemistry is a little more complicated than this simplified reaction suggests and will be considered later in this topic.

LEARNING CHECK 8.1

DESCRIBING

1 **Define**:
- **a** oxidation
- **b** reduction
- **c** half-equation.

2 **Explain** why oxidation and reduction must always occur as a pair.

APPLYING

3 Consider the following reactions.
- **i** $4K(s) + O_2(g) \rightarrow 2K_2O(s)$
- **ii** $Cu(s) + Cl_2(g) \rightarrow CuCl_2(s)$
- **iii** $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$
- **iv** $Zn(s) + Fe(NO_3)_2(aq) \rightarrow Fe(s) + Zn(NO_3)_2(aq)$
- **v** $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$
- **vi** $Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$

- **a** **Determine** which are redox reactions.
- **b** For each identified redox reaction, **identify** the element that has been oxidised and the element that has been reduced.
- **c** For the reactions given, **determine** if any can also be classified as metal displacement, combustion or corrosion.

4 **Identify** the oxidation and reduction half-equations for the following reactions.
- **a** Magnesium metal in an aqueous solution containing iron(II) ions
- **b** Copper metal in an aqueous solution containing silver ions

5 **a** Write a balanced equation for the corrosion of aluminium in air to produce aluminium oxide.
b **Identify** the element that is oxidised and the one that is reduced.

ANALYSING

6 Use the reactivity series of metals on page 182 or in the *Formula and Data Book* to **justify** whether a chemical reaction will occur for the following solutions.
a Zinc metal in a silver ion solution
b Zinc metal in a sodium ion solution
c Magnesium metal in a copper(II) ion solution
d Iron metal in a copper(II) ion solution

7 Consider the following:
i Mg(s) in a solution of $FeSO_4(aq)$
ii Fe(s) in a solution of $ZnSO_4(aq)$
Use the reactivity series of metals to:
a **predict** the direction electrons will move
b **identify** the species being oxidised and the one being reduced.

8 The following reactions are considered redox reactions by the 'loss or gain of oxygen' definition.
i $CuO(s) + C(s) \rightarrow Cu(s) + CO(g)$
ii $2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$
a **Explain** how they are redox reactions by the 'loss or gain of electrons' definition.
b **Deduce** which element in each reaction has been oxidised and which has been reduced.

8.2 Identification in redox reactions

Oxidising and reducing agents

'Oxidising agent' or 'oxidant' and 'reducing agent' or 'reductant' are two terms often used in connection with redox reactions.

An **oxidising agent** (or **oxidant**) is a substance that brings about the oxidation of another substance. A **reducing agent** (or **reductant**) is a substance that brings about the reduction of another substance.

oxidising agent or oxidant a substance that causes another substance to be oxidised

reducing agent or reductant a substance that causes another substance to be reduced

Consider the reaction between zinc metal and copper(II) sulfate solution:

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

As discussed earlier, we can write half-equations that clearly show which substance is being oxidised and which substance is being reduced:

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

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad \text{reduction}$$

In this reaction, Zn(s) has been oxidised by $Cu^{2+}(aq)$. $Cu^{2+}(aq)$ is the oxidising agent or oxidant. Note that the oxidising agent gets reduced (Cu^{2+} to Cu).

In turn, $Cu^{2+}(aq)$ have been reduced by Zn(s). Zn(s) is the reducing agent or reductant. Note that the reducing agent gets oxidised (Zn to Zn^{2+}).

Oxidising and reducing agents are the substances or chemical species that cause the processes of oxidation and reduction that happen to the elements in substances or chemical species.

In the reaction:

$$CuO(s) + CO(g) \rightarrow Cu(s) + CO_2(g)$$

the element copper is reduced while the element carbon is oxidised; carbon monoxide is the reducing agent and copper(II) oxide is the oxidising agent.

WORKED EXAMPLE 8.2.1

Calcium metal reacts with hydrochloric acid to produce hydrogen gas.

a Write the balanced neutral species equation for this reaction (including states).
b Explain which substance is the oxidising agent and which is the reducing agent.

ANSWERS

a **1** **Determine the products of the reaction.**

Products are calcium chloride ($CaCl_2$) and hydrogen gas (H_2).

2 **Write the balanced equation.**

$Ca(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$

b **1** **Identify which element has been oxidised and which has been reduced.**

Calcium has been oxidised ($Ca \rightarrow Ca^{2+}$) and H has been reduced ($H^+ \rightarrow H$).

2 **Determine the oxidising and reducing agents.**

Ca metal is the reducing agent; HCl is the oxidising agent.

Deducing the oxidation state

In the examples examined so far, it has been relatively easy to determine which species is being oxidised and which is being reduced. However, sometimes it is difficult to determine whether an oxidation–reduction reaction is occurring, especially when the species involved are covalent molecular compounds.

To assist with this, chemists have developed numbers, referred to as 'oxidation states', also called 'oxidation numbers'.

KEY FORMULA

Oxidation state

Oxidation state is an indication of the number of electrons an atom would gain or lose to get to its present state. It assumes that each species is completely ionic.

The oxidation state always indicates whether it has a positive or negative charge. As shown earlier, it is straightforward to determine the oxidation states of simple ionic compounds such as sodium sulfide (Na_2S). The sodium ion is written as Na^+. It has a +1 oxidation state. The sulfide ion is written as S^{2-}. It has a –2 oxidation state.

However, in covalent molecular compounds, electrons are shared by different species. It is more difficult to determine the oxidation states, and hence to determine if a redox reaction has occurred. Consider a combustion reaction between carbon and oxygen gas that produces CO_2. The compound formed is covalent so there is no clear loss or gain of electrons.

It is important to remember that the oxidation state is not necessarily the charge on the atom concerned. It is an arbitrary way of tracking electrons in redox reactions. Because it is an arbitrary number, it may even be a fraction.

The following rules are used when determining the oxidation states of various species.

1. The oxidation state of any element is zero regardless of its structure or formula.
2. The oxidation state of a monatomic ion is the same as the charge on that ion.
3. The oxidation state of fluorine is always –1.
4. The oxidation state of hydrogen in compounds is always +1, except when forming metal hydrides (e.g. NaH), when it is –1.
5. The oxidation state of oxygen in any compound is always –2, except when forming peroxides (e.g. H_2O_2), where it is –1, and in F_2O, where it is +2.
6. In a neutral compound, the sum of the oxidation states must always equal zero.
7. In polyatomic ions, the sum of the oxidation states must always equal the charge on the ion.
8. The most electronegative species in a compound is assigned the negative oxidation state; the less electronegative species is assigned the positive oxidation state.

WORKED EXAMPLE 8.2.2

Determine the oxidation state of the various elements in:

a methane (CH_4)
b the phosphate ion (PO_4^{3-}).

ANSWERS

a **1** **Refer to the rule for determining oxidation state of hydrogen.**
Rule 4 says that H must have an oxidation state of +1. There are 4 hydrogens, so the total oxidation state of hydrogen in methane is +4.

2 **Refer to the rule for neutral compounds.**
Rule 6 says that the sum of the oxidation states of the neutral compound must equal zero. Therefore, the oxidation state of carbon must be –4.

b **1** **Refer to the rule for oxygen.**
Rule 5 says that oxygen has an oxidation state of –2. There are 4 oxygens, so the total oxidation state of oxygen is –8.

2 **Refer to the rule for polyatomic ions.**
Rule 7 says that in ions, the sum of the oxidation states must equal the charge on the ion. Hence, the sum of the oxidation states for the phosphate ion (PO_4^{3-}) must equal –3.
Therefore, the oxidation state of the phosphorus must be +5 since oxygens total –8 and the overall charge of the ion is –3.

Using oxidation states to identify redox reactions

An understanding of how oxidation states are assigned can help you recognise redox equations. An increase in oxidation state corresponds to a loss of electrons from an atom and indicates oxidation has occurred. A decrease in oxidation state corresponds to a gain of electrons by an atom and indicates reduction has occurred.

These changes can be used to identify whether a particular reaction is a redox reaction.

WORKED EXAMPLE 8.2.3

Use oxidation states to decide whether the following are redox reactions.

a $MgO(s) + HCl(aq) \rightarrow MgCl_2(s) + H_2O(l)$

b $HOCl(aq) + KI(aq) + HCl(aq) \rightarrow I_2(g) + KCl(aq) + H_2O(l)$

ANSWERS

a **1** **Identify the type of compounds.**

MgO and $MgCl_2$ are ionic compounds; HCl and H_2O are covalent molecular compounds.

2 **Refer to the periodic table or the oxidation state rules to determine the charge on the ions and hence the oxidation state in each ionic compound.**

Oxidation state of Mg in MgO = +2, oxidation state of O in MgO = –2.
Oxidation state of Mg in $MgCl_2$ = +2, oxidation state of Cl in $MgCl_2$ = –1.

3 **Refer to the rules to determine the oxidation states for the covalent molecular compounds.**

Oxidation state of H in HCl = +1 (Rule 4), oxidation state of Cl in HCl = –1 (Rule 6).
Oxidation state of H in H_2O = +1 (Rule 4), oxidation state of O in H_2O = –2 (Rule 5 or 6).

4 **Identify if the oxidation state of any element has changed.**

There is no change for magnesium, chlorine, hydrogen or oxygen.

5 **Determine if the reaction is redox.**

As none of the oxidation states have changed this is not a redox reaction.

b **1** **Identify the types of compounds.**

KI and KCl are ionic. HCl, HOCl and H_2O are covalent molecular. I_2 is an element.

2 **Refer to the periodic table or oxidation state rules to determine the charge on the ions and hence the oxidation state in each ionic compound.**

K in KI = +1, I in KI = –1

K in KCl = +1, Cl in KCl = –1

3 **Refer to the rules to determine the oxidation states of covalent molecular compounds.**

H in HCl = +1 (Rule 4), Cl in HCl = –1 (Rule 6)

H in HOCl = +1 (Rule 4), O in HOCl = –2 (Rule 5), Cl in HOCl = +1 (Rule 6)

4 **Refer to rule for elements.**

I in I_2 = 0 (Rule 1)

5 **Identify if the oxidation state of any element has changed.**

There is no change for K, H and O.

There is a change in Cl and I. Cl changes from +1 to –1 and I changes from –1 to 0.
Therefore, this is a redox reaction.

Worksheets

Perspectives on redox reactions

Redox reactions

Oxidation states of transition metals

The oxidation states of main group metals such as sodium, magnesium and aluminium are predictable. They correspond to the group in the periodic table to which they belong. Transition metals, on the other hand, have varying oxidation states. Iron can have oxidation states of +2 and +3. Chromium can have +2, +3 and +6. Manganese can have +2, +3, +4 and +6.

It is meaningless, therefore, to refer to iron oxide or tin chloride. It is necessary to specify the oxidation state of the transition metal in the compound. This is done using roman numerals.

For example, FeO is called iron(II) oxide and Fe_2O_3 is called iron(III) oxide.

Manganese(IV) oxide has the formula MnO_2.

LEARNING CHECK 8.2

DESCRIBING

1 **Define**:

a oxidising agent **b** reducing agent **c** oxidation state.

2 **Explain** why transition metals have roman numerals in the name of their compounds.

APPLYING

3 **Identify** the oxidising agent in each of the following reactions.

a $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

b $CuO(s) + H_2(g) \rightarrow Cu(s) + 3H_2O(l)$

4 **Identify** the reducing agent in each of the following reactions.

a $2Fe^{2+}(aq) + Cl_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$

b $V_2O_5(aq) + 3H_2(g) \rightarrow 2VO^{2+}(aq) + H_2O(l)$

5 **Determine** the oxidation state of the underlined species.

a $\underline{I}O_3^-$

b $\underline{C}_2H_2$

c $\underline{Cl}O_3^-$

d $\underline{Cr}O_4^{2-}$

e $H_3\underline{As}O_4$

6 **Determine** the oxidation state of:

a chromium in the dichromate ion ($Cr_2O_7^{2-}$)

b nitrogen in dinitrogen tetroxide (N_2O_4)

c oxygen in hydrogen peroxide (H_2O_2)

d hydrogen in aluminium hydride (AlH_3).

7 For each of the underlined elements **identify** whether it is being oxidised, reduced or neither.

a $\underline{N}O_2(g) \rightarrow NO_3^-(aq)$

b $\underline{S}_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq)$

c $HO\underline{Cl}(aq) \rightarrow Cl_2(g)$

d $\underline{C}_2O_4^{2-}(aq) \rightarrow CO_2(g)$

e $\underline{Cr}(NO_3)_3(aq) \rightarrow Cr_2(SO_4)_3(aq)$

f $\underline{C}H_4(g) \rightarrow CH_4O(g)$

8 Write the name of each transition metal compound.

a Cu_2O

b $V(NO_3)_4$

c $NiCl_3$

ANALYSING

9 **Distinguish** the redox reactions in those below.

a $Cl_2(g) + 2HBr(aq) \rightarrow 2HCl(aq) + Br_2(l)$

b $6Mn^{3+}(aq) + I^-(aq) + 6OH^-(aq) \rightarrow 6Mn^{2+} + IO_3^-(aq) + 3H_2O(l)$

c Sulfuric acid + sulfur trioxide → oleum ($H_2S_2O_7$)

d Silver sulfide + oxygen → silver oxide + sulfur dioxide

e Phosphorus trichloride + chlorine → phosphorus pentachloride

10 For each of the reactions in Question 9 that are redox reactions **deduce** the:

a element that has been oxidised and give its change in oxidation state

b substance that is the oxidising agent.

8.3 Balancing redox reactions

In the relatively straightforward examples of redox reactions discussed in the previous sections, it has been quite easy to balance the equations. However, many redox reactions are complex, so a systematic approach to balancing equations is needed. There are two main approaches: one is to use oxidation states, and the other is to use half-equations.

Balancing using oxidation states

This method is outlined below and illustrated in Worked example 8.3.1.

1. Determine the oxidation states of the species that have been oxidised and reduced and calculate the change in oxidation state for each.
2. Balance these changes by putting coefficients in front of the formulas so that the total changes in electrons for the oxidised and reduced species are the same. (In essence, you are multiplying the equation by a multiple to make sure the number of electrons in each half-equation is the same.)
3. Balance oxygen by adding water to the side of the equation that is deficient in O.
4. Balance hydrogen by adding H^+ to the side that is deficient in H.
5. Double check that charge and elements are balanced.
6. Add state symbols if necessary.

WORKED EXAMPLE 8.3.1

a Aqueous permanganate oxidises nitrous acid solution to nitrate. The skeletal equation is:

$MnO_4^- + HNO_2 \rightarrow Mn^{2+} + NO_3^-$

Write a balanced equation for this reaction, using oxidation numbers.

b Nitric acid is an important industrial chemical. The first step in its synthesis is the gas phase oxidation of ammonia by oxygen. The skeletal equation for this reaction is:

$NH_3 + O_2 \rightarrow NO$

Write the balanced equation for this reaction, using oxidation numbers.

ANSWERS

a **1** **Determine the change in oxidation state for species being oxidised and reduced.**

$MnO_4^- \rightarrow Mn^{2+}$ For Mn = +7 → +2 = gain of $5e^-$

$HNO_2 \rightarrow NO_3^-$ For N = +3 → +5 = loss of $2e^-$

2 **Change the coefficients of oxidised and reduced species to make the loss and gain of electrons the same.**

Add a coefficient of 2 to Mn species and a coefficient of 5 to N species so that 10 electrons are lost and 10 are gained.

$2MnO_4^- + 5HNO_2 \rightarrow 2Mn^{2+} + 5NO_3^-$

3 **Balance O by adding H_2O.**

There are 18 O atoms on the left and 15 on the right. Add $3H_2O$ to the right. By doing so, you have added 3 O atoms to the right.

$2MnO_4^- + 5HNO_2 \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

4 **Balance H by adding H^+.**

There are 5 H atoms on the left and 6 on the right. Add one H^+ to the left.

$2MnO_4^- + 5HNO_2 + H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

5 Check that charge and elements are balanced.
Overall charge on the left equals –1; overall charge on the right equals –1 so charge is balanced. Elements are balanced.

6 Add states.
$2MnO_4^-(aq) + 5HNO_2(aq) + H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5NO_3^-(aq) + 3H_2O(l)$

b 1 Determine the changes in oxidation numbers.
$NH_3 \rightarrow NO$ For N = –3 to +2 = loss of $5e^-$
$O_2 \rightarrow NO$ For O = 0 to –2 = gain of $2e^-$

2 Balance loss and gain of electrons.
Need 2 N atoms and 5 O atoms but oxygen is present as O_2; this means $5O_2$ so need 4 N.
$4NH_3 + 5O_2 \rightarrow 4NO$

3 Balance O by adding H_2O.
$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

4 Balance H by adding H^+.
Hydrogen is balanced so no action needed.

5 Check charge and elements are balanced.
No charges, elements balanced.

6 Add states.
$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Balancing using half-equations

Weblink
Balancing a redox equation in acidic solution

This method is outlined below and illustrated in Worked examples 8.3.2 and 8.3.3.

1. Identify the species being oxidised and reduced.
2. Write oxidation and reduction half-equations.
3. Balance all elements except O and H.
4. Balance O by adding H_2O to the side that is deficient in O.
5. Balance H by adding H^+ to the side that is deficient in H.
6. Balance charge by adding electrons to the side with excess positive charge.
7. Equate electrons in both half-equations by adding coefficients.
8. Add half-equations, cancelling common species on each side.

WORKED EXAMPLE 8.3.2

Write the half-equation for the reduction of dichromate ($Cr_2O_7^{2-}$) to Cr^{3+} in acidic solution.

ANSWER

1 Write the skeletal half-equation.
$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$

2 Balance all elements except O and H.
$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$

3 Balance O by adding H_2O.
$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

4 Balance H by adding H^+.
$14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

5 Check charge and elements are balanced.

$14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

+12 charge +6 charge

Since there is an imbalance of charge, we need to add 6 electrons to the left-hand side to make the charges of both sides 6+.

$6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

6 Write the half-equation for the reduction of dichromate.

$14H^+(aq) + 6e^-(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

When determining the full equations for redox reactions, the half-equations need to be added, making sure electrons cancel according to Rules 5 and 6. If you are told the reaction is taking place in acidic solution, it means there will be $H^+(aq)$ ions in the final equation, as shown in Worked example 8.3.3.

WORKED EXAMPLE 8.3.3

Write the balanced equation for the following redox reaction in acidic solution:

$Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$

ANSWER

1 Identify the species being oxidised and the species being reduced.

$Fe^{2+}(aq)$ is oxidised to $Fe^{3+}(aq)$.

$MnO_4^-(aq)$ is reduced to $Mn^{2+}(aq)$.

2 Write oxidation and reduction half-reactions.

$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$ reduction

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$ oxidation

3 Balance elements (except oxygen).

(no change)

4 Balance O by adding H_2O.

$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$

5 Balance H by adding H^+.

$8H^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$

6 Check that charge and elements are balanced.

$5e^- + 8H^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

7 Multiply half-equations so the numbers of electrons are the same.

$5e^- + 8H^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$

8 Add half-equations, cancelling electrons.

$8H^+(aq) + 5Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

LEARNING CHECK 8.3

APPLYING

Worksheet
Balancing redox reactions

1 **Construct** oxidation and reduction half-equations and the net ionic equations for the following reactions.
   - **a** Reaction between magnesium and bromine to give magnesium bromide
   - **b** Reaction between sodium and oxygen to give sodium oxide
   - **c** Reaction between aluminium and nitrogen to give aluminium nitride

2 **Devise** balanced half-equations for the following processes. State whether each one is oxidation or reduction.
   - **a** $NO_2(g) \rightarrow NO_3^-(aq)$
   - **b** $S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq)$
   - **c** $HOCl(aq) \rightarrow Cl_2(g)$
   - **d** $C_2O_4^{2-}(aq) \rightarrow CO_2(g)$
   - **e** Sulfur dioxide reacting in acidic solution to form the sulfate ion
   - **f** Chlorate (ClO_3^-) reacting in an acidic solution to form chlorine dioxide (ClO_2)

3 **Derive** overall balanced equations using oxidation numbers for the following reactions given their skeleton equations.
   - **a** Reaction between dichromate ($Cr_2O_7^{2-}(aq)$) and $Sn^{2+}(aq)$
     $Cr_2O_7^{2-}(aq) + Sn^{2+}(aq) \rightarrow Cr^{3+}(aq) + Sn^{4+}(aq)$
   - **b** Reaction between oxalate ($C_2O_4^{2-}(aq)$) and permanganate ($MnO_4^-(aq)$)
     $C_2O_4^{2-}(aq) + MnO_4^-(aq) \rightarrow CO_2(g) + Mn^{2+}(aq)$
   - **c** Reaction of calcium with phosphorus to give calcium phosphide
   - **d** Reaction of potassium metal with fluorine to produce potassium fluoride

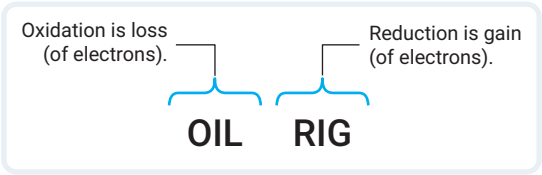
4 **Derive** overall balanced equations using half-equations for the following reactions given their skeleton half-equations.
   - **a** The reaction between $SO_2(g)$ and dichromate:
     $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$
     $SO_2(g) \rightarrow SO_4^{2-}(aq)$
   - **b** The reaction between nitrate ($NO_3^-(aq)$) and nickel:
     $NO_3^-(aq) \rightarrow NO_2(g)$
     $Ni(s) \rightarrow Ni^{2+}(aq)$

5 **Generate** a balanced equation for the following redox reactions using half-equations.
   - **a** The reaction between permanganate and chloride ions:
     $MnO_4^-(aq) + Cl^-(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g)$
   - **b** The reaction between dichromate and sulfite ions:
     $Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$

CHAPTER SUMMARY

Redox terminology

- A redox reaction is a reaction that involves the oxidation of one atom and the reduction of another atom.
- Oxidation is the loss of electrons from an atom, which is said to be oxidised.
- Reduction is the gain of electrons by an atom, which is said to be reduced.
- The mnemonic OIL RIG can be used to remember which process is oxidation and which is reduction.



- An oxidising agent or oxidant is a substance that brings about the oxidation of another substance.
- A reducing agent or reductant is a substance that brings about the reduction of another substance.

Redox reactions

- Metal-displacement reactions (also called single-displacement reactions), combustion reactions and corrosion reactions are all types of redox reactions.
- Redox reactions can be represented by half-equations where the full equation is split into its two components: the oxidation reaction and the reduction reaction. In half-equations, charge is balanced by adding the appropriate number of electrons to the more positive side of the equation so the overall charge on both sides of the equation is the same.

Oxidation state

- The oxidation state is an indication of the number of electrons an atom would gain or lose to get to its present state. It assumes that each species is completely ionic.
- Rules for determining oxidation state:
  1. The oxidation state of any element is zero regardless of their structure or formula.
  2. The oxidation state of a monatomic ion is the same as the charge on that ion.
  3. The oxidation state of fluorine is always –1.
  4. The oxidation state of hydrogen in compounds is always +1, except when forming metal hydrides (e.g. NaH), where it is –1.
  5. The oxidation state of oxygen in any compound is always –2, except when forming peroxides (e.g. H_2O_2), where it is –1, and in F_2O, where it is +2.
  6. In a neutral compound, the sum of the oxidation states must always equal zero.
  7. In polyatomic ions, the sum of the oxidation states must always equal the charge on the ion.
  8. The most electronegative species in a compound is assigned the negative oxidation state; the less electronegative species is assigned the positive oxidation state.
- The oxidation state of a transition metal is written in roman numerals following the name of the metal in the name of its compound.

Balancing redox reactions

- Redox reactions can be balanced using oxidation states or half-equations.
- Rules for balancing using oxidation numbers:
  1. Determine the oxidation states of the species that have been oxidised and reduced and calculate the change in oxidation state for each.
  2. Balance these changes by putting coefficients in front of the formulas so that the total changes in electrons for the oxidised and reduced species are the same.
  3. Balance oxygen by adding water to the side of the equation that is deficient in O.
  4. Balance hydrogen by adding H^+ to the side that is deficient in H.
  5. Double check that charge and elements are balanced.
  6. Add state symbols if necessary.
- Rules for balancing using half-equations:
  1. Identify the species being oxidised and reduced.
  2. Write oxidation and reduction half-equations.
  3. Balance all elements except O and H.
  4. Balance O by adding H_2O to the side that is deficient in O.
  5. Balance H by adding H^+ to the side that is deficient in H.
  6. Balance charge by adding electrons to the side with excess positive charge.
  7. Equate electrons in both half-equations by adding coefficients.
  8. Add half-equations, cancelling common species on each side.

CHAPTER EXAM

MULTIPLE CHOICE

1. In a metal-displacement reaction, the metal:
- **A** is oxidised.
- **B** ion loses electrons.
- **C** gains electrons.
- **D** ion is oxidised.

2. During a redox reaction:
- **A** the oxidation state becomes more positive for the species being reduced.
- **B** the oxidation state increases for the species being oxidised.
- **C** the oxidation state becomes more negative for the species being reduced.
- **D** there is no change in oxidation state for the species being reduced.

3. Use this reactivity series to determine which statement is correct.

K > Na > Ca > Mg > Zn > Fe > Cu > Ag

- **A** Iron will react in a solution of magnesium nitrate.
- **B** Magnesium is more likely to be reduced than copper.
- **C** There will be no reaction if zinc is placed in copper nitrate.
- **D** Sodium is more likely to be oxidised than zinc.

4. Which of the following reactions is not a redox reaction?
- **A** $2NaCl(l) \rightarrow 2Na(s) + Cl_2(g)$
- **B** $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$
- **C** $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
- **D** $Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$

5. In the following reaction, which species is reduced?

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

- **A** Ag^+
- **B** Br^-
- **C** Ag
- **D** Br_2

6. What is the oxidation state of chlorine in $KClO_4$?
- **A** +7
- **B** +3
- **C** −1
- **D** −3

Questions 7 and 8 relate to the following information.

In the following reaction molecular bromine gives the aqueous solution a reddish brown colour.

$Br_2(aq) + 2OH^-(aq) \rightarrow OBr^-(aq) + Br^-(aq) + H_2O(l)$

7. Which of the following shows the correct oxidation state of bromine in Br_2, Br^- and OBr^- in that order?
- **A** −1, +1, 0
- **B** 0, −1, +1
- **C** 0, −1, −1
- **D** +2, 0, 0

8. Which of the following statements is correct?

A OBr^- is a reducing agent.
B Oxygen is reduced.
C OH^- is reduced to H_2O.
D Br_2 is oxidised.

9. To balance the following skeletal half-equation:
$MnO_4^- \rightarrow Mn^{2+}$

A 4 water molecules would be written in the products.
B 4 water molecules would be written in the reactants.
C 3 electrons would be written in the products.
D 1 electron would be written in the reactants.

10. When sulfur reacts with sodium hydroxide, it is both oxidised and reduced to produce sulfide ions (S^{2-}) and sulfite ions (SO_3^{2-}).
Which of the following correctly shows the mole ratio of the species S : S^{2-} : SO_3^{2-} in the balanced equation for the reaction?

A 2 : 1 : 1
B 3 : 1 : 2
C 3 : 2 : 1
D 4 : 1 : 3

SHORT RESPONSE

11. **Identify** whether the following statements are true or false. Correct any false statements and rewrite them to make them true.

a Oxidation occurs when a species gains electrons.
b A metal reacting with an acid is an example of a redox reaction.
c Magnesium is more reactive than copper and reduces preferentially in the presence of copper.
d A reducing agent gains electrons.
e In the compound iron(III) oxide, iron has an oxidation state of +3.

12. The following equation shows the combustion of propane in air:

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

a Using oxidation states, **explain** why this is a redox reaction.
b **Identify** the oxidising agent.

CROSS-CHAPTER QUESTION

 Modified from VCAA 2000 SA Q5

13. The label of a 750 mL bottle of white wine states the alcohol content is 13.5% alc/vol.

a **Calculate** the volume of ethanol in one 750 mL bottle of wine.

One way to determine the alcohol content in wine involves the oxidation of ethanol to ethanoic acid (CH_3COOH), using acidified dichromate as the oxidising agent. The equation for the oxidation of ethanol with dichromate in acid solution is:

$2Cr_2O_7^{2-}(aq) + 16H^+(aq) + 3C_2H_5OH(aq) \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$

b The half-equation for dichromate as an oxidising agent is:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

Determine the half-equation for the oxidation of ethanol to ethanoic acid in acid solution.

c A 10.0 mL sample of this white wine was diluted to 250 mL in a volumetric flask. Then 25.0 mL aliquots of the diluted wine were titrated against 0.0750 M acidified potassium dichromate solution ($K_2Cr_2O_7$).

The titration data is shown on the table below.

Trial	1	2	3	4
Titre (mL)	20.60	20.20	20.64	20.62

i **Explain** why more than three trials were necessary to calculate the average titre value.

ii The mean titre was 20.62 mL. **Explain** how this value was arrived at.

iii **Calculate** the number of moles of $Cr_2O_7^{2-}$ reacting with the 25.0 mL aliquot.

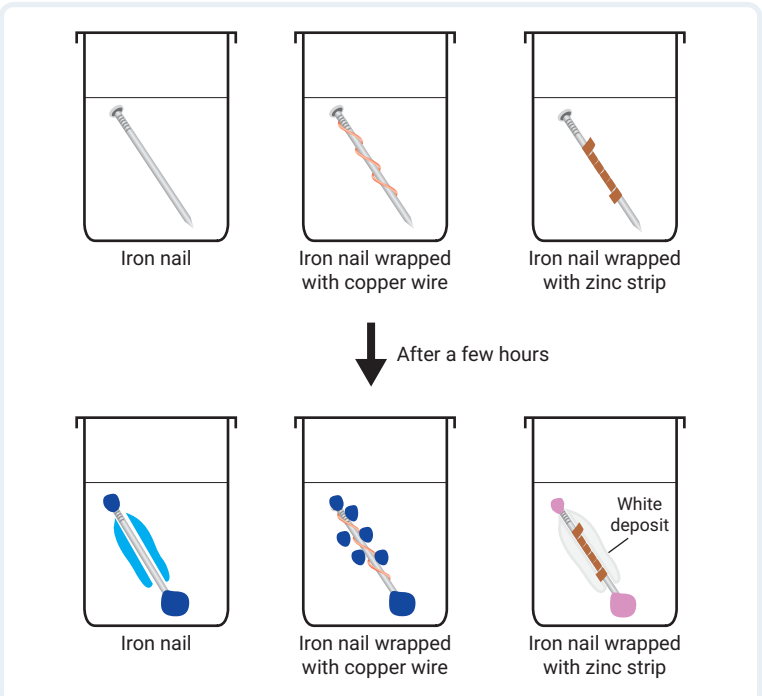
iv **Calculate** the number of moles of ethanol in the 25.0 mL aliquot.

v **Calculate** the number of moles of ethanol in the 10.0 mL sample of white wine.

DATA ANALYSIS

14. Analyse data

An experiment was carried out in which an iron nail, an iron nail with copper wire wrapped around it and an iron nail with a zinc strip wrapped around it were placed in separate beakers. The beakers were filled with warm ferroxyl jelly, covered and left for a few hours for the jelly to set. The results are shown in the diagram.



Ferroxyl jelly is made by adding a hexacyanoferrate indicator and phenolphthalein indicator to agar jelly. Hexacyanoferrate indicator turns dark blue in the presence of $Fe^{2+}(aq)$ ions. Phenolphthalein indicator turns pink in the presence of $OH^-(aq)$ ions. Hydroxide ions (OH^-) are produced when oxygen gas ($O_2(aq)$) is reduced in the presence of water.

a With the aid of half-equations, **explain** the colour changes in each beaker.

b Suggest why a white deposit formed in the beaker that contained the iron nail wrapped in zinc.

15. Interpret evidence

The following half-equations represent the reduction reactions of three substances: X^{3+}, Y^{2+} and Z_2.

$X^{3+}(aq) + e^- \rightarrow X^{2+}(aq)$

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

$Z_2(aq) + 2e^- \rightarrow 2Z^-(aq)$

Pairs of the six species shown in the half-equations were mixed in test tubes and the observations recorded. The following table shows some of the results. The combinations indicated by I, II and III in the table were not investigated.

	$X^{2+}(aq)$	$Y(s)$	$Z^-(aq)$
$X^{3+}(aq)$	NT	✓	I
$Y^{2+}(aq)$	II	NT	III
$Z_2(aq)$	x	✓	NT

✓ reaction occurred
x no reaction occurred
NT not tested

a Write the fully balanced equations for the two reactions that occurred.

b **Explain** whether there would be a reaction for I, II and III.

c **Determine** the strengths of oxidising agents from strongest to weakest. **Justify** your answer.

CHAPTER 9

Galvanic cells

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SYLLABUS DOT POINTS

SCIENCE UNDERSTANDING

- 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.

- 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).

SCIENCE INQUIRY

- Investigate galvanic cells.

Introduction

Galvanic cells are a type of electrochemical cell that uses a spontaneous redox chemical reaction to generate an electric current. They are sometimes referred to as voltaic cells, but most people know them by their common name – batteries.

The importance of galvanic cells is beyond question. But the more we become aware of the dangers that fossil fuels pose to the climate, the more we are searching for ways to make battery technology more efficient – to produce more power from smaller batteries. This chapter will discuss how galvanic cells are constructed and the role of each component in the cell.

ASSUMED KNOWLEDGE

- ✓ Oxidation is loss of electrons and reduction is gain of electrons.
- ✓ Half-equations are written to show oxidation and reduction reactions.
- ✓ Oxidation states are used to identify species being oxidised and reduced, and the oxidising agent and reducing agent.
- ✓ The reactivity series of metals lists metals in order from most reactive to least reactive.
- ✓ A more reactive metal reacts with ions of a less reactive metal.
- ✓ An electrolyte is a solution that conducts electricity.
- ✓ Roman numerals are used in the names of transition metal compounds to show the oxidation state of the metal.
- ✓ Redox reactions can be balanced using oxidation states and half-equations.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ identify the two types of electrochemical cells
- ✓ distinguish between galvanic (voltaic) cells and electrolytic cells in terms of energy transformation and spontaneity of chemical reactions occurring in the cells
- ✓ apply the reactivity series of metals to determine the species being oxidised and the species being reduced
- ✓ explain that a galvanic cell consists of two half-cells, one being the site of oxidation and the other the site of reduction
- ✓ recognise a galvanic cell consists of an external circuit and an internal circuit and will only operate when there is a complete circuit
- ✓ identify the components of the external circuit and the internal circuit
- ✓ identify the electrodes in each half-cell and classify them as anode and cathode
- ✓ explain the chemical processes occurring at the anode and cathode, and identify their polarity and direction of electron flow between them
- ✓ explain the purpose of a salt bridge and identify cation and anion flow
- ✓ draw a fully labelled diagram of a galvanic cell, including half-equations
- ✓ apply and interpret shorthand notation used to represent a galvanic cell
- ✓ recognise different types of galvanic cells
- ✓ apply knowledge of galvanic cells to interpret the operation of fuel cells.

9.1 Introduction to galvanic cells

Types of electrochemical cells

electrochemical cell a device that transforms energy between electrical energy and chemical potential energy

galvanic cell (or voltaic cell) an electrochemical cell that transforms chemical potential energy to electrical energy in a spontaneous chemical reaction

electrolytic cell an electrochemical cell that transforms electrical energy into chemical potential energy

Electrochemical cells allow for the transformation of energy between chemical potential energy and electrical energy. There are two types of electrochemical cells: **galvanic cells** and **electrolytic cells**.

Galvanic cells, also called **voltaic cells**, are a type of electrochemical cell that produces a flow of electrons by a spontaneous chemical reaction. The electric potential produced is then harnessed to power machines. The most familiar type of galvanic cell is a battery **(Figure 9.1.1)**.

Electrolytic cells are a type of electrochemical cell that uses electricity to produce a chemical reaction that would not occur spontaneously. Electrolytic cells are widely used in industry.

Galvanic cells use chemical processes to produce electricity, and electrolytic cells use electricity to produce chemical processes. This chapter will focus on galvanic cells and Chapter 11 will focus on electrolytic cells.

Age fotostock/Alamy Stock Photo

FIGURE 9.1.1 Batteries are galvanic cells.

Germany Feng/Shutterstock.com

FIGURE 9.1.2 These copper-plated pots were given their shiny metallic coating in an electrolytic process known as electroplating.

Metal displacement reactions and galvanic cells

As you learnt in Chapter 8, metal displacement oxidation and reduction reactions occur when a metal is in direct contact with a solution containing the ions of a less reactive metal. The reactivity series of metals can be used to identify the oxidation and reduction half-equations when a metal is in contact with ions of a different metal.

REACTIVITY SERIES OF METALS

K > Na > Li > Ba > Ca > Mg > Al > Zn > Fe > Sn > Pb > (H) > Cu > Ag > Pt > Au

FORMULA AND DATA BOOK

A more comprehensive list is provided in the *Formula and Data Book*.

An example of a metal displacement reaction is the reaction that occurs when a piece of zinc is placed in a copper(II) sulfate solution. In this spontaneous reaction, the zinc gives up electrons to the copper ions and the products are copper metal and zinc ions.

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

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

KEY CONCEPT

Galvanic cells involve spontaneous chemical reactions. The overall cell voltage is positive.

If the reacting species (Zn and Cu^{2+}) are put into two separate beakers and connected in a specific way to form a complete circuit, then the same reaction will occur but the electrons can be used to do work in the process. This is the principle of galvanic cells.

This simple galvanic cell is shown in Figure 9.1.3.

One beaker contains zinc metal in a zinc sulfate solution and the other beaker contains copper metal in a copper(II) sulfate solution. The two beakers are called **half-cells**.

half-cell the part of a galvanic cell where oxidation or reduction occurs

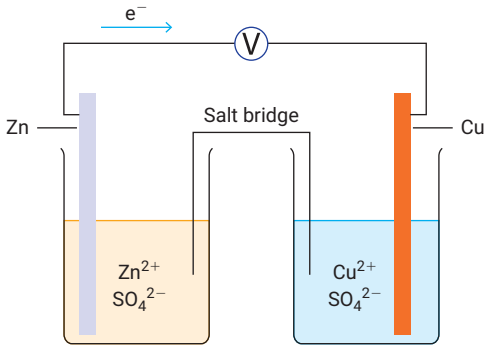


FIGURE 9.1.3 The galvanic cell between zinc and copper

Worksheet
Electrochemical cells

Oxidation occurs in one of the half-cells (in this case, the Zn, Zn^{2+} half-cell) and reduction occurs in the other (in this case, the Cu, Cu^{2+} half-cell).

The electrons flow through a wire connecting the metals in the different half-cells. Because copper has a greater potential to be reduced than zinc, electrons are transferred from the zinc atoms in the zinc half-cell to the copper half-cell where the copper ions are reduced. The flow of electrons produces a current, which is measured in amperes (amps). Voltage (also known as electrical potential difference) is a measure of the work needed to move a charge between two points and is measured in volts (V). If a voltmeter is included in the circuit, as seen in Figure 9.1.3, the electrical potential difference between the two half-cells can be measured in volts. Electrical potential difference will be covered in detail in Chapter 10.

LEARNING CHECK 9.1

DESCRIBING

1 **Describe** the purpose of an electrochemical cell.

2 **a** **Identify** the two types of electrochemical cells.

b **Construct** a table comparing these two cells type in terms of energy transformation and reaction spontaneity.

3 **Describe** what information a metal reactivity series provides and **explain** how it can be used.

APPLYING

4 **a** **Identify** if a reaction will occur in each of the following set-ups.

i A granule of zinc is dropped into a solution of lead(II) nitrate.
ii A piece of tin is dropped into a solution of silver nitrate.
iii A strip of magnesium is dropped into a solution of sodium chloride.

b Write equations for the reactions that occurred in part a.

5 **Explain** why the blue solution decolourises when a galvanic cell is set up using a strip of copper in a copper(II) sulfate solution and a strip of magnesium in a magnesium nitrate solution.

6 **a** **Identify** in which direction (left to right or right to left) the following reactions occur.

i $Sn(s) + Cu^{2+}(aq) - Sn^{2+}(aq) + Cu(s)$
ii $Fe(s) + Mg^{2+}(aq) - Fe^{2+}(aq) + Mg(s)$
iii $Al^{3+}(aq) + Zn(s) - Al(s) + Zn^{2+}(aq)$

b **Determine** the oxidation and reduction half-equations for the reactions in part a and write them in the directions in which they occur.

c **Suggest** two half-cells that could be used to construct a galvanic cell for the reaction in part a(iii).

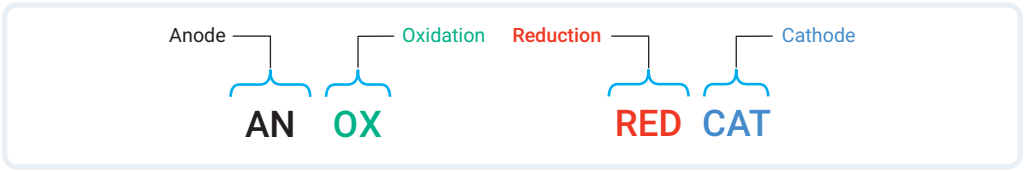
9.2 The essential components of a galvanic cell

Figure 9.1.3 shows a galvanic cell connecting a Zn, Zn^{2+} half-cell to a Cu, Cu^{2+} half-cell. For electricity to flow there needs to be a complete circuit. In a galvanic cell, there is an **external circuit** consisting of the connecting wires and voltmeter (or appliance) connected to an **internal circuit**, which consists of the strips of metal, solutions and **salt bridge**. The voltmeter measures the difference in cell potential of the two half-cells and can therefore measure the electrical energy generated by the cell (in volts), indicating that the cell is working.

The conductors of the cell, usually pieces of metal, which get connected to the external circuit, are called **electrodes**. In the cell in Figure 9.1.3 there is a zinc electrode and a copper electrode. Sometimes the term 'electrode' is also used to refer to the combination of conductor and associated ions in solution. In the example, these would be the Zn, Zn^{2+} electrode and the Cu, Cu^{2+} electrode.

Oxidation occurs at one of the electrodes and reduction occurs at the other electrode. The electrodes are given specific names – the electrode where oxidation occurs is the **anode** and the electrode where reduction occurs is the **cathode**. In a galvanic cell, the anode is negatively charged because it is the source of electrons, and the cathode is positively charged because it attracts the electrons.

The mnemonics, **an ox** and **red cat** may help you remember which process occurs at which electrode:



In the mnemonic red cat, thinking of the 't' as a plus sign helps you remember the cathode is positive (+) in galvanic cells. Table 9.2.1 summarises the key concepts related to the electrodes.

TABLE 9.2.1 The reactions and polarity of each electrode

Electrode	Reaction	Electrode sign
Anode	Oxidation (loss of electrons)	Negative
Cathode	Reduction (gain of electrons)	Positive

Figure 9.2.1 shows the electrode processes occurring in each half-cell.

In the zinc half-cell, the zinc atoms at the surface of the zinc electrode are oxidised to Zn^{2+} ions, which move into solution. The electrons produced in the oxidation of zinc move up through the electrode and into the wire of the external circuit. Since negatively charged electrons are produced at this electrode, the zinc strip is the negative electrode. It is the anode because oxidation occurs here.

external circuit the circuit of an electrochemical cell consisting of the connecting wires and voltmeter or electrical appliance

internal circuit the circuit of an electrochemical cell consisting of the strips of metal, solutions and salt bridge

salt bridge a link containing an electrolyte between the oxidation and reduction half-cells of a galvanic cell

electrode the conductor of a cell connected to the external circuit; also the combination of conductor and associated ions in solution

anode the electrode where oxidation occurs

cathode the electrode where reduction occurs

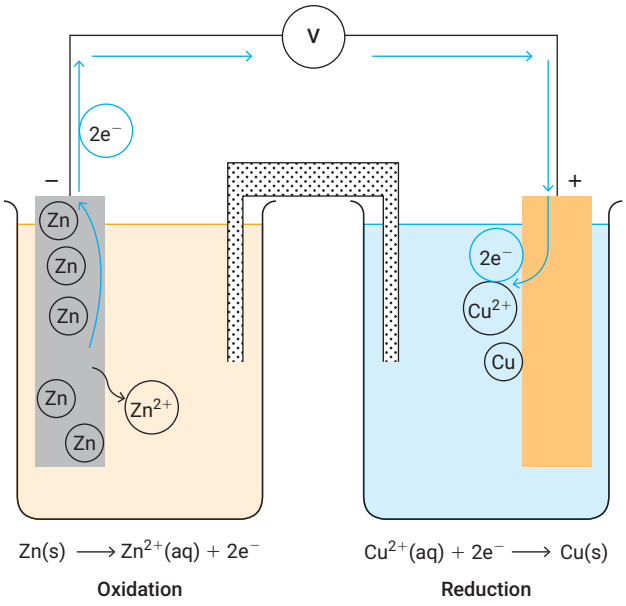


FIGURE 9.2.1 Electrode processes of a galvanic cell

The electrons, having moved through the wires of the external circuit, enter the copper strip. The positively charged copper ions in solution are attracted to the build-up of negative charge in the copper strip. Here, they pick up the electrons that travelled from the zinc strip and are reduced to copper atoms. The copper strip is the positive electrode. It is the cathode because reduction occurs here.

Purpose of the salt bridge

As mentioned previously, a salt bridge is necessary to complete the circuit and to maintain neutrality in each half-cell. It is important to understand how this is achieved.

Consider the oxidation half-cell:

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

Typically, the concentration of electrolyte, in this case zinc sulfate, is 1 mol L^{-1}. The positive $Zn^{2+}(aq)$ ions are balanced out by the $SO_4^{2-}(aq)$ ions.

If the cell were able to operate without a salt bridge, then as the Zn metal atoms are oxidised, the resulting Zn^{2+} ions would move into solution. This would increase the number of $Zn^{2+}(aq)$ ions, thereby producing a build-up of positive charge within the half-cell. This is not possible.

A salt bridge contains a solution of positive and negative ions that must not interfere chemically with the components of either half-cell. Typically, potassium nitrate is used as the solution for the salt bridge because neither potassium nor nitrate ions form any precipitates. In this example, for every Zn^{2+} ion that moves into solution, two NO_3^- ions move from the salt bridge into the solution. This keeps the charges balanced.

Similarly, in the reduction half-cell:

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

If the cell were able to operate without a salt bridge, then as the $Cu^{2+}(aq)$ ions are reduced, they are effectively removed from the solution, resulting in a build-up of negative charge within the half-cell. This is not possible.

For every Cu^{2+} that is lost from the half-cell, two K^+ ions move from the salt bridge into the solution. This keeps the charges balanced.

This is shown in **Figure 9.2.2**.

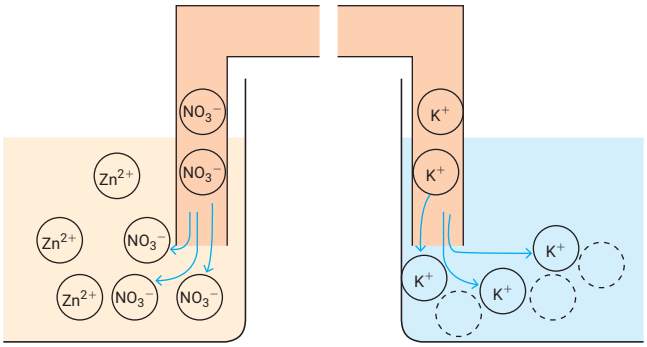


FIGURE 9.2.2 The role of the salt bridge in a galvanic cell

An easy way to remember which direction the ions in the salt bridge move is:

'Anions in the salt bridge move towards the anode and cations in the salt bridge move towards the cathode.'

Although this may seem contradictory given the anode is negative and the cathode is positive, it is important to remember the ions of the salt bridge are moving to balance charge in the solution of the half-cell. The anode is the site of oxidation, which produces positive ions so these need to be balanced by anions. The cathode is the site of reduction where positive ions leave the solution, so more cations are needed to balance this loss.

Weblink
Structure of a voltaic/galvanic cell

LEARNING CHECK 9.2

DESCRIBING

1 **Define**:
   - **a** anode
   - **b** cathode
   - **c** electrolyte.

2 **Explain** why the mass of the magnesium electrode decreases during the operation of a magnesium–lead galvanic cell.

3 **Explain** why the reactants in a galvanic cell such as aluminium and tin must be placed in separate beakers.

4 **Describe** two properties a salt must have to be used in a salt bridge.

5 **Identify** which ions from the salt bridge electrolyte, K^+ or NO_3^-, move into the oxidation half-cell. **Explain** your choice.

APPLYING

6 If a galvanic cell was left to run indefinitely, it would go 'flat'; that is, it would stop working. With reference to the zinc–copper galvanic cell, **deduce** a reason why this could occur.

ANALYSING

7 **Justify** whether each of the following would produce a galvanic cell.
   - **a** $2Ag(s) + Pb^{2+}(aq) \rightarrow Pb(s) + 2Ag^+(aq)$
   - **b** $Zn(s) + Fe^{2+}(aq) \rightarrow Fe(s) + Zn^{2+}(aq)$

9.3 Galvanic cell diagrams

A labelled diagram of a galvanic cell makes it easy to determine what is happening in the overall cell as well as the half-cells. The following are steps in the process to follow when sketching a galvanic cell.

1. Identify the species being oxidised and the species being reduced and then write oxidation and reduction half-equations.
2. Identify the electrode and ion solution for each half-cell.
3. Sketch the basic form of the cell.
4. Label the anode and the cathode and add the minus sign and plus sign.
5. Add the salt bridge and name the salt.
6. Add an external circuit to the cell, consisting of wires and a voltmeter.
7. Show the direction of electron flow through the external circuit.
8. Show the direction of positive ion flow through the cell.
9. Show the direction of positive and negative ion flow from the salt bridge.

WORKED EXAMPLE 9.3.1

The displacement reaction between manganese and iron is given by the equation:

$Mn(s) + Fe(NO_3)_2(aq) \rightarrow Mn(NO_3)_2(aq) + Fe(s)$

From this information, draw and label the galvanic cell represented by this equation.

ANSWER

1 Identify the species being oxidised and the species being reduced then write oxidation and reduction half-equations.

The Mn oxidation state goes from 0 to +2, so it is oxidised.
The oxidation state of Fe goes from +2 to 0, so it is reduced.

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

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

2 Identify the electrode and ion solution for each half-cell.

The metals are Mn and Fe and the solutions are $Mn(NO_3)_2(aq)$ and $Fe(NO_3)_2(aq)$.
The oxidation half-cell is Mn in a $Mn(NO_3)_2$ solution.
The reduction half-cell is Fe in a $Fe(NO_3)_2$ solution.

3 Sketch the basic form of the cell.

Draw two separate beakers side by side, add electrodes and solution to each.

4 Label the anode and the cathode and add the minus sign and plus sign.

Mn electrode is the anode because it is where oxidation is occurring and it is negative.
Fe electrode is the cathode because it is where reduction is occurring and is positive.

5 Add the salt bridge and name the salt.

Draw in the salt bridge. Label it with 'KNO_3' and 'salt bridge'.

6 Add an external circuit to the cell, consisting of wires and a voltmeter.

Draw a wire from one metal electrode to the other and show a voltmeter (V) as part of this circuit.

7 Show the direction of electron flow through the external circuit.

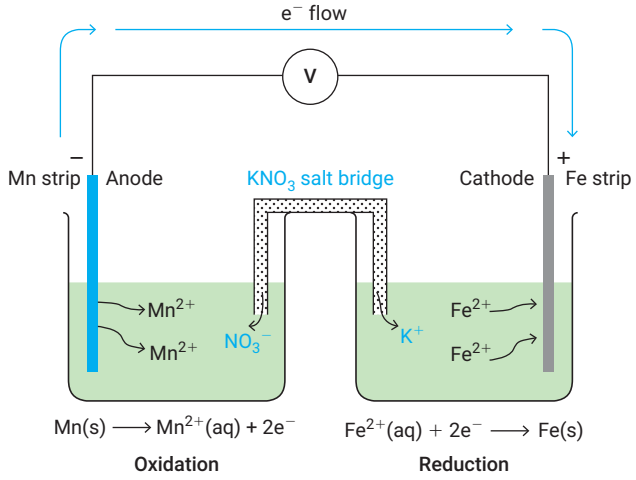
Add an arrow on or above the wire showing electrons flowing from the anode (Mn) to the cathode (Fe).

8 Show the direction of positive ion flow through the cell.

Positive ions are produced at the anode and removed from solution at the cathode. Show Mn^{2+} ions moving into solution from the anode and Fe^{2+} ions moving out of solution to the cathode.

9 Show the direction of positive and negative ion flow from the salt bridge.

Show the NO_3^- anions moving into the anode half-cell and the K^+ cations moving into the cathode half-cell.



Shorthand representations of galvanic cells

To have to draw a galvanic cell every time one is discussed can be tedious, so chemists have devised a shorthand way of representing cells. In this way, the cell in Worked example 9.3.1 can be represented as:

$$Mn(s) \mid Mn^{2+}(aq) \parallel Fe^{2+}(aq) \mid Fe(s)$$

This galvanic cell representation is read as this: a piece of manganese metal dips into a solution containing manganese ions. This half-cell is connected by a salt bridge to a half-cell containing a solution of iron ions into which dips a piece of iron.

The rules for writing this shorthand representation are:

- different phases are separated by a single vertical line |
- the salt bridge is represented by double vertical lines ||
- the anode reaction is written to the left of the salt bridge
- the cathode reaction is written to the right of the salt bridge
- the electrodes always appear on the far left and the far right
- species in the same phase (state) are separated by a comma.

The same shorthand can be used for identifying different individual electrodes. For example, in Figure 9.2.1 the electrodes are $Zn(s) \mid Zn^{2+}(aq)$ and $Cu^{2+}(aq) \mid Cu(s)$

Note: State symbols (s), (aq), (g) may not always be included.

Weblink
Cell diagrams for galvanic cells

Worksheet
Sketching galvanic cells

Using different electrodes

A large variety of galvanic cells can be constructed in the laboratory. So far, we have only considered electrodes that consist of a piece of metal dipped into a solution containing the ions of that metal, such as $Zn(s) \mid Zn^{2+}(aq)$ and $Cu^{2+}(aq) \mid Cu(s)$.

However, this tends to limit the variety of redox reactions that can be used to form galvanic cells. Two other types of electrodes include the following:

- Electrodes consisting of an inert conductor such as a piece of platinum wire or a graphite rod dipping into a solution containing both an oxidised and reduced form of the same element such as Fe^{2+} and Fe^{3+}. Using shorthand, this electrode is shown as $Fe^{2+}(aq)$, $Fe^{3+}(aq)$ | Pt(s). Note: $Fe^{2+}(aq)$, $Fe^{3+}(aq)$ are separated by a comma because they are both in the same phase
- Electrodes consisting of a gas bubbling into a solution containing the oxidised or reduced form of the gas with an inert electrode such as platinum wire dipping into the solution; for example, H_2 and H^+ with a Pt wire electrode as represented by $H^+(aq)$ | $H_2(g)$ | Pt(s). Note: Even though $H_2(g)$ and Pt are part of the same electrode $H_2(g)$ | Pt(s), they are different phases so are separated by a vertical line.

PRACTICAL ACTIVITY 9.3.1

CONSTRUCTING GALVANIC CELLS

Introduction

Galvanic cells involve joining two half-cells by a salt bridge and an external circuit. In this experiment, you will use different combinations of half-cells.

Research question

How is the electrical potential difference of a galvanic cell affected when different half-cells are used?

Aim

To measure the cell voltage for a variety of galvanic cells

Materials

- 50 mL of 1 mol L^{-1} $CuSO_4$
- 50 mL of 1 mol L^{-1} $MgSO_4$
- 50 mL of 1 mol L^{-1} acidified $FeSO_4$
- 50 mL of 1 mol L^{-1} $ZnSO_4$
- 50 mL of 1 mol L^{-1} KNO_3
- strip of Cu metal
- strip of Mg ribbon
- ungalvanised iron nail
- strip of zinc metal
- 7 cm × 7 cm piece of sandpaper
- voltmeter
- 2 electrical wires with banana plugs on each end
- 2 alligator clips – place one on each electrical wire
- strips of filter paper about 1 cm wide and 10 cm long
- 4 × 100 mL beakers
- 250 mL beaker
- 5 labels for beakers
- small piece of Blu-Tack
- forceps
- waste bottle for heavy metals

RISK ASSESSMENT

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Potassium nitrate is a moderately toxic salt.	Use forceps to handle filter paper soaked with potassium nitrate.

Copy and complete the risk assessment table in your write-up. Add any more risks you can think of, and ways to manage them. Ask your teacher to check your risk assessment before you proceed.

Procedure

1 Pour 50 mL of each solution (except KNO_3) into separate labelled 100 mL beakers.
2 Clean the pieces of metal with sandpaper.
3 Stand a piece of metal in the beaker with its corresponding solution so that it is partly submerged. You may use a small piece of Blu-Tack to hold the metal in place.
4 Put strips of filter paper into a 250 mL beaker, add KNO_3 solution and leave it to soak.
5 Connect the Cu, $CuSO_4$ half-cell with the Zn, $ZnSO_4$ half-cell, using a piece of soaked filter paper as the salt bridge with one end in each of the solutions.
6 Connect the zinc strip and copper strip to the voltmeter with electrical wires.
7 Record the voltage. If the needle drops below zero, connect the wires to the opposite terminals of the voltmeter.
8 Repeat for all other combinations for galvanic cells: copper–magnesium, copper–iron, magnesium–zinc, magnesium–iron and zinc–iron.
9 Dispose of copper(II) sulfate by pouring it into the heavy metals waste bottle. Do not pour it down the drain.

Results

Construct a table like the one below and record the voltage for each galvanic cell.

Beaker 1	Beaker 2	Voltage (V)	Direction of electron flow	Anode reaction	Cathode reaction
$Zn(s) \mid Zn^{2+}(aq)$	$Cu(s) \mid Cu^{2+}(aq)$				

Analysis of results

1 Complete the results table by identifying the direction of electron flow and writing the anode and cathode reaction for each combination.
2 Identify the galvanic cell that had the largest cell voltage.
3 Identify the galvanic cell that had the smallest cell voltage.

Interpretation

4 Construct a reactivity series of the metals used based on the cell voltages.

Evaluation

5 Compare the reactivity series you constructed with the one given earlier in the chapter. Suggest reasons for any differences.
6 Determine if there is a relationship between relative positions of metals in the reactivity series and the size of cell potential.

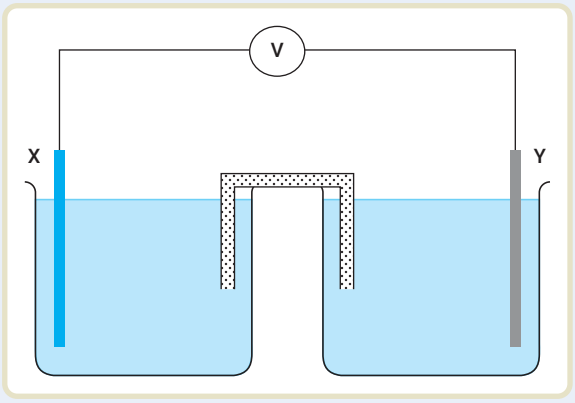
LEARNING CHECK 9.3

APPLYING

1 Draw and fully label, including half-equations, the galvanic cells based on the metal displacement reaction between:
   a lead and copper(II) nitrate
   b cadmium and silver nitrate.

2 Write the shorthand representations for each of the galvanic cells in Question 1.

3 A galvanic cell was set up as shown with metal electrodes X and Y dipping into solutions of $X(NO_3)_2$ and $Y(NO_3)_2$ respectively. The electrodes were weighed before they were placed into the cell.



After several minutes, the electrodes were taken out and weighed again. Electrode X had gained mass, while electrode Y had lost mass.

Redraw the cell from this information, labelling the anode, cathode, sign (+ or –) of the electrodes, direction of current flow, movement of positive ions, salt used in the salt bridge, movement of ions from the salt bridge, and oxidation and reduction half-equations.

4 Consider the following shorthand representation:

$Fe(s) \mid Fe^{2+}(aq) \parallel Pb^{2+}(aq) \mid Pb(s)$

a **Identify** the anode and cathode.

b **Construct** the oxidation and reduction half-equations.

ANALYSING

5 A galvanic cell was set up as shown. The chloride electrode in the right-hand arm was made by bubbling chlorine gas over a platinum electrode that dipped into a $NiCl_2$ solution. The left-hand arm contained a nickel rod dipping into the same solution. The platinum wire is positive.

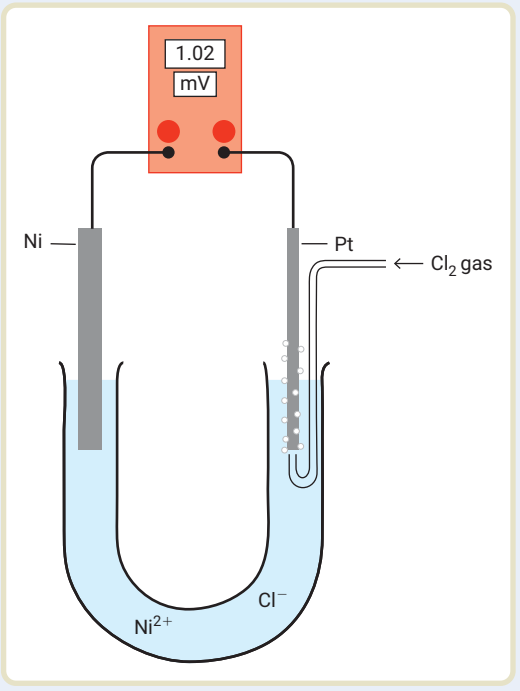
a **Identify** the anode and cathode and their polarity (positive and negative).

b Write and **identify** the oxidation and reduction half-equations.

c **Determine** the direct of electron and ion flow as the cell operates.

d **Explain** why a salt bridge is not needed in this galvanic cell. Use the term 'oxidising agent' in your explanation.

e **Construct** the shorthand representation for the chlorine electrode



CHAPTER SUMMARY

Types of electrochemical cells

- There are two types of electrochemical cells: galvanic cells and electrolytic cells.
- Galvanic cells, also called voltaic cells, produce a flow of electrons by a spontaneous chemical reaction.
- Electrolytic cells use electricity to produce a chemical reaction that would not occur spontaneously.

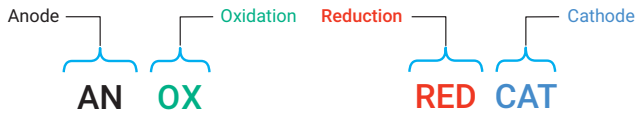
Reactivity series of metals

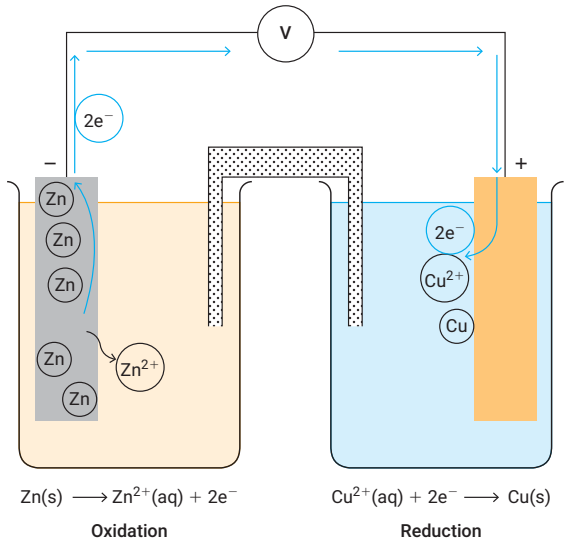
- The reactivity series of metals can be used to identify the oxidation and reduction half-equations when a metal is in contact with ions of a different metal.

  K > Na > Li > Ba > Ca > Mg > Al > Zn > Fe > Sn > Pb > (H) > Cu > Ag > Pt > Au

Components of galvanic cells

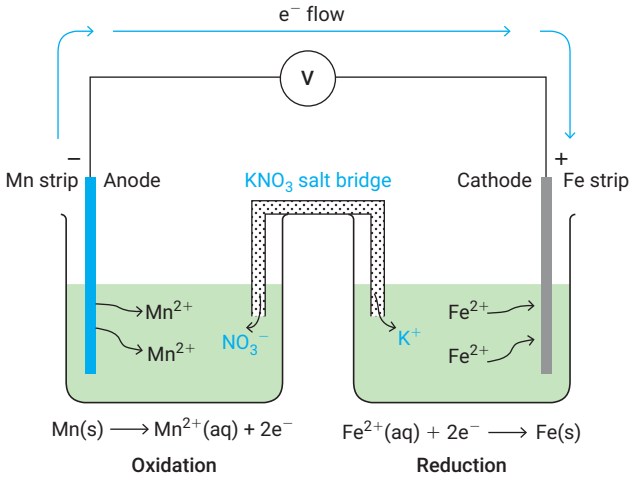
- Galvanic cells consist of:
  - two half-cells
  - external circuit – the connecting wires and the voltmeter or electrical appliance
  - internal circuit – strips of metal, solutions and salt bridge
  - salt bridge – a link containing an electrolyte that joins the oxidation and reduction half-cells
  - electrodes – conductors of the half-cell, also referred to combination of conductors and associated ions in solution; may be a piece of metal or inert conductor such as platinum or a graphite rod
  - anode – negative electrode where oxidation occurs
  - cathode – positive electrode where reduction occurs.





Representing a galvanic cell

- A galvanic cell can be represented by a labelled diagram showing all components and half-equations.



- Shorthand representation is also used to represent a galvanic cell, e.g. $Mn(s) \mid Mn^{2+}(aq) \,||\, Fe^{2+}(aq) \mid Fe(s)$.

CHAPTER EXAM

MULTIPLE CHOICE

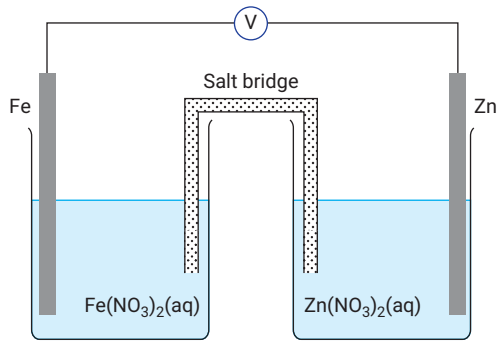
1. In a galvanic cell, it is important that the half-cells are separated because:
- **A** oxidation and reduction are two separate reactions.
- **B** oxidation and reduction cannot happen at the same time.
- **C** this allows ions to flow through the salt bridge.
- **D** this allows electrons to flow through the external wire.

2. Which of the following is *not* true? The salt bridge in a galvanic cell must:
- **A** contain ions.
- **B** be an electrolyte.
- **C** connect the two half-cells.
- **D** react with the half-cells.

3. How is the circuit completed in an electrochemical cell?
- **A** Electrons go through the wire and positive ions go through the solution from anode to cathode.
- **B** Electrons go through the solution and positive ions go through the wire from anode to cathode.
- **C** Positive ions go through the solution and electrons go through the wire from cathode to anode.
- **D** Positive ions go through the wire and electrons go through the solution from cathode to anode.

4. Which of the following materials would be least suitable to use as an electrode in a $Fe^{3+}(aq)$, $Fe^{2+}(aq)$ half-cell?
- **A** Carbon
- **B** Iron
- **C** Platinum
- **D** Silver

Questions 5 and 6 relate to the following galvanic cell.



Adapted from WA SCSA ATAR Chemistry course examination, 2022 Question 15, https://senior-secondary.scsa.wa.edu.au/__data/assets/pdf_file/0016/1042027/2022-CHE-Examination-Web-version.PDF

5. Which of the following best represents the cell?

	Anode	Cathode	Direction of electron flow	Direction of cation flow
A	Iron	Zinc	←	→
B	Iron	Zinc	→	←
C	Zinc	Iron	→	→
D	Zinc	Iron	←	←

6. Which of the following is the correct representation of this cell using shorthand notation?

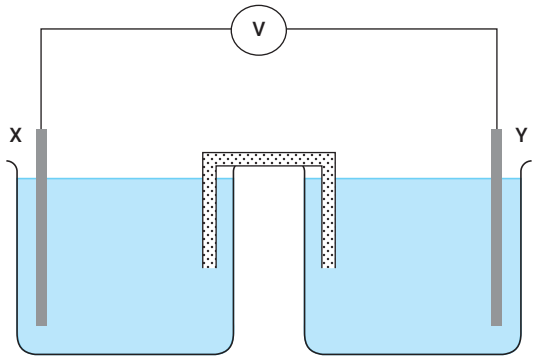
A $Fe(s) \mid Fe^{2+}(aq) \,||\, Zn(s) \mid Zn^{2+}(aq)$

B $Zn^{2+}(aq) \mid Fe^{2+}(aq) \,||\, Zn(s) \mid Fe(s)$

C $Zn(s) \mid Zn^{2+}(aq) \,||\, Fe^{2+}(aq) \mid Fe(s)$

D $Fe(s) \mid Fe^{2+}(aq) \,||\, Zn^{2+}(aq) \mid Zn(s)$

7. The following diagram shows a standard voltaic cell.



Which combination of electrodes and electrolyte solution will result in a reading on the voltmeter?

	Left half-cell		Right half-cell	
	Electrode X	Electrolyte solution	Electrode Y	Electrolyte solution
A	Platinum	$MgSO_4(aq)$	Magnesium	$CuSO_4(aq)$
B	Copper	$MgSO_4(aq)$	Platinum	$CuSO_4(aq)$
C	Magnesium	$CuSO_4(aq)$	Copper	$MgSO_4(aq)$
D	Magnesium	$MgSO_4(aq)$	Copper	$CuSO_4(aq)$

8. Which of the following statements are correct for a galvanic cell?

I Reaction is spontaneous
II Reaction is non-spontaneous
III Produces an electric current
IV Used for electroplating

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

9. Which half-reaction occurs at the positive electrode of a voltaic cell composed of the half-cells, $Sn(s)|Sn^{2+}(aq)$ and $Al(s)|Al^{3+}(aq)$?

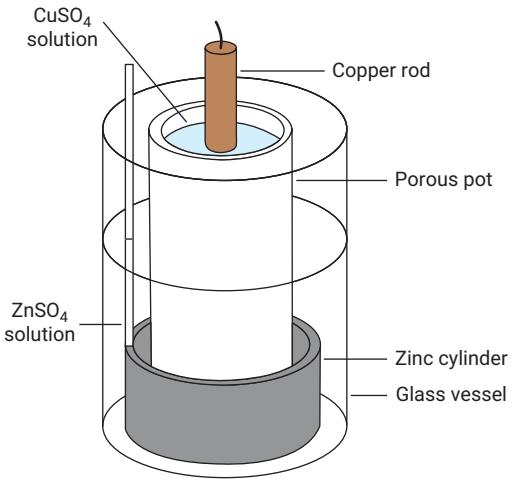
A $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

B $Al^{3+}(aq) + 3e^- \rightarrow Al(s)$

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

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

10. The following diagram shows a galvanic cell in which the two half-cells are kept separate with a porous pot that takes the place of a salt bridge.



In this galvanic cell, which reactant is the reducing agent?

A $CuSO_4$

B $ZnSO_4$

C Zn

D Cu

SHORT RESPONSE

11. A student was given the task of constructing a functioning galvanic cell. They were provided with all the necessary equipment and the following substances:

- A piece of magnesium
- A piece of zinc
- A 6 cm piece of platinum wire
- 1.0 mol L^{-1} magnesium carbonate solution
- 1.0 mol L^{-1} zinc nitrate solution
- 1.0 mol L^{-1} sodium carbonate solution

The student was told there was no need to use all the substances.

a **Identify** which substances the student should use and the purpose of each substance

b **Construct** a fully labelled diagram of the galvanic cell the student should construct. Labels should include anode, cathode, polarity of electrodes, electrolyte solutions and direction of cation and anion flow

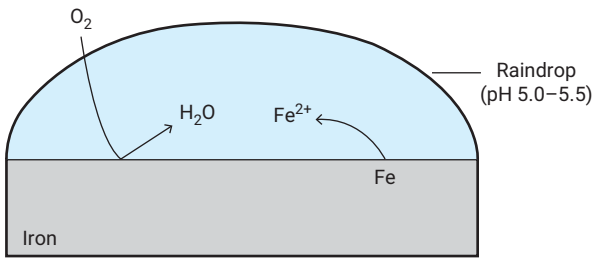
c Write the anode and cathode half-equations for the cell, **identifying** the oxidation and reduction reactions.

d Suggest up to two changes in substances that could be made and **explain** why they would not affect the operation of the cell.

 Modified from SCSA 2021 SA Q31

12. Corrosion involves a redox reaction. When an iron object is exposed to water it will corrode to form rust, Fe_2O_3. In the presence of water, this exists in the hydrated form $Fe_2O_3.H_2O(s)$.

The corrosion of iron occurs in two stages. During the first stage of the corrosion process, a galvanic cell is established on the iron surface. The following diagram shows the reactants and products for each half-cell.



a **Deduce** the:

i oxidation half-equation

ii reduction half-equation

iii overall balanced equation.

b Copy the diagram and **identify** and label the anode site, cathode site and direction of electron transfer.

c **Justify** why this process is considered to be a galvanic cell.

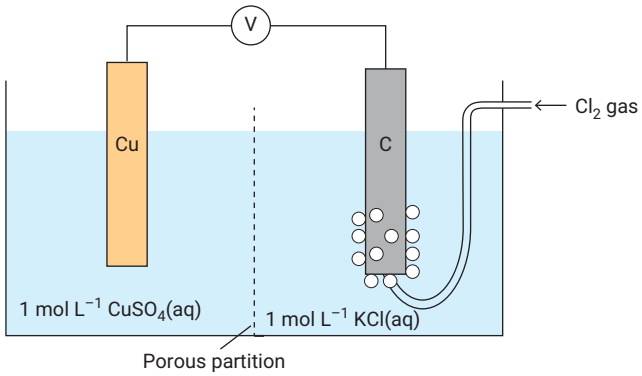
d During the second stage of iron corrosion, the Fe^{2+} ions migrate away from the iron surface and react with water and dissolved oxygen to form rust. This is shown in the following equation:

$$4Fe^{2+}(aq) + O_2(g) + 6H_2O(l) \rightarrow 2Fe_2O_3.H_2O(s) + 8H^+(aq)$$

Explain why this stage is a redox process.

CROSS-CHAPTER QUESTION

13. An experimental investigation was conducted to determine the purity of a piece of copper. The following diagram shows the voltaic cell used in the investigation. An inert graphite rod was used as one of the electrodes.



The shorthand hand representation for this cell is:

$Cu(s) \mid Cu^{2+}(aq) \mid\mid Cl^{-}(aq) \mid Cl_2(g) \mid C(s)$

a **Identify** the anode and cathode.

b **Determine** equations for the:

- **i** half-reaction that occurs in the left-hand cell
- **ii** half-reaction that occurs in the right-hand cell
- **iii** overall cell reaction.

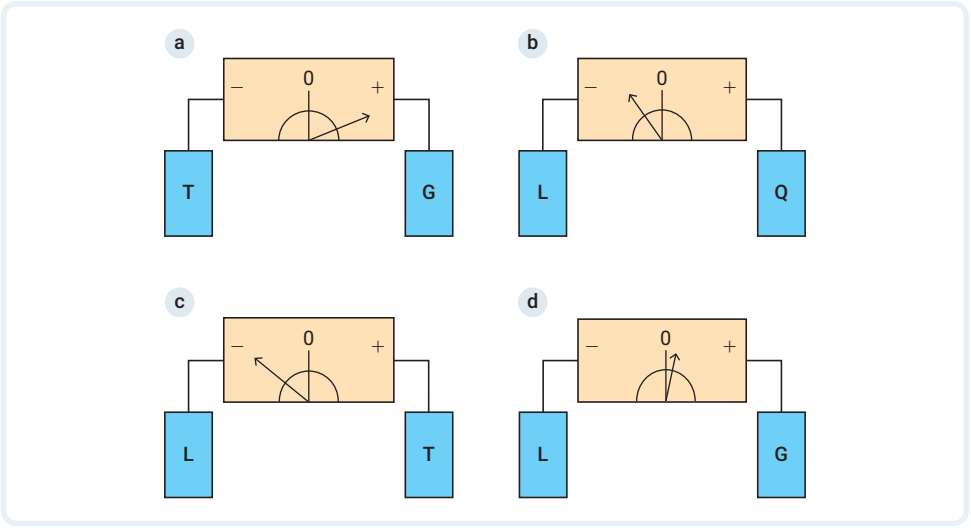
c The copper metal was weighed before constructing the cell. 283.3 mL of chlorine gas (at 100 kPa and 25°C) was bubbled over the graphite electrode. After the reaction ceased, the copper electrode was dried and reweighed. The mass of the electrode had decreased by 0.761 g.

- **i** **Calculate** the number of moles of $Cl_2(g)$ that reacted.
- **ii** **Calculate** the mass of Cu(s) that reacted.
- **iii** **Determine** the percentage of copper by mass in the electrode.
- **iv** **Infer** the purity of the copper electrode.

DATA ANALYSIS

14. Analyse data

An experiment is carried out to develop a reactivity series for a group of unknown metals: T, Q, L and G. A number of galvanic cells are set up using the given metals dipping into solutions of their respective ions. In each cell, a galvanometer is used to measure the voltage in the cell as well as the direction of current flow. The results are shown in the following diagram.



a **Construct** a reactivity series for the metals T, Q, L and G based on the experimental results.

b For each experiment a–d:

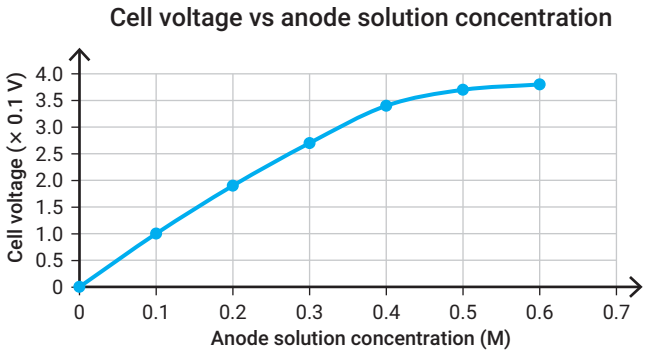
i **identify** the anode and cathode

ii **determine** oxidation and reduction half-equations (assume all the metals produce 2+ ions).

15. Interpret evidence

A student carried out a series of experiments in which they set up a galvanic cell. The student varied the concentration of the solution of the metal in the anode half-cell and recorded the corresponding cell voltage.

The results are recorded in the following graph.



a **Deduce** whether there is a relationship between concentration of anode solution and cell voltage

b **Determine** a reason for any relationship identified in part a.

c **Explain** why the graph plateaus after about 0.4 M concentration.

d **Infer** what the graph would look like if the cathode solution concentration was varied instead.

CHAPTER 10

Standard electrode potential

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SYLLABUS DOT POINTS

SCIENCE UNDERSTANDING

- 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, $E°_{cell}$ (Formula: $E°_{cell} = E°_{reduction\ half\text{-}cell} - E°_{oxidation\ half\text{-}cell}$)
- 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.

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Introduction

Galvanic cells consist of two half-cells. If a half-cell is connected to a reference cell, its standard electrode potential can be measured. The standard electrode potential of substances is a very useful property. Standard electrode potentials enable the relative strength of oxidising and reducing species to be determined, they can be used to predict whether or redox reactions will take place and they can be used to calculate the voltage produced by galvanic cells.

Worksheets

- Predicting reactions using $E°$ values
- Calculating half-cell potentials

Nelson MindTap

To access resources above, visit **cengage.com.au/nelsonmindtap**

ASSUMED KNOWLEDGE

- ✓ The reactivity series of metals can be used to predict whether reactions will occur between different metals and metal ions.
- ✓ Galvanic cells consist of two half-cells in which reactions occur spontaneously to generate an electric current.
- ✓ A galvanic cell has characteristic components and structure.
- ✓ Electrochemical processes occurring in galvanic cells include site of oxidation and reduction, direction of electron flow and direction of ion flow.
- ✓ A galvanic cell can be represented by a diagram or shorthand representation.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ describe a standard hydrogen electrode
- ✓ explain the purpose of having a standard electrode
- ✓ identify standard half-cell conditions
- ✓ explain the term 'standard electrode potential' ($E°$)
- ✓ use a table of standard electrode potentials
- ✓ calculate cell potential ($E°$) from half-cell electrode potentials
- ✓ examine limitations associated with standard electrode potentials
- ✓ apply standard electrode potentials to:
  - predict whether reactions will occur spontaneously
  - determine relative strength of oxidising and reducing agents
  - compare galvanic cells.

10.1 The relative strength of oxidising and reducing agents

Using a standard to rank oxidising strength

reference cell an electrode used for reference on half-cell potential reactions

Practical activity 8.1.1 compared the oxidising strength of a variety of metals in solutions containing cations of other metals. This enabled you to verify the reactivity of different metals. If chemists continued to perform experiments with different combinations of metals and solutions, they could put together a table showing the ability to be oxidised for all elements on the periodic table; however, this would be very time consuming. Instead, chemists compare all other species to a **reference cell**. The reference cell is a hydrogen half-cell. It contains a solution with hydrogen ions, hydrogen gas and a piece of platinum as the electrode to connect this cell to the electric circuit. The hydrogen gas is bubbled into the solution. Platinum is used because it is a good conductor of electricity and is relatively inert. It is also a catalyst for the dissociation of H_2 gas. Therefore, it provides a pathway for the electric charge, while not taking part in the chemical reaction, as shown in Figure 10.1.1.

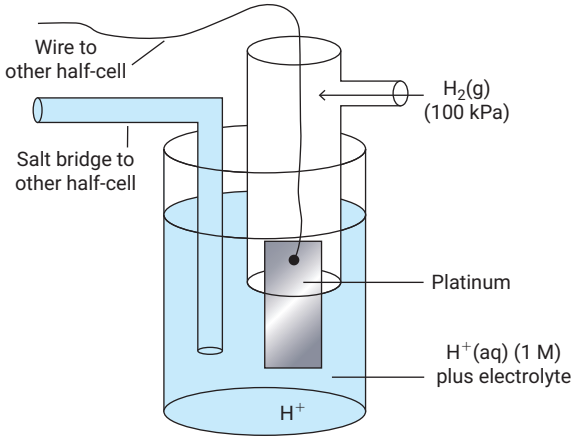


FIGURE 10.1.1 The standard hydrogen electrode

The test cell consists of a solution containing ions of the element being tested and a metal electrode, or the non-metal with a platinum or graphite electrode. The test cell and the reference cell are connected by external wires to a voltmeter. A salt bridge completes the circuit. The simplest salt bridge is a piece of filter paper soaked in an electrolyte such as potassium nitrate, since it will not react with any of the test or reference solutions. **Figure 10.1.2** shows how this galvanic cell is set up.

Conditions for half-cells

To ensure the validity of the data being collected, standard conditions must be used:

- Solutions must contain 1 mol L^{-1} of ions of the species being tested.
- Solutions must be at 25°C (298 K).
- Gases must be at 100 kPa and 25°C (298 K).

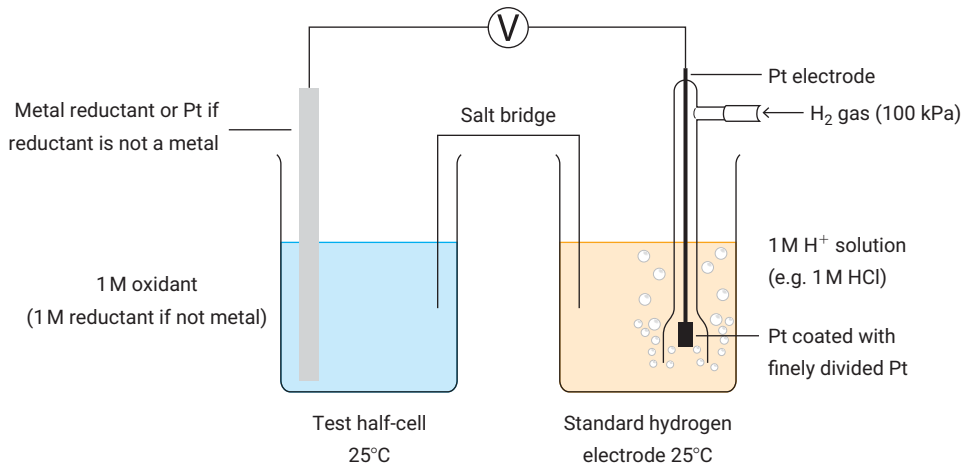


FIGURE 10.1.2 The set-up for determining standard electrode potentials

FORMULA AND DATA BOOK

standard electrode potential ($E°$) the potential of an electrode (measured in volts) in its standard state relative to the standard hydrogen electrode

Determining standard test half-cell potentials

All values are measured relative to the hydrogen half-cell. The hydrogen half-cell is given a value of 0.00 V. Hence, the reading on the voltmeter becomes the value of the test half-cell. This method has been used to produce a table of standard electrode potentials at 298 K **(Table 10.1.1)**.

Elements that are more likely than hydrogen to gain electrons have positive **standard electrode potential ($E°$)** values. Elements that are more likely than hydrogen to lose electrons have negative $E°$ values. Standard electrode potentials are assigned not only to the electrodes but also to the reduction half-reactions associated with the electrodes, as can be seen in Table 10.1.1. If conditions are not those of the standard state, then the term used is simply 'electrode potential' and the symbol used is E rather than $E°$.

As shown in Table 10.1.1, the half-equations are written in the same format. They are all written as reduction reactions; hence, it is easy to compare their relative strengths as oxidising or reducing agents.

Table 10.1.1 can be used to compare the relative abilities of metals to be oxidised. Consider magnesium and copper:

$$Mg^{2+} + 2e^- \rightarrow Mg \qquad E° = -2.36\ V$$

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E° = +0.34\ V$$

In the table, the Mg half-equation is above the Cu half-equation. It has a smaller $E°$ value. Therefore, Mg is a stronger reducing agent and more easily oxidised than Cu.

Similarly, we can compare the relative abilities of non-metals to be reduced. Consider fluorine and bromine:

$$Br_2 + 2e^- \rightarrow 2Br^- \qquad E° = +1.08\ V$$

$$F_2 + 2e^- \rightarrow 2F^- \qquad E° = +2.89\ V$$

The F_2 half-equation is lower in the table than the Br half-equation. It has a larger $E°$ value. F_2 is a stronger oxidising agent and is therefore more easily reduced than Br_2.

Some important generalisations can be made from the table:

- Metals 'prefer' to lose electrons to be oxidised. The most reactive metals, such as lithium, sodium, potassium and calcium, are towards the top of the table and have the lowest $E°$ values.
- Non-metals 'prefer' to gain electrons to be reduced. The most reactive non-metals, such as fluorine, chlorine and bromine, are towards the bottom of the table and have the highest $E°$ values.
- Any species on the left will be reduced by any species above it on the right.

In the standard electrode potentials table, the species on the left are the oxidising agents, whereas the species on the right act as the reducing agents. The strength of the oxidising agent increases as you go down the left-hand side of the table (due to the increase in $E°$), whereas the strength of the reducing agent increases as you go up the right-hand side of the table. (You could annotate the table of standard electrode potentials in the *Formula and Data* Book to show increasing strengths of oxidising and reducing agents. See the chapter summary.)

TABLE 10.1.1 Standard electrode potentials at 298 K

Oxidised species ⇌ 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

Weblink
Table of standard reduction potentials

WORKED EXAMPLE 10.1.1

In the reaction between potassium dichromate solution ($K_2Cr_2O_7$) and tin(II) nitrate solution ($Sn(NO_3)_2$), which one is the oxidising agent? Write the half-equation associated with each reactant.

ANSWER

1 Identify the reactants in the form that they appear in Table 10.1.1.

$K_2Cr_2O_7$ appears as $Cr_2O_7^{2-}$.

$Sn(NO_3)_2$ appears as Sn^{2+}.

2 Write the reduction half-equations as they appear in the table, along with their *E*° values.

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $\quad E° = +1.36$ V

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $\quad E° = -0.14$ V

3 Identify which species is reduced and which is oxidised.

The *E*° value for $Cr_2O_7^{2-}$ half-equation is higher than that of Sn^{2+}. This means that $Cr_2O_7^{2-}$ is reduced. Therefore, $K_2Cr_2O_7$ is the oxidising agent.

Sn must be oxidised, so it is the reducing agent:

4 Write the half-equations for each reactant as they occur in the cell.

Reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

Because Sn is being oxidised, the reduction half-equation given above must be reversed.

Oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$

LEARNING CHECK 10.1

DESCRIBING

1 Define:

- **a** standard electrode potential
- **b** hydrogen electrode
- **c** oxidising agent
- **d** reducing agent.

2 Identify the conditions under which standard electrode potentials are measured.

3 Explain why chemists have used a reference cell to develop the table of standard electrode potentials.

APPLYING

4 The *E*° value for the reduction of species A is –1.4 V, while the *E*° value for the reduction of species B is +0.70 V. **Justify** whether species A or B is more likely to be reduced.

5 a In the reaction between iron(II) nitrate solution ($Fe(NO_3)_2$) and potassium permanganate solution ($KMnO_4$), which one is the oxidising agent? **Construct** the half-equation associated with each reactant.

b In the reaction between nickel (Ni) and lead(II) nitrate solution ($Pb(NO_3)_2$), **identify** the reducing agent. **Construct** the half-equations associated with each reactant.

10.2 Calculating standard cell potentials

Table 10.1.1 can be used to identify the half-equations for the reactions in a galvanic cell. Remember, all the half-equations are written as reduction reactions:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E° = +0.34\ V$$

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad E° = -0.76\ V$$

However, there must always be an oxidation reaction and a reduction reaction. Hence, one of the reactions will be reversed. Galvanic cells involve spontaneous reactions; hence, they have an overall positive cell voltage. For this to occur, the strongest oxidising agent in the cell must have a higher $E°$ than the reducing agent. In the metal-displacement reactions in Chapter 8, you saw that zinc is more likely to be oxidised whereas copper ions are more likely to be reduced. This is supported by the $E°$ values for their half-equations. The reduction of zinc ions to zinc solid has a negative $E°$ value. The $E°$ value for the reduction of Cu^{2+} is larger than the $E°$ value for the reduction of Zn^{2+}, so Cu^{2+} will be reduced. Subsequently, the zinc metal will be oxidised.

For the overall galvanic cell the **standard cell potential** is calculated by using standard electrode potentials for each half-cell directly from the table of standard electrode potentials.

standard cell potential the difference in electrode potential between the two half-cells that make up a galvanic cell

$$E°_{cell} = E°_{reduction\ half\text{-}cell} - E°_{oxidation\ half\text{-}cell}$$

In the case of the $Zn(s)\,|\,Zn^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)$:

$$E°_{cell} = +0.34 - (-0.76) = +1.10\ V$$

To obtain the overall equation for the galvanic cell, the $Cu^{2+}(aq)\,|\,Cu(s)$ electrode half-equation is as written because this is the half-cell in which reduction is occurring. The half-equation for the $Zn(s)\,|\,Zn^{2+}(aq)$ electrode will be reversed because zinc solid oxidises to form zinc ions. Therefore, zinc will be oxidised at the anode and copper will be reduced at the cathode:

FORMULA AND DATA BOOK

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

$$\text{Cathode: } Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

Syllabus link
Chapter 8 outlines the steps to balance half and full redox reactions.

The overall reaction for this galvanic cell can be determined by adding the two equations together. Remember to check that the number of electrons in each half-cell is the same.

Since two electrons appear on each side of the equation, they can be cancelled out.

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

The equation becomes:

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

Using the $E°_{cell}$ value of +1.10 V calculated from Table 10.1.1.

Hence, the final reaction is written as:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq) \qquad E° = +1.10\ V$$

The positive sign indicates that the reaction occurs spontaneously. In this reaction, energy is transformed from chemical potential energy to electrical energy.

WORKED EXAMPLE 10.2.1

Determine the standard cell potential, $E°_{cell}$, for a galvanic cell made of aluminium and tin electrodes.

ANSWER

1 Identify the relevant equations from Table 10.1.1.

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $\quad E° = -0.14$ V

$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ $\quad E° = -1.68$ V

2 Determine the species being oxidised (anode) and the species being reduced (cathode).

The standard electrode potential for Al^{3+}, –1.68 V, is lower than that for Sn^{2+}, –0.14 V. Therefore, $Sn^{2+}(aq)$ is being reduced at the cathode while Al(s) is being oxidised at the anode.

3 Calculate the cell potential.

Use $E°_{cell} = E°_{reduction\ half\text{-}cell} - E°_{oxidation\ half\text{-}cell}$ to determine the cell potential.

$E°_{cell} = -0.14 - (-1.68) = +1.54$ V

$E°_{cell} = +1.54$ V

This type of calculation requires the subtraction of two standard electrode potentials. Given that two electrons are transferred in the Sn half-equation and three electrons are transferred in the Al half-equation, it might be tempting to multiply the $E°$ values to reflect that the same number of electrons are transferred. Remember that when multiplying the equations, $E°$ values are *not* multiplied.

Weblink
Calculating $E°$ using standard reduction potentials

Worksheet
Calculating half-cell potentials

KEY CONCEPT

When multiplying the equations, the $E°$ values are not multiplied. The $E°$ values indicate the difference in electrical potential energy between the two sides of the equation – this does not change when the quantities in the equation change.

LEARNING CHECK 10.2

DESCRIBING

1 Define:

- **a** standard cell potential
- **b** positive cell potential
- **c** negative cell potential.

2 Identify the three steps required to determine the standard cell potential for a galvanic cell.

3 Explain how you can predict if a spontaneous chemical reaction will occur in a galvanic cell.

4 Use Table 10.1.1 to **determine** the $E°$ value for each of the following half-equations.

- **a** $Mn(s) \rightarrow Mn^{2+}(aq) + 2e^-$
- **b** $Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$
- **c** $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

5 **Explain** why $E°$ values must not be multiplied when determining the standard cell potential for a galvanic cell.

APPLYING

6 The standard cell potential for a galvanic cell that included an iron electrode was found to be +1.95 V. Use Table 10.1.1 to **determine** the other electrode. **Identify** the cathode.

7 **a** **Determine** the standard cell potential using a chlorine gas | Pt electrode and an $Fe(NO_3)_2(aq)$, $Fe(NO_3)_3(aq)$ | Pt electrode.

b **Determine** the standard cell potential using a hydrogen gas | Pt electrode and a $AgNO_3(aq)$ | silver electrode.

10.3 The limitations associated with standard electrode potentials

In sections 10.1 and 10.2, we showed that the table of standard electrode potentials (Table 10.1.1) was useful when predicting whether a redox reaction would occur or not and the voltage produced by redox reactions in a galvanic cell. However, there are some limitations to this method.

Kinetic stability

Consider the oxidation of magnesium by water:

$$Mg(s) + 2H_2O(l) \rightarrow Mg^{2+}(aq) + H_2(g) + 2OH^-(aq)$$

Writing the oxidation and reduction half-equations gives:

$$\text{Oxidation: } Mg(s) \rightarrow Mg^{2+}(aq) + 2e^- \qquad E° = -(-2.36)\text{ V}$$

$$\text{Reduction: } 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83\text{ V}$$

Finding the difference between the half-cell potentials of the half-equations:

$$E°_{cell} = -0.83 - (-2.36) = +1.53\text{ V}$$

(Note: For the oxidation half-equation, the sign of $E°$ has been reversed because the equation was reversed.) A positive value for cell potential indicates that the reaction will occur. However, the reaction occurs so slowly that it is imperceptible. In *QCE Chemistry Units 1 & 2*, you learnt that reactions that have a high activation energy occur very slowly. In this case, the cell potential indicates that a reaction will occur but, in practice, there will be no perceptible reaction because of the high activation energy – this means the reactants are **kinetically stable**. However, you can speed up the rate of this reaction by reacting the magnesium with steam.

kinetically stable where the cell potential indicates that a reaction will occur but, in practice, there is no perceptible reaction because of the high activation energy

Non-standard conditions

The table of standard reduction potentials is only useful if reactions are conducted under standard conditions:

- Solutions must contain 1 mol L^{-1} of ions of the species being tested.
- Solutions must be at 25°C (298 K).
- Gases must be at 100 kPa and 25°C (298 K).

If the solutions are either very concentrated or very dilute, then the electrode potentials will not be the standard electrode potentials, and the magnitude or sign of the cell potential may be different from that predicted under standard conditions.

Consider the reaction between manganese dioxide and hydrochloric acid:

$$MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$$

Writing the oxidation and reduction half-equations gives:

$$\text{Oxidation: } 2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \qquad E° = -(+1.36)\,V$$

$$\text{Reduction: } MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l) \qquad E° = +1.22\,V$$

$$E°_{cell} = +1.22\,V - (+1.36) = -0.14\,V$$

A negative sign for cell potential indicates that the reaction will *not* occur. However, if we use concentrated hydrochloric acid, the high concentration of chloride ions means that more electrons can be transferred from these ions. This gives rise to a smaller negative value for the oxidation of chloride ions, resulting in a positive electrode potential. Under these conditions, the reaction *will* occur.

Other issues

If the oxidising and reducing species are very close to each other in the table, it can be difficult to predict whether a reaction will occur under standard conditions.

Consider the reaction between tin and lead(II) nitrate solution:

$$Sn(s) + Pb(NO_3)_2(aq) \rightarrow Sn(NO_3)_2(aq) + Pb(s)$$

$$\text{Oxidation: } Sn(s) \rightarrow Sn^{2+}(aq) + 2e^- \qquad E° = -(-0.14)\,V$$

$$\text{Reduction: } Pb^{2+}(aq) + 2e^- \rightarrow Pb(s) \qquad E° = -0.13\,V$$

$$E°_{cell} = -0.13 - (-0.14) = +0.01\,V$$

According to the cell potential, the reaction should occur but, because of the proximity of the half-equations in the table, the reaction will be very slow.

Some of the more reactive metals can react with oxygen in the air to form an impervious oxide layer. The most notable example is aluminium. When it is exposed to oxygen and water, the following reaction occurs:

$$4Al(s) + 3O_2(aq) + 6H_2O(l) \rightarrow 4Al(OH)_3(s)$$

$$\text{Oxidation: } Al(s) \rightarrow Al^{3+}(s) + 3e^- \qquad E° = -(-1.68)\,V$$

$$\text{Reduction: } O_2(aq) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \qquad E° = +0.40\,V$$

$$E°_{cell} = +0.40 - (-1.68) = +2.08\,V$$

This is a relatively high positive value, and so the reaction should occur. However, aluminium is widely used in the construction industry and is one of the major components in the manufacture of aircraft. The reaction above would prove catastrophic to both industries! Fortunately, because aluminium is such a reactive metal, it immediately forms a thin coating of aluminium oxide (Al_2O_3) when exposed to air. This coating prevents any further reactions.

LEARNING CHECK 10.3

DESCRIBING

1 **Define**:
   - **a** kinetic stability
   - **b** non-standard conditions.

2 Apart from kinetic stability of reactants and non-standard conditions, **identify** other situations that can cause problems when using the table of standard electrode potentials to predict whether a redox reaction will occur.

APPLYING

3 The reaction between potassium dichromate solution ($K_2Cr_2O_7(aq)$) and hydrochloric acid solution (HCl(aq)) has a cell potential of 0.00 V. **Deduce** conditions under which this reaction will have a positive cell potential and will occur.

10.4 Applying standard electrode potential

Standard electrode potentials have several applications:
- comparing the relative strengths of oxidising and reducing agents
- predicting whether a reaction will occur spontaneously or not
- calculating the standard cell potential of a galvanic cell.

Comparing the relative strengths of oxidising and reducing agents

All standard electrode potentials are measured relative to the hydrogen electrode, which has an $E°$ value of 0.00 V. The half-equation in the standard hydrogen electrode is represented by the equation:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

This reaction is reversible, the direction of the reaction depending on the half-cell it is attached to. Consider the hydrogen half-cell connected to a zinc half-cell:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \qquad E° = 0.00\ V$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E° = -0.76\ V$$

The value of −0.76 V for the zinc half-equation indicates that the zinc has a greater tendency to be oxidised than hydrogen. Alternatively, hydrogen ions have a greater tendency to be reduced. Therefore, the zinc is a stronger reducing agent (tends to lose its electrons) than hydrogen. Hydrogen ions are a stronger oxidising agent (tends to gain electrons) than zinc.

If the hydrogen half-cell is connected to a copper half-cell:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \qquad E° = 0.00\ V$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E° = +0.34\ V$$

In this case, the hydrogen half-cell is less positive than the copper half-cell. Therefore, hydrogen has a greater tendency to lose electrons than copper. Hydrogen gas is a stronger reducing agent than copper.

The table of standard electrode potentials is produced in this way – a wide variety of substances are connected to the standard hydrogen electrode and the cell potential measured. The magnitude and sign of the voltage produced indicates the ability of each substance to lose electrons relative to hydrogen.

Therefore, substances with a higher (more positive) $E°$ value than hydrogen are stronger oxidising agents. Those with a lower (less positive) $E°$ value than hydrogen are stronger reducing agents.

Predicting whether a reaction will occur spontaneously

If two half-cells are connected and a current flows, the electrode with the smaller $E°$ value, as shown in Table 10.1.1, will be oxidised and the electrode with the higher $E°$ value will be reduced.

If the zinc half-cell and the copper half-cell are connected:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E° = -0.76\ V$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E° = +0.34\ V$$

The lower value for the zinc half-cell indicates that Zn(s) is oxidised and the higher value for the copper half-cell shows $Cu^{2+}(aq)$ is reduced, giving an overall reaction represented by:

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

Worksheet
Predicting reactions using $E°$ values

According to the standard electrode potentials given above, this reaction occurs electrochemically.

Adding the half-equations and their associated $E°$ values gives the standard cell potential:

$$E°_{cell} = +0.34 - (-0.76) = +1.10\ V$$

The positive $E°_{cell}$ value means the reaction occurs spontaneously. Therefore, if a piece of zinc was added to a test tube containing a copper(II) nitrate solution, the above reaction would occur.

If a piece of copper was added to a zinc sulfate solution, the above equation would be reversed:

$$Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s) \qquad E° = -1.10\ V$$

The negative $E°_{cell}$ value means there would be no reaction. Therefore, a reaction with a *positive* $E°_{cell}$ value occurs *spontaneously*.

WORKED EXAMPLE 10.4.1

Predict whether nickel metal will displace manganese from a solution of manganese(II) nitrate solution according to the equation:

$Ni(s) + Mn(NO_3)_2(aq) \rightarrow Ni(NO_3)_2(aq) + Mn(s)$

ANSWER

1 Write the relevant half-equations from Table 10.1.1.

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \qquad E° = -0.24\ V$

$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s) \qquad E° = -1.18\ V$

2 From the equation in the question, decide which metal is being oxidised and which is being reduced.

According to the given equation, Ni(s) is being oxidised and $Mn^{2+}(aq)$ is being reduced.

3 Calculate $E°_{cell}$.

Using $E°_{cell} = E°_{red} - E°_{ox}$:

$E°_{cell} = -1.18 - (-0.24) = -0.94$ V

The negative $E°_{cell}$ value indicates that this reaction will *not* occur spontaneously.

The reaction will not occur as written.

Calculating the standard cell potential of a galvanic cell

Any spontaneous redox reaction can be used to produce a galvanic cell. The half-cell containing the oxidising agent has the more positive standard electrode potential. The half-cell containing the reducing agent has the more negative standard electrode potential.

Weblink
Determining spontaneity of a reaction using E_{cell} values

WORKED EXAMPLE 10.4.2

Calculate the cell potential for the galvanic cell represented by the equation:
$Fe(s) + Sn(NO_3)_2(aq) \rightarrow Fe(NO_3)_2(aq) + Sn(s)$

ANSWER

1 Write the relevant half-equations from Table 10.1.1.

$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $\quad E° = -0.44$ V

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $\quad E° = -0.14$ V

2 From the equation in the question, decide which species is being oxidised and which is being reduced.

In the equation given, $Sn^{2+}(aq)$ is being reduced and Fe(s) is being oxidised.

Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

Reduction: $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

3 Calculate $E°_{cell}$.

Using $E°_{cell} = E°_{red} - E°_{ox}$:

$E°_{cell} = -0.14 - (-0.44) = +0.30$ V

$E°_{cell} = +0.30$ V

WORKED EXAMPLE 10.4.3

Calculate the cell potential for the galvanic cell represented by the equation:
$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

ANSWER

1 Write the relevant half-equations from Table 10.1.1.

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(s)$ $\quad E° = +0.77$ V

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $\quad E° = +1.36$ V

2 From the equation in the question, decide which substance is being oxidised and which is being reduced.

According to the equation given, $Cr_2O_7^{2-}(aq)$ is being reduced and $Fe^{2+}(aq)$ is being oxidised.

Oxidation: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

Reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

3 Calculate $E°_{cell}$.

Using $E°_{cell} = E°_{red} - E°_{ox}$:

$E°_{cell} = +1.36 - (+0.77) = +0.59$ V

$E°_{cell} = +0.59$ V

Weblink
Using reduction potentials

LEARNING CHECK 10.4

DESCRIBING

1 **Explain** why an oxidising agent has a higher standard electrode potential than the hydrogen electrode.

2 List the following elements in order of decreasing reducing strength:

Fe, Br_2, Ag, O_2, Cu, Cl_2

APPLYING

3 **Predict** whether a spontaneous reaction will occur between lead and acidified potassium permanganate solution, according to the equation:

$5Pb(s) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 5Pb^{2+}(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$

4 **Determine** if potassium iodide crystals will decolourise bromine water.

$2I^-(aq) + Br_2(aq) \rightarrow 2Br^-(aq) + I_2(aq)$

5 **a** **Calculate** the cell potential for the galvanic cell represented by the shorthand notation:

$Pt \mid Cl_2(g) \mid Cl^-(aq) \parallel Ag^+(aq) \mid Ag(s)$

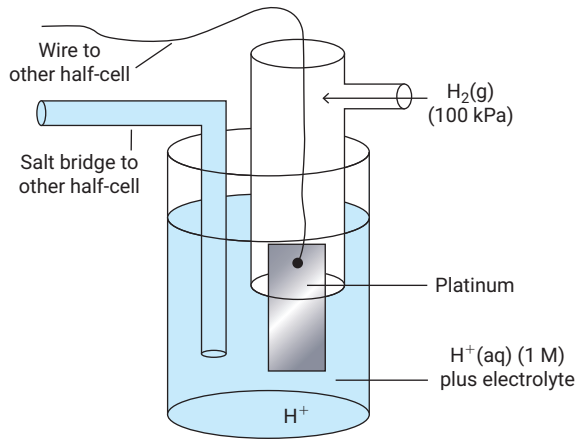
b **Explain** if this cell will operate.

6 A half-cell consists of a piece of platinum dipping into a mixture of copper(I) nitrate and copper(II) nitrate solutions. **Deduce** what half-cell it needs to be connected to produce a galvanic cell with $E° = 1.24$ V.

CHAPTER SUMMARY

Standard hydrogen electrode

- A standard hydrogen electrode is assigned an electrode potential of zero ($E° = 0.00$ V) It is used as the reference half-cell for determining the $E°$ value of all other half-cells.



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Standard electrode potential

- The standard electrode potential ($E°$) is the potential of that electrode (measured in volts) in its standard state relative to the standard hydrogen electrode.
- Standard electrode potentials can be used to:
  - compare the relative strength of oxidising and reduction agents
  - predict if a reaction will occur spontaneously
  - calculate standard cell potential using $E°_{\text{cell}} = E°_{\text{reduction half-cell}} - E°_{\text{oxidation half-cell}}$.

Limitations

- Limitations of applying standard electrode potentials include:
  - not considering kinetic stability of reactants
  - using non-standard conditions
  - reactions that impede electrode availability.

Standard electrode potentials at 298 K

Oxidised species ⇌ 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

Increasing strength of oxidising agent. These are reduced at the cathode.

Increasing strength of reducing agent. These are oxidised at the anode.

CHAPTER EXAM

MULTIPLE CHOICE

1. Which one of the following is *not* used as part of a standard hydrogen electrode?

A H^+ ions
B Pt
C OH^- ions
D Hydrogen gas

2. Which one of the following is the strongest oxidising agent?

A Br_2
B Cu^{2+}
C Ag^+
D Cu

3. For the galvanic cell composed of the Sn^{2+}, Sn and Cu^+, Cu^{2+} half-cells, which one of the following identifies the anode and gives the correct cell potential?

A Sn, +0.30 V
B Cu, +0.02 V
C Sn, −0.30 V
D Cu, +0.30 V

4. Which one of the following represents a non-spontaneous redox reaction?

A $Pb(s) + 2AgNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + 2Ag(s)$
B $2Cl^-(aq) + Cu^{2+}(aq) \rightarrow Cl_2(g) + Cu(s)$
C $6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$
D $6I^-(aq) + 2MnO_4^- + 4H_2O(l) \rightarrow 3I_2(aq) + 2MnO_2(aq) + 8OH^-(aq)$

5. If a value of –1.0 V was assigned to the standard hydrogen half-cell instead of the currently accepted value of zero, the $E°$ of a particular galvanic cell would be:

A unchanged.
B increased by 1.0 V.
C increased by 2.0 V.
D decreased by 1.0 V.

6. The $E°$ of a new dry galvanic cell is normally 1.5 V. If, in a particular cell, the species involved in the cell reaction are at equilibrium what would the $E°$ of the cell be?

A More than 1.5 V
B 1.5 V
C Between 1.5 V and 0 V
D 0 V

7. A galvanic cell has an $E°$ value of +1.48 V for the reaction:

$2X(s) + 2H_2O(l) + O_2(g) \rightleftharpoons 2X(OH)_2(aq)$

What is the standard reduction potential for the half-equation below?

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

A –1.08 V
B –0.68 V
C +0.68 V
D +1.88 V

8. The $E°$ of a cell composed of a Sn^{4+}, Sn^{2+} half-cell and a Cl_2, Cl^- standard half-cell is 1.25 V. A cell composed of an I_2, I^- half-cell and a Cl_2, Cl^- standard half-cell has an $E°$ of 0.78 V. In each cell, the Cl_2 acts as the oxidising agent.

What would be the $E°$ of a cell formed from the I_2, I^- half-cell and the Sn^{4+}, Sn^{2+} half-cell?

A 0.47 V
B 2.03 V
C 0.16 V
D Cannot be determined from information provided

 SCSA 2020 MCQ Q19

9. The following half-equations show some predicted standard reduction potentials for seaborgium (Sg) oxides:

$2SgO_3(s) + 2H^+(aq) + 2e^- \rightarrow Sg_2O_5(s) + H_2O(l)$ $\quad E° = -0.046$ V

$Sg_2O_5(s) + 2H^+(aq) + 2e^- \rightarrow 2SgO_2(s) + H_2O(l)$ $\quad E° = +0.11$ V

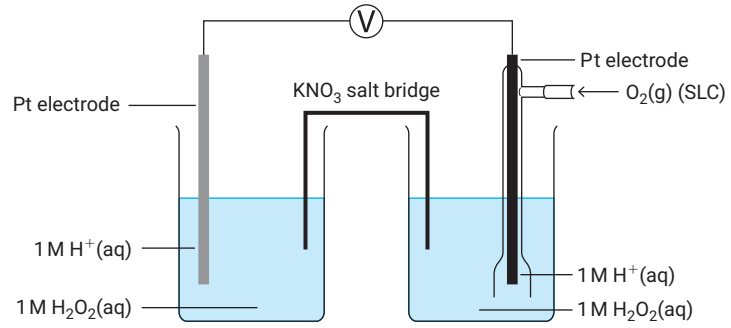
$SgO_2(s) + 4H^+(aq) + e^- \rightarrow Sg^{3+}(aq) + 2H_2O(l)$ $\quad E° = -1.34$ V

The strongest reducing agent is:

A SgO_3
B Sg_2O_5
C SgO_2
D Sg^{3+}

 Modified from VCAA 2013 MCQ Q25

10. A student constructs the following galvanic cell.



Given the half-equation:

$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$ $\quad E° = +1.78$ V

The student predicts that the following overall reaction will occur:

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

However, no reaction is observed.

This is most likely because:

A the difference between the $E°$ values is too small for a reaction to occur.
B hydrogen peroxide will oxidise water in preference to itself.
C the student did not construct standard half-cells.
D the rate of the reaction is extremely slow.

SHORT RESPONSE

11. Use the table of standard electrode potentials (Table 10.1.1) to **determine** which of the following reactions will occur spontaneously:

a $2Ag(s) + Zn(NO_3)_2(aq) \rightarrow 2AgNO_3(aq) + Zn(s)$

b $Pb(s) + SO_4^{2-}(aq) + 4H^+(aq) \rightarrow Pb^{2+}(aq) + SO_2(aq) + 2H_2O(l)$

c $10I^-(aq) + 16H^+(aq) + 2MnO_4^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5I_2(s)$

12. The purple colour of a solution of $KMnO_4$ is due to the presence of MnO_4^- ion. When MnO_4^- ions are reduced, the purple colour disappears as colourless Mn^{2+} ions are formed. **Justify**, using reduction potentials, which solution(s) to choose to decolourise the solution.

a $FeC1_2$ solution, which will provide Fe^{2+}

b $FeC1_3$ solution, which will provide Fe^{3+}

c KI solution, which will provide I^-

d $C1_2$ water, which will provide $C1_2$

CROSS-CHAPTER QUESTION

13. X is a non-metallic element that does not appear as X in the table of standard reduction potentials. A galvanic cell is constructed. One half-cell consisting of a piece of platinum wire dipping into a solution containing both X_2 and X^- is connected by a salt bridge to another half-cell consisting of a piece of silver wire dipping into a 1 mol L^{-1} $AgNO_3$ solution. The X_2/X^- half-cell is positive.

a Draw a labelled diagram of the galvanic cell, identifying the:

- anode
- cathode
- direction of electron flow
- direction of ion flow.

b **Construct** balanced half-equations for the oxidation and reduction reactions and the equation for the overall reaction occurring in this cell.

c The $E°$ of the cell is 0.28 V.

i **Calculate** the $E°$ of the X_2/X^- electrode.

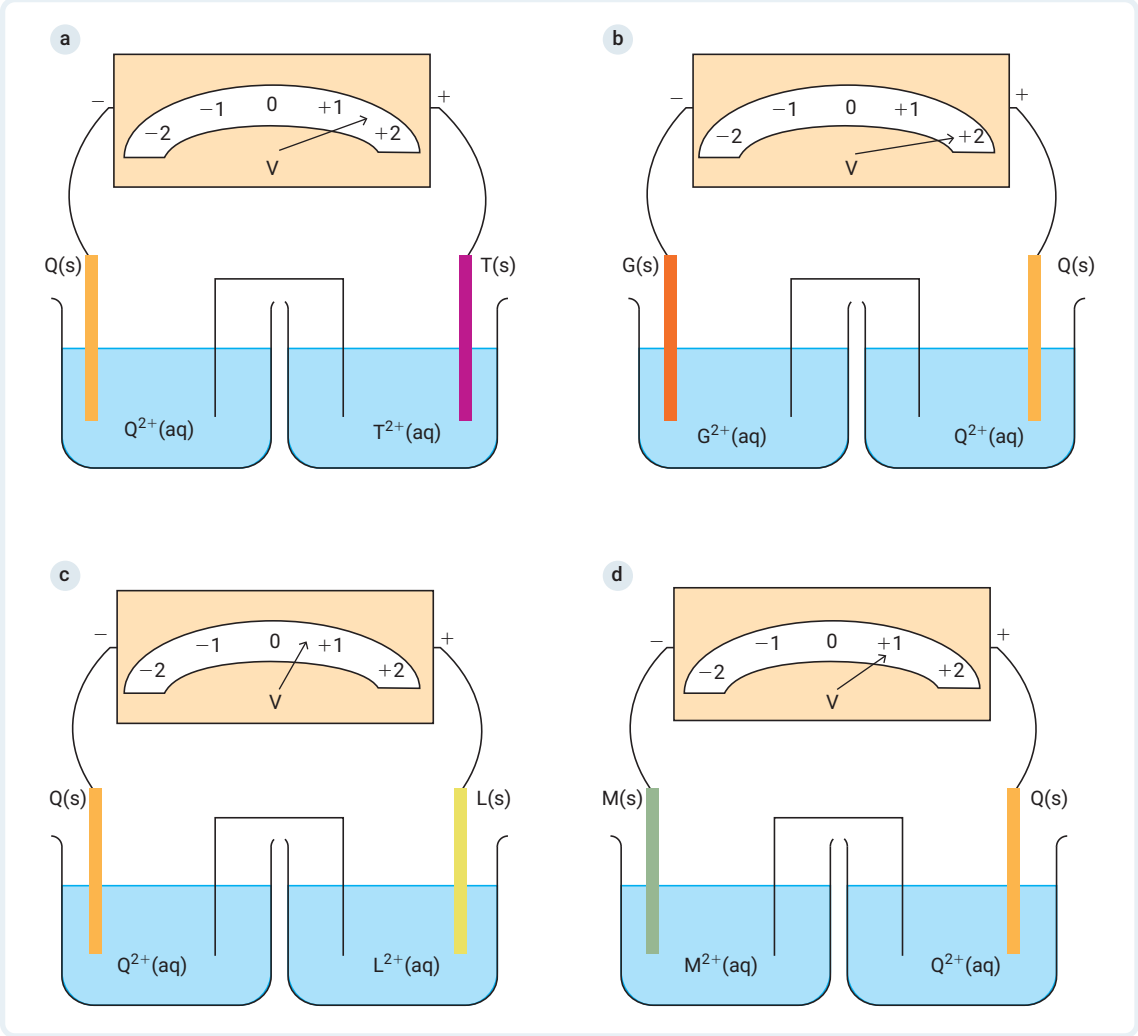
ii **Identify** X_2.

d After operating for 10 min, the mass of the silver electrode decreases by 1.09 g. **Calculate** the change in mass of X_2 during this time.

DATA ANALYSIS

14. Analyse data

An experiment was designed to compare the relative electrode potentials of five unknown metals, T, Q, M, G and L. For each experiment, a galvanic cell was constructed using a pair of metals and the voltage measured. The experimental set-up is shown below.



Use this information to **construct** a table of electrode potentials, choosing an appropriate half-cell as the reference half-cell.

15. Analyse data

A scientist carried out several experiments in which strips of unknown metals were dipped into solutions of the unknown metal nitrates.

The standard electrode potentials of the unknown metals are given in the following table.

Oxidised form	Reduced form	$E°$ (V)
X^{2+}	X	–2.11
Q^{2+}	Q	–1.14
T^{2+}	T	+0.12
R^{2+}	R	+1.17
M^{2+}	M	–2.19
G^{2+}	G	–1.62

Use this table of standard electrode potentials to **predict** whether each combination will react spontaneously.

Indicate your decision in each case with a ✓ or a ×.

Copy the following table below in your workbook. For each ✓, **construct** the balanced equation and **calculate** the cell potential.

	$X(NO_3)_2(aq)$	$Q(NO_3)_2(aq)$	$T(NO_3)_2(aq)$	$R(NO_3)_2(aq)$	$M(NO_3)_2(aq)$	$G(NO_3)_2(aq)$
X						
Q						
T						
R						
M						
G						

CHAPTER 11

Electrolytic cells

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SYLLABUS DOT POINTS

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 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 concentration sodium chloride(aq) and copper sulfate(aq).
- Describe that 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 INQUIRY

- Investigate:
  - factors that affect electrolysis
  - electroplating using an electrolytic cell.

Introduction

During electrolysis, electrical energy is converted to chemical potential energy. Since electrical energy is used to produce a chemical reaction, the reaction is not spontaneous. Electrolysis is used to force chemical reactions to occur. As discussed, batteries are galvanic cells; they convert chemical energy to electrical energy. But some batteries are rechargeable – electrical energy helps us to use them again.

ASSUMED KNOWLEDGE

- ✓ Galvanic cells consist of two half-cells in which reactions occur spontaneously to generate an electric current.
- ✓ Galvanic cells have a basic structure that includes electrodes, half-cells, a salt bridge and an external wire.
- ✓ Electrochemical processes in galvanic cells include site of oxidation and reduction, direction of electron flow and direction of ion flow.
- ✓ A table of standard electrode potentials can be used to:
  - predict whether reactions will occur spontaneously
  - determine relative strength of oxidising and reducing agents
  - determine preferred reaction
  - calculate cell potential.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ identify that electrolytic cells use electrical energy to produce a chemical reaction
- ✓ identify the essential components of an electrolytic cell
- ✓ construct a labelled diagram of an electrolytic cell showing anode, cathode, electrolyte, positive and negative electrodes, direction of ion and electron flow
- ✓ discriminate between galvanic and electrolytic cells
- ✓ determine the half-reactions that occur at the anode and the cathode
- ✓ state the factors that affect the products of an electrolytic cell
- ✓ determine the products of electrolysis of a molten salt
- ✓ apply $E°$ values to determine the probable products of electrolysis an aqueous salt solution
- ✓ explain how concentration affects the products of the electrolysis of an aqueous salt solution
- ✓ describe the electrolytic processes of metal electroplating and the purification of copper
- ✓ state Faraday's first law of electrolysis
- ✓ recall the value and meaning of the Faraday constant
- ✓ apply the formula $q = I \times t$ and $q = n(e^-) \times F$ to calculate the number of moles of electrons, current, time, mass or volume of substance related to the products of electrolysis.

11.1 Introduction to electrolytic cells

Dr_cloudberry/Shutterstock.com

FIGURE 11.1.1 A copper-plated leaf and coffee bean, produced by electroplating

As you learnt in Chapter 9 there are two types of electrochemical cells: galvanic cells and electrolytic cells. Chapter 9 focused on galvanic (voltaic) cells. This chapter will focus on electrolytic cells.

An electrolytic cell is a type of electrochemical cell that uses electricity to produce a chemical reaction that would not occur spontaneously. Electrolytic cells are widely used in small-scale and industrial situations. Electroplating is also used in the decorative arts **(Figure 11.1.1)**.

In the mining industry, electrolysis is used to both extract metals from their ores and purify the extracted metal, particularly copper, zinc and aluminium. Metal plating, the production of chemicals such as chlorine gas, and the electrolysis of water to produce hydrogen and oxygen are also widely used electrolytic processes. Another use of electrolysis is to

restore metal objects recovered from shipwrecks. Rechargeable batteries are also recharged using an electrolytic process.

The electrode processes

In its simplest form, an electrolytic cell consists of two inert electrodes, usually carbon or platinum, connected to a power source and dipped into a molten salt such as lithium bromide, as shown in **Figure 11.1.2**.

Lithium bromide is a stable salt. Its decomposition, even in its molten state, is a non-spontaneous reaction:

$$2LiBr(l) \rightarrow 2Li(l) + Br_2(g)$$

The half-equations for this reaction are:

Reduction: $Li^+(l) + e^- \rightarrow Li(l)$

Oxidation: $2Br^-(l) \rightarrow Br_2(g) + 2e^-$

The Li^+ and Br^- ions are far too stable to spontaneously react in this way. However, if an electric current is passed through molten lithium bromide in the apparatus shown in Figure 11.1.2, the half-equations shown above are forced to occur.

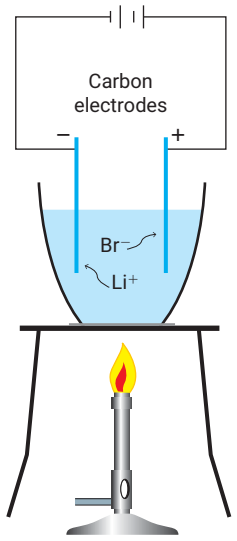


FIGURE 11.1.2 The apparatus used for the electrolysis of molten lithium bromide

In this process, electrons are provided by an external power source such as a powerpack or a battery. This is represented in Figure 11.1.2 by $|\,||$, where the shorter line represents the negative (–) terminal and the longer line the positive (+) terminal. The charge on an electrode corresponds to the terminal to which it is connected.

The electrons flow from the negative terminal of the power source, through the external circuit to a carbon electrode, making it negatively charged.

The positively charged lithium ions in the molten electrolyte move towards the negative electrode, where they pick up an electron:

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

This is *reduction*, so this electrode is the *cathode*.

As the Li^+ ions are reduced to Li(l), more are attracted to the negative cathode, producing a flow of positive ions (cations) through the electrolyte towards the cathode.

The lithium metal produced melts because of the high temperature of the molten salt and forms a pool on the surface of the electrolyte around the cathode.

Completing the circuit is the other carbon electrode, which is connected to the positive terminal of the external power source, so is positively charged. Negatively charged bromide ions move towards this electrode. When they contact the electrode, they release their extra electrons:

$$2Br^-(l) \rightarrow Br_2(g) + 2e^-$$

This is *oxidation*, so this electrode is the *anode*.

As the Br^- ions are oxidised, more are attracted to the anode, producing a flow of negative ions (anions) through the electrolyte towards the anode. The molecular bromine that is produced vaporises because of the high temperature of the molten salt and dissipates away.

Figure 11.1.3 shows the processes occurring in the electrolytic cell.

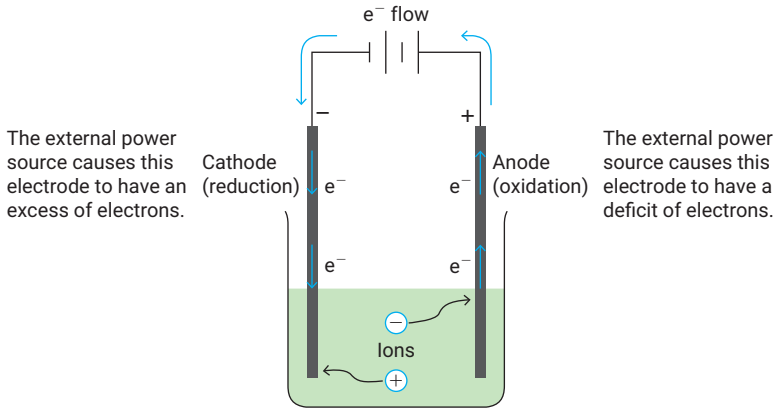


FIGURE 11.1.3 The processes occurring in the electrolytic cell

The anode and cathode

The anode is still defined as the electrode at which oxidation occurs, and the cathode is still defined as the electrode at which reduction occurs (**an ox** and **red cat**). This is the same as for galvanic cells.

However, in an electrolytic cell, the polarity of the electrodes is determined by the external power source. The electrode that is connected to the negative terminal of the power source is negatively charged and the electrode that is attached to the positive terminal of the power source is positively charged. This is opposite to galvanic cells.

In the electrolyte cell, the negative ions (anions) are attracted to positive electrode (anode) and lose electrons, so are oxidised (OIL). The positive ions (cations) move towards the negative electrode (cathode) and gain electrons, so are reduced (RIG). This is the same as in galvanic cells.

The products of the reaction

The net electrolytic cell reaction is:

$$2Li^+(l) + 2Br^-(l) \rightarrow 2Li(l) + Br_2(g)$$

It is important to note that the electrolytic cell is a single cell whereas a galvanic cell consists of two half-cells. This is because the Li^+ ions and the Br^- ions do not react with each other so do not need to be kept apart. However, the products, Li(l) and $Br_2(g)$, do react together quite violently so it is important they are kept apart.

In large commercial electrolytic cells, a porous separator is often placed between the two electrodes to keep the products apart. If a gas is produced, this is immediately drawn off by a gas intake system.

Galvanic and electrolytic cells – a comparison

The fundamental difference between galvanic and electrolytic cells is the spontaneity of their cell reactions. This comparison is shown in **Table 11.1.1**. Cell diagrams showing direction of electron and ion flow are shown in **Figure 11.1.4**.

TABLE 11.1.1 Comparing galvanic and electrolytic cells

	Galvanic cells	Electrolytic cells
Reaction type	Spontaneous	Non-spontaneous
Reactions at each electrode	Oxidation at anode, reduction at cathode	Oxidation at anode, reduction at cathode
Polarity of each electrode	Anode negatively charged; cathode positively charged	Anode positively charged; cathode negatively charged
Electron flow	Electrons flow from anode to cathode	Electrons flow from anode to cathode
Ion flow	Positive ions flow to cathode half-cell	Positive ions flow towards cathode

Some of this can be confusing, but it can help to remember that, in both kinds of cell, *oxidation* occurs at the *anode* and *reduction* occurs at the *cathode*.

Weblink
Electrolytic cells

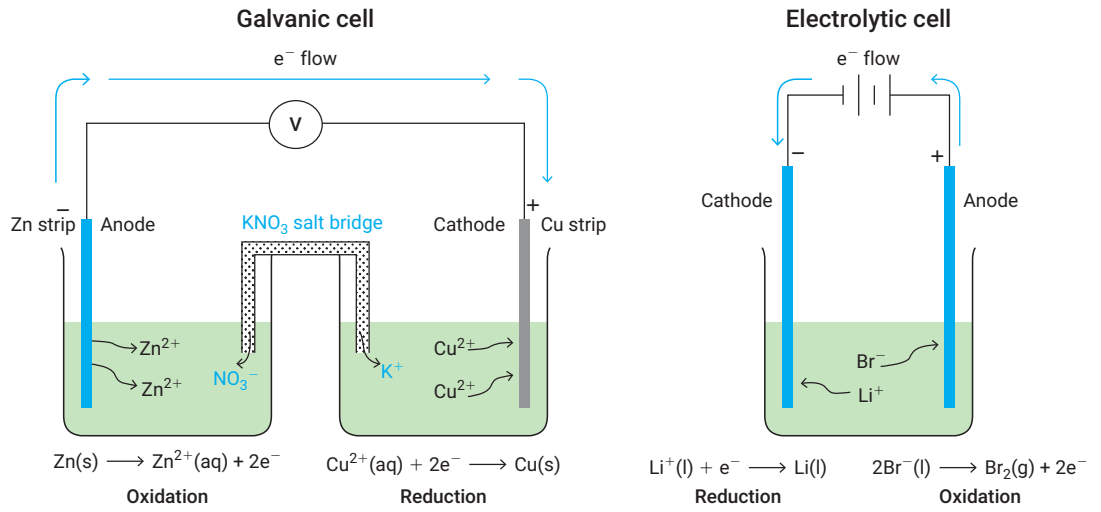


FIGURE 11.1.4 The similarities and differences between galvanic and electrolytic cells

LEARNING CHECK 11.1

DESCRIBING

1 **Explain** why the anode and cathode in an electrolytic cell have different polarities from those in a galvanic cell.

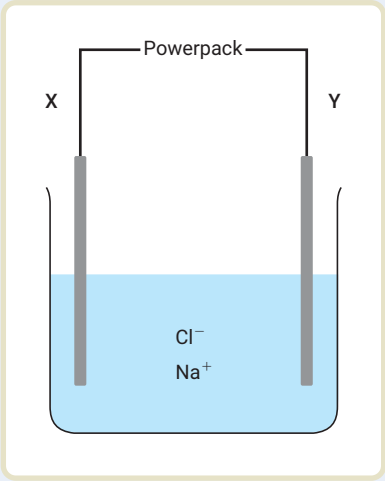
2 **Explain** why an electrolytic cell does not need two half-cells.

3 Copy and complete the following table.

	Cell reaction	Anode	Cathode
Galvanic	Spontaneous		
Electrolytic	Non-spontaneous		

APPLYING

4 The following diagram shows the electrolysis of molten sodium chloride.



It was observed that when an electric current was applied to the molten sodium chloride, a pale green, noxious gas was produced at electrode Y.

a From this information, **identify** and label the:

- **i** anode
- **ii** cathode
- **iii** direction of electron flow
- **iv** direction of positive ion flow
- **v** charges of the electrodes.

b Write the oxidation and reduction half-equations.

11.2 Predicting and explaining products

When carrying out electrolysis of a molten salt or aqueous salt solution, the three factors that affect the products that are formed are the:

- nature of the electrolyte
- concentration of the ions present
- nature of the electrodes.

These factors will be examined for the electrolysis of a molten salt and an aqueous salt solution.

Electrolysis of molten salts

Molten salts are the liquid form of ionic compounds, such as magnesium chloride. When carrying out the electrolysis of molten binary salts (those that contain the ions of just two elements), the electrolyte is the ions of the salt. As this is a pure liquid, concentration does not affect what products are formed.

Generally, inert electrodes are used because this ensures the products are simply the elements produced by the ions in the molten salt. This was discussed in section 11.1 where the electrolysis of molten lithium bromide was shown to produce lithium metal and bromine gas. Similarly, molten sodium chloride produces sodium metal and chlorine gas, molten aluminium oxide produces aluminium metal and oxygen gas, and so on.

If non-inert electrodes were used, it would be important to consult a table of standard electrode potentials to ensure the chosen electrode substance would not react with either of the ions of the molten salt.

Electrolysis of molten salts is the method used industrially for extracting magnesium and sodium from their salts **(Figure 11.2.1)**.

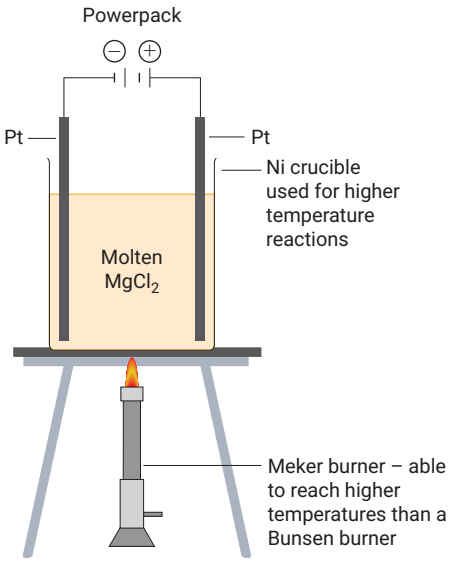


FIGURE 11.2.1 The set-up for electrolysis of molten magnesium chloride

Molten magnesium chloride ($MgCl_2$) contains Mg^{2+} and Cl^- ions, so these are the reactants for electrolysis. Remember that oxidation occurs at the anode and reduction occurs at the cathode.

FORMULA AND DATA BOOK

We can use Table 10.1.1 (p. 227) or the table in the *Formula and Data Book* to find the $E°$ values for these half-equations to help determine which species is being oxidised and reduced.

$$Mg^{2+}(l) + 2e^- \rightarrow Mg(l) \qquad E° = -2.36\,V$$

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(l) \qquad E° = +1.36\,V$$

Although Mg^{2+} has a lower $E°$, it is the only oxidising agent in the cell. As a result, it will be reduced (with the help of an external power supply). Similarly, since Cl^- is the only reducing agent present, it will be oxidised (again with the help of an external power supply). Therefore, the reactions occurring at each electrode are:

$$\text{Anode:} \quad 2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

$$\text{Cathode:} \quad Mg^{2+}(l) + 2e^- \rightarrow Mg(l)$$

Since the electrons are balanced, the half-equations can be combined. Using the formula to calculate the cell potential:

$$E°_{cell} = E°_{reduction\ half\text{-}cell} - E°_{oxidation\ half\text{-}cell}$$

$$E°_{cell} = -2.36 - (+1.36V) = -3.72\,V$$

The overall reaction is:

$$Mg^{2+}(l) + 2Cl^-(l) \rightarrow Cl_2(g) + Mg(l) \qquad E° = -3.72\,V$$

The negative sign for the voltage indicates that this is not a spontaneous reaction. This is the approximate voltage that must be applied to the system; that is, it must be provided by a battery or powerpack. Since the species present are not under standard conditions, this voltage is a guide only.

Electrolysis of aqueous salt solutions

Aqueous salt solutions contain ionic salts dissolved in water. Although electrolysis of aqueous solutions is easier to conduct in the laboratory, the chemistry is a little more complicated because as well as the ions in the electrolyte, water is also present, and it could be electrolysed in place of either of the ions. There are competing reactions occurring and you need to be able to determine which is the main reaction taking place at each electrode.

Again, the electrode reactions depend on the:

- nature of the electrolyte
- concentration of the electrolyte
- nature of the electrodes.

Nature of the electrolyte

The electrolyte is the solution that is used in the electrolytic cell. Different solutions have different ions, which have different $E°$ values for their half-equations. The water present could also be oxidised at the anode and/or reduced at the cathode. We will again use Table 10.1.1 to assist with understanding which reactions will occur. To ensure that we are only investigating the effect of the nature of the electrolyte, the other factors must be kept constant. Therefore, the concentration of solution for all examples will be kept constant and the electrodes will be kept constant. Graphite electrodes will be used for each of these examples. Graphite electrodes are used in school experiments because they conduct electricity, they do not take part in the reaction (they are inert) and they are relatively cheap.

Consider the electrolysis of an aqueous solution of copper(II) chloride ($CuCl_2$) as shown in **Figure 11.2.2**.

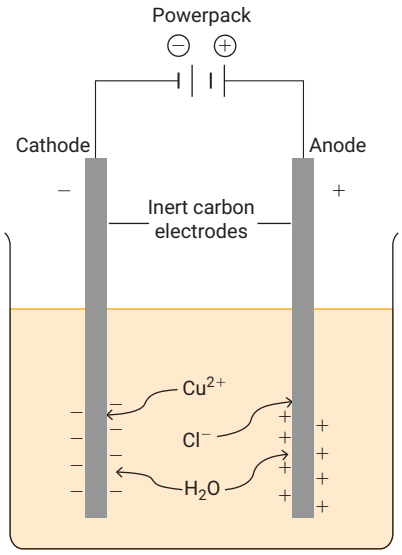


FIGURE 11.2.2 The set-up for the electrolysis of copper(II) chloride solution

The ions $Cu^{2+}(aq)$ and $Cl^-(aq)$ are present, since it is a solution. The half-equations for these ions can be determined from Table 10.1.1.

Oxidation: $2Cl^-(aq) \rightarrow Cl_2(l) + 2e^-$ $\quad E° = -(+1.36)\,V$

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

However, as stated earlier, water is also present. When water is electrolysed, it decomposes to form hydrogen gas and oxygen gas. The half-equations for the oxidation and reduction of water to form oxygen and hydrogen gases, respectively, can be determined from Table 10.1.1.

Oxidation: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad E° = -(+1.23)\,V$

Reduction: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\quad E° = -0.83\,V$

Close inspection of Table 10.1.1 shows that water can act as both an oxidising ($E° = -0.83\,V$) and reducing agent ($E° = +1.23\,V$).

Therefore, in this cell there are two possible oxidation reactions at the anode:

$2Cl^-(aq) \rightarrow Cl_2(l) + 2e^-$ $\quad E° = -1.36\,V$

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad E° = -1.23\,V$

There are also two possible reduction reactions at the cathode:

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

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\quad E° = -0.83\,V$

- At the anode, the preferred reaction is the oxidation of water because the voltage for this reaction is less negative than that of the oxidation of chloride ions.
- At the cathode, the preferred reaction is the reduction of copper ions because the voltage for this reaction is greater than that of the reduction of water.

For the electrolytic cell for the aqueous solution of copper(II) chloride where graphite electrodes are used, the half-equations for the reactions occurring are:

Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad E° = -1.23\,V$

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

Weblink
Electrolysis of solutions

KEY CONCEPT

The reaction that is more likely to occur is the one that requires the least input of energy; that is, the least negative voltage.

The electrons are balanced by multiplying the reduction equation by 2, and then the equations and $E°$ values can be used to determine the overall reaction and cell voltage for this electrolytic cell. So the overall reaction is:

$$2Cu^{2+}(aq) + 2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 2Cu(s) \qquad E° = -0.89\,V$$

Therefore, more than 0.89 V must be supplied for this reaction to occur.

Consider a different example for a solution of copper(II) bromide ($CuBr_2$). The ions $Cu^{2+}(aq)$ and $Br^-(aq)$ are present since it is a solution. Water is also present. Therefore, the possible reactions for both the anode and cathode reactions are determined.

- Oxidation (at the anode):

$$2Br^-(aq) \rightarrow Br_2(g) + 2e^- \qquad E° = -1.08\,V$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E° = -1.23\,V$$

- Reduction (at the cathode):

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

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83\,V$$

The preferred reactions are those with the less negative voltage at each electrode. Bromide ions will be oxidised at the anode and copper will be reduced at the cathode.

$$\text{Anode:} \quad 2Br^-(aq) \rightarrow Br_2(g) + 2e^- \qquad E° = -1.08\,V$$

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

The electrons are balanced, and then the equations and $E°$ values can be used to determine the overall reaction and cell voltage for this electrolytic cell. So the overall reaction is:

$$Cu^{2+}(aq) + 2Br^-(aq) \rightarrow Br_2(l) + Cu(s) \qquad E° = -0.74\,V$$

Polyatomic anions, such as sulfate (SO_4^{2-}), nitrate (NO_3^-) and phosphate (PO_4^{3-}), are much more stable than monatomic anions. Hence, much larger voltages are required for them to be oxidised. Thus, when polyatomic anions are present in solution, the water will always be oxidised preferentially to the polyatomic anions, because it has a less negative voltage.

So, the overall reaction for the electrolysis of a copper(II) sulfate solution ($CuSO_4$) would be the same as the equation for the electrolysis of copper(II) chloride:

$$2Cu^{2+}(aq) + 2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 2Cu(s) \qquad E° = -0.89\,V$$

Concentration of the electrolyte

As mentioned, in the electrolysis of aqueous salt solutions, there are competing reactions at both the anode and the cathode. The reaction at each electrode that has the less negative voltage – the reaction where the least voltage must be applied – is the favoured reaction. This is almost always true. However, where the $E°$ values for the competing reactions are very similar, we may need to consider the concentration of the solution.

Consider the example of sodium chloride (NaCl). At the cathode, there is a large difference between the $E°$ values for the reduction of sodium ions and the reduction of water.

$$Na^+(aq) + e^- \rightarrow Na(s) \qquad E° = -2.71\,V$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83\,V$$

This indicates that the reduction of water is much more likely to occur than the reduction of sodium ions, which are much more stable. Hence, the concentration of the solution does not affect the preferred reaction for this electrode.

However, at the anode, there is only a small difference between the $E°$ values for the oxidation of chloride ($E° = -1.36\,V$) and the oxidation of water ($E° = -1.23\,V$). This indicates that there is little difference in the likelihood of each of these reactions occurring. Hence, the concentration of the solution does affect the preferred reaction for this electrode.

In a more concentrated solution (greater than about $2\,mol\,L^{-1}$), there are more chloride ions in the same volume of solution, so it is more likely that the chloride ions will be oxidised. In a more dilute solution (less than about $0.1\,mol\,L^{-1}$), there are fewer chloride ions in the same volume of solution, and it is less likely that the chloride ions will be oxidised. The water will be oxidised in this case. In solutions with concentrations between these two values, both reactions may occur at the anode.

So, in more *dilute* chloride solutions, the anode reaction will be:

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

whereas in more *concentrated* chloride solutions, the anode reaction will be:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

This is the most common example of where the concentration of the solution can affect the preferred reaction occurring at one of the electrodes.

Overall reactions would be:

Concentrated solution **(Figure 11.2.3a)**:

$$2Cl^-(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2OH^-(aq)$$

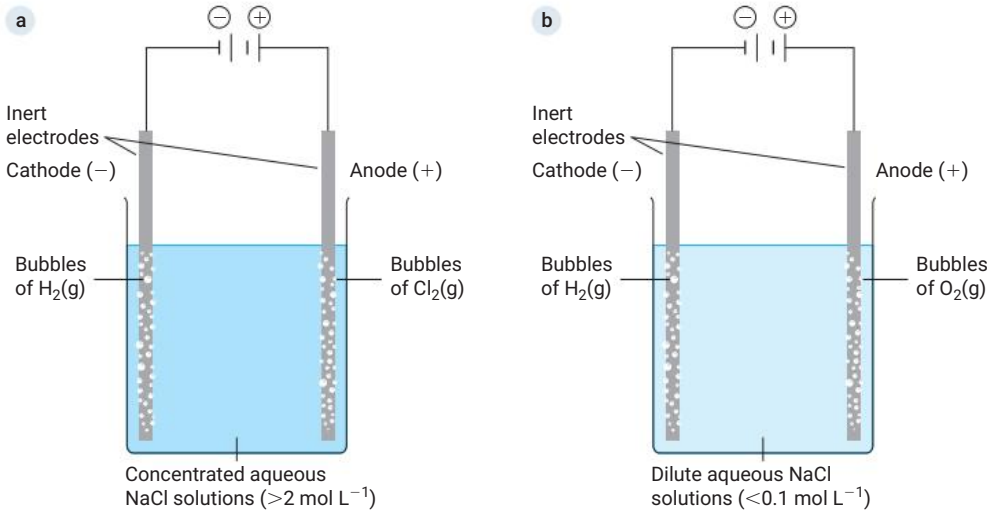
Adding the spectator $Na^+(aq)$ ions, the equation would be:

$$2NaCl(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2NaOH(aq)$$

The electrolysis of a concentrated sodium chloride solution is used industrially to produce sodium hydroxide, and chlorine gas with hydrogen gas also being a useful product.

Dilute solution **(Figure 11.2.3b)**:

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



Source: Smith, D. R. et al (2006). *Chemistry in Use Book 2*.

FIGURE 11.2.3 Electrolysis of sodium chloride of different concentrations: (a) concentrated NaCl(aq) and (b) dilute NaCl(aq)

Worksheet
Electrolytic cells

Another, less common, example is where zinc solutions are used.

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad E° = -0.76\,V$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83\,V$$

Again, the $E°$ values are very close together, which indicates that each of the reactions is equally likely to occur. Generally, the reduction of zinc ions would be the preferred reaction because it has the less negative $E°$ value; that is, less voltage must be applied for this reaction to occur. However, for very dilute zinc solutions, there would be very few zinc ions present in the solution. In this case, water would be reduced.

WORKED EXAMPLE 11.2.1

With reference to Table 10.1.1, predict the products formed from the electrolysis of a concentrated aluminium iodide solution with inert electrodes. Write an equation for the overall reaction and determine the voltage required to enable this reaction to occur.

ANSWER

1 Identify the relevant electrode reactions.

Cathode:

$Al^{3+}(aq) + 3e^- \rightarrow Al(s) \qquad E° = -1.68\,V$

or

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83\,V$

Anode:

$2I^-(aq) \rightarrow I_2(g) + 2e^- \qquad E° = -0.54\,V$

or

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E° = -1.23\,V$

2 Use the fact that the reaction with the least negative *E°* value is the preferred reaction to determine which will occur.

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83\,V$

Anode: $2I^-(aq) \rightarrow I_2(g) + 2e^- \qquad E° = -0.54\,V$

Because the two $E°$ values at the reactions at both the anode and cathode are quite different, these are the most likely reactions even when concentration of $Al^{3+}(aq)$ ions is considered.

3 Balance electrons.

Electrons are balanced in these half-equations.

4 Add the half-equations to give the overall equation (cancelling electrons).

$2H_2O(l) + 2I^-(aq) \rightarrow H_2(g) + 2OH^-(aq) + I_2(g)$

5 Determine the voltage required.

$E°_{cell} = -0.83 + (-0.54) = -1.37\,V$

Therefore, the minimum voltage required is –1.37 V.

Nature of the electrodes

In each of the examples given for electrolysis so far, inert electrodes have been used. Graphite electrodes are used in school experiments because they are good conductors of electricity, inert and relatively cheap. Platinum electrodes are generally used in industry because they are also inert and are good electrical conductors. Since both graphite and platinum are chemically inert under these conditions, they did not need to be considered in terms of anode and cathode reactions. However, if other more reactive electrodes are used, then they must also be considered when determining the preferred reactions at the anode and cathode.

Consider the copper(II) chloride cell again, this time, using copper electrodes instead of graphite electrodes. Once again, ions $Cu^{2+}(aq)$ and $Cl^{-}(aq)$ are present because it is a solution. Water is also present. However, Cu(s) is also present in the electrodes and could be oxidised. It must also be considered as a possible reaction at the anode. The method used is the same as the previous examples. However, one extra half-equation must be considered at the anode.

Anode – oxidation:

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

$$2Cl^{-}(aq) \rightarrow Cl_2(g) + 2e^{-} \qquad E° = -1.36\,V$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 4e^{-} \qquad E° = -1.23\,V$$

Cathode – reduction:

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

$$2H_2O(l) + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq) \qquad E° = -0.83\,V$$

The preferred reactions are those with the less negative voltage at each electrode. Copper will be oxidised at the anode and copper will be reduced at the cathode.

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

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

The electrons are balanced, then the equations and $E°$ values are added to determine the overall reaction and cell voltage for this electrolytic cell.

Overall reaction: $Cu^{2+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + Cu(s) \qquad E° = 0.00\,V$

Therefore, if any voltage is applied to the cell, the above reactions will occur. The anode will decrease in mass as the copper electrode is oxidised while the cathode will increase in mass as copper metal is deposited on the electrode.

PRACTICAL ACTIVITY 11.2.1

FACTORS THAT AFFECT ELECTROLYSIS

Introduction

The products of electrolysis are determined by the nature and concentration of the electrolyte as well as the electrodes used. In this investigation, you will investigate each of these factors to determine how they affect what products are formed.

Research question

How does the nature and concentration of the electrolyte and the type of electrodes affect the products of electrolysis?

Aim

To investigate the products formed by the electrolysis of different aqueous solutions and the use of different electrodes

Materials

- U-tube
- retort stand and clamp
- DC power source (0–12 V)
- 2 electrical leads with alligator clips
- 2 carbon electrodes (at least 4 cm long) or 2 platinum electrodes
- 2 copper electrodes (1 cm × 7 cm)
- 2 × 100 mL beakers
- 100 mL measuring cylinder
- 50 mL saturated sodium chloride solution
- 50 mL of 0.1 mol L^{-1} sodium chloride solution
- 150 mL of 0.5 mol L^{-1} copper(II) sulfate solution
- universal indicator (solution or paper)
- paper towel
- sandpaper
- distilled water
- electronic balance
- marking pen

RISK ASSESSMENT

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Chlorine gas is poisonous.	Work in a fume cupboard; avoid breathing the vapour.
Copper(II) sulfate is toxic.	Dispose of as directed by your teacher. Do not pour down the sink.

Copy and complete the risk assessment table in your write-up. Add any more risks you can think of, and ways to manage them. Ask your teacher to check your risk assessment before you proceed.

Procedure

Part A Electrolysis of saturated sodium chloride solution with inert electrodes

1 Use the clamp to secure the U-tube to a retort stand as shown Figure 11.2.4. Half-fill the U-tube with the saturated sodium chloride solution.

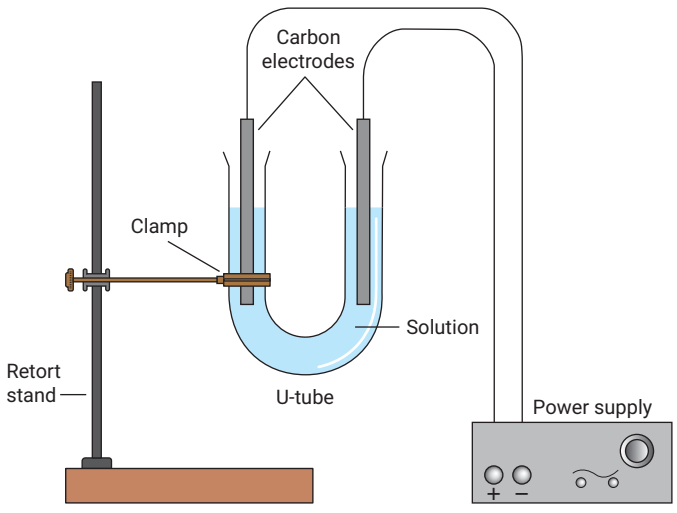


FIGURE 11.2.4 The experimental set-up

2 Insert the carbon (or platinum) electrodes, which have been connected to the DC power supply using the electrical leads provided. Ensure the electrodes are about half covered with solution.

3 Set the power supply to 6–8 V and switch on the power. You may need to adjust the power output. Electrolyse the solution for 2–3 minutes.

4 In a results table, observe and record any changes, such as colour of the solution or electrode, evolution of a gas or deposition of a solid, at each electrode. Caution: Do not try to smell any gas being produced.

5 Switch off the power. Remove the electrodes, examine them and note any change.

6 Determine the pH of the solution at each electrode by using universal indicator paper or solution.

7 Record your observations and pH results in a table.

8 Dispose of the solution in the U-tube by flushing it down the sink with plenty of water. Rinse the U-tube. Rinse and dry the graphite electrodes.

Part B Electrolysis of 0.1 mol L^{-1} sodium chloride solution

1 Repeat Part A steps 1–8 but use a dilute sodium chloride solution.

Part C Electrolysis of copper(II) sulfate solution with inert electrodes

1 Repeat Part A steps 1–7 but use copper(II) sulfate solution.

2 Dispose of the copper(II) sulfate solution as directed by your teacher.

Part D Electrolysis of copper(II) sulfate using copper electrodes

1 Thoroughly clean both strips of copper with sandpaper, wash them with distilled water and wipe them clean with paper towel. Hold the strips by their edges. Do not handle the surface at all during the investigation.

2 Place the strips on a clean piece of paper and label one A for anode and the other C for cathode. Weigh each strip and record its mass.

3 Place 80 mL of the copper(II) sulfate solution in a 100 mL beaker.

4 Bend the top of each copper strip so it can be slipped over the side of the beaker and held in place.

5 Place each piece of copper on opposite sides of the beaker. Attach the piece marked A to the positive terminal and piece marked C to the negative terminal of the powerpack.

6 Set the power supply to 8 V and switch on the power. You may need to adjust the power output. Electrolyse the solution for 5–10 minutes.

7 In the results table, observe and record any changes, such as colour of the solution or electrode, evolution of a gas or deposition of a solid, at each electrode. Caution: Do not try to smell any gas being produced.

8 Turn off the power, remove the electrodes and place them in a clean dry 100 mL beaker to dry.

9 Weigh the dry electrodes and record their weight.

Results

	Observations (e.g. colour change, gas or solid production, pH)	
	Anode	Cathode
Part A Electrolysis of saturated NaCl solution		
Part B Electrolysis of dilute NaCl solution		
Part C Electrolysis of copper(II) sulfate solution with inert electrodes		
Part D Electrolysis of copper(II) sulfate solution with copper electrodes		
Initial mass (g)		
Final mass (g)		
Change in mass (g)		

Analysis of results

1 Calculate the change in mass for each of the electrodes in Part D and record in the results table.

2 Copy and complete the following table, giving all possible electrode reactions.

	Electrode reactions	
	Anode	Cathode
Part A Saturated NaCl solution		
Part B Dilute NaCl solution		
Part C Copper(II) sulfate with inert electrodes		
Part D Copper(II) sulfate with copper electrodes		

3 From the possible electrode reactions for each electrolyte cell, use your experimental results to decide which of the reactions took place.

4 Write the overall reaction for each cell.

Evaluation

5 Suggest possible differences in the solution and electrodes in parts A and B after both solutions had been electrolysed for 30 minutes. Give reasons for these differences.

6 Use experimental results to support or refute the statement: 'Products of electrolysis are affected by the concentration of the electrolyte used'.

7 Compare the change in mass of each of the electrodes in Part D and use these to evaluate whether these changes align with expected theoretical results.

8 Construct a summary statement relating products of electrolysis and factors investigated.

LEARNING CHECK 11.2

DESCRIBING

1 a **Identify** the factors that affect the products of electrolysis.

b **Explain** how these factors can affect the electrolysis of a molten salt.

2 **Identify** why inert electrodes such as carbon and platinum are used in electrolysis.

3 **Explain** why electrolysis of an aqueous solution is more complicated than electrolysis of a molten salt.

4 When electrolysis of aqueous solutions of salts containing polyatomic ions such as nitrates, carbonates and sulfates is carried out, **explain** why oxygen gas is always produced at the anode.

5 When electrolysing aqueous solutions, **describe** the principle that determines the products formed at each electrode.

6 **Explain** why, when electrolysing concentrated and dilute chloride solutions, the concentrated chloride solution produces chlorine gas at the anode while the dilute chloride solution produces oxygen gas.

APPLYING

7 **Construct** the oxidation and reduction half-equations for the reactions occurring at the anode and cathode during the electrolysis of molten copper(II) bromide.

8 A student set up an electrolysis experiment using a dilute solution of aqueous iron(II) iodide and inert electrodes.

- **a** **Identify** the possible anode reactions.
- **b** **Identify** the possible cathode reactions.
- **c** The student made the following observations for each electrode.
  The solution around the anode becomes yellow, some dark coloured crystals sink to the bottom of the beaker. A red-brown solid coats the cathode.
  Deduce which of the possible reactions occurred at each of the electrodes.
- **d** **Determine** the voltage that would need to be applied to operate this electrolytic cell.

9 A student set up an electrolysis experiment using a dilute solution of aqueous calcium chloride and inert graphite electrodes.

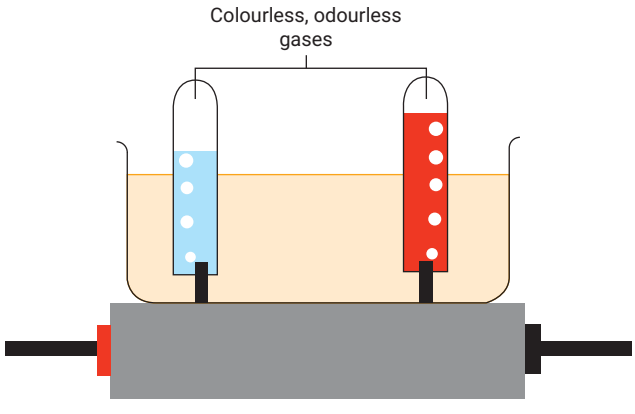
- **a** **Identify** the anode reaction.
- **b** **Identify** the cathode reaction.
- **c** **Outline** the observations for each electrode.
- **d** **Describe** how could you identify the products forming at each electrode.
- **e** **Determine** the voltage that would need to be applied to operate this electrolytic cell.

10 With reference to a table of standard electrode potentials, **determine** the minimum voltage that must be applied to electrolyse a 1.0 M solution of zinc(II) nitrate solution.

11 With reference to a table of standard electrode potentials (such as Table 10.1.1), **predict** the products formed from the electrolysis of a concentrated sodium nitrate solution. Write an equation for the overall reaction and **determine** the voltage required to enable this reaction to occur.

12 An experiment was carried out in which a 1 M sodium chloride solution was electrolysed. A few drops of universal indicator were placed into the solution. The set-up for this experiment is shown in the following diagram.

- **a** **Describe** what chemical tests could a student perform to identify the unknown gases.
- **b** Using the information given, **identify** the anode and the cathode.
- **c** **Determine** a reason to explain why the amounts of gases produced are not the same.



11.3 Applying electrolytic processes

Electrolysis is widely used in small-scale and industrial situations. As you learnt in the previous section, sodium hydroxide, and chlorine gas are produced industrially by the electrolysis of a concentrated sodium chloride solution.

In the mining industry, chemical and physical processes are used to extract metals from their ores. Electrolysis is one of the chemical processes used to obtain pure metals, particularly aluminium and copper.

Electrorefining

electrorefining a process used to produce a pure sample of a metal from an impure sample using electrolysis

The method shown in section 11.2 where inert electrodes are replaced with copper electrodes is called **electrorefining**. It is used industrially to purify copper. A similar method is used to obtain pure aluminium from alumina (Al_2O_3).

Electrorefining is the final step in extracting copper from its ore to produce the pure copper necessary for electrical applications. The process starts with 'blister copper', which is about 98 per cent pure copper from the smelting process. The blister copper is at the anode. A sample of pure copper, about 99.9 per cent pure, is the cathode. The copper from the anode is oxidised and goes into solution. Pure copper is deposited on the cathode. The electrolyte is a mixture of copper(II) sulfate and sulfuric acid. The impurities either stay in solution or fall to the bottom of the electrolytic cell as seen in Figure 11.3.1.

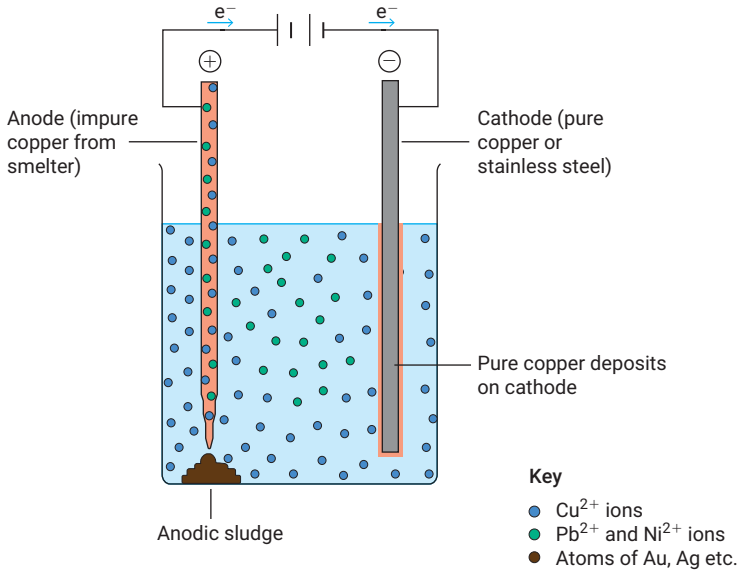


FIGURE 11.3.1 The electrolytic cell used for electrorefining impure copper from a copper smelter

Electroplating

The principles of electrorefining can also be applied to electroplating. Electroplating is an electrochemical process that enables a thin coating of a metal to be deposited on a metal object. The applications of this process include:

- Jewellery: gold and silver jewellery can be manufactured much more cheaply and made more durable by plating a hard metal object with a metal such as gold or silver.

- Car parts: metals such as chromium and nickel are plated onto car parts to provide low-friction surfaces that enhance a car's performance. These metals also protect the car parts and can make them look attractive.
- Cutlery: plating knives, forks and spoons with silver or gold can increase their durability and make them look more attractive.

The metallic object that is to be plated is the cathode in the electrolytic cell. The electrolyte is a solution containing the metal to be plated on the object. The anode is either an inert electrode or the metal to be plated on the object – this is dependent on the reactivity of the metal.

The set-up for silver-plating a metal fork is shown in **Figure 11.3.2**.

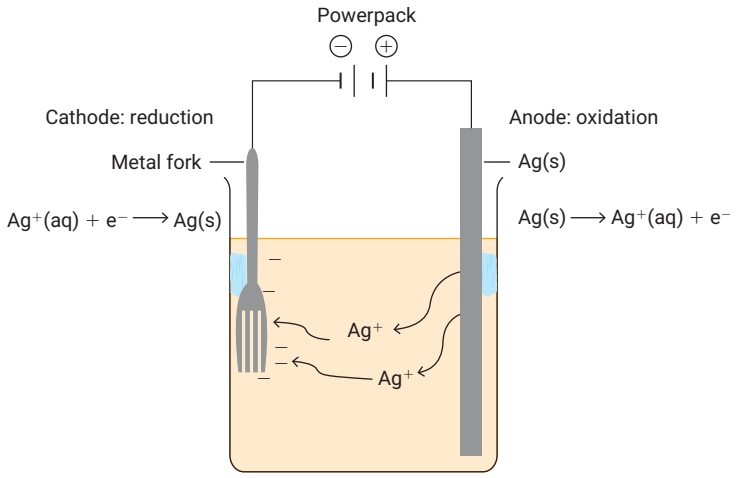


FIGURE 11.3.2 The set-up for silver-plating a metal fork

In this case, the anode is a piece of silver. During electrolysis, the silver is oxidised to silver ions. These silver ions move into the silver nitrate electrolyte solution and migrate towards the metal fork cathode where they are reduced to silver metal. This forms a thin layer of silver on the fork.

PRACTICAL ACTIVITY 11.3.1

ELECTROPLATING

Introduction

Electroplating is an important industrial process. In this activity, you will model the process.

Research question

How can a piece of copper be plated with a layer of silver?

Aim

To silver-plate a piece of copper using electrolysis

Materials

- 20 mL of a saturated potassium nitrate (KNO_3)
- 30 mL of a 0.1 mol L^{-1} silver nitrate solution ($AgNO_3$)
- stirring rod
- sandpaper
- warm solution of detergent
- 100 mL beaker
- graphite electrode
- strip of copper
- powerpack
- 2 electrical leads with banana plugs
- 2 alligator clips, one to be placed on each electrical wire
- waste bottle for heavy metals
- 50 mL measuring cylinder

RISK ASSESSMENT

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Chemicals may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Silver nitrate stains skin.	Avoid getting silver nitrate on your skin.

Copy and complete the risk assessment table in your write-up. Add any more risks you can think of, and ways to manage them. Ask your teacher to check your risk assessment before you proceed.

Procedure

1. Measure 30 mL of silver nitrate solution into a 100 mL beaker.
2. While stirring, add 20 mL of saturated potassium nitrate to the silver nitrate solution until the precipitate that forms is dissolved.
3. Clean the piece of copper with sandpaper, then wash it in a warm solution of detergent and rinse it thoroughly. Hold the copper by the sides. Do not touch the surface.
4. Place the piece of copper and graphite electrode on opposite sides to the 100 mL beaker containing the silver nitrate electrolyte.
5. Attach the piece of copper to the negative terminal and the graphite electrode to the positive terminal of the powerpack.
6. Set the powerpack to 4 V and turn it on.
7. Record your observations.
8. Dispose of the electrolyte solution by pouring it into the heavy metals waste bottle. Do not pour it down the drain.

Results

Record all your observations.

Analysis of results

1. Identify the anode in this electrolytic cell.
2. Identify the cathode in this electrolytic cell.
3. Write the half-equation for the reaction occurring at the anode.
4. Write the half-equation for the reaction occurring at the cathode.

Interpretation

5. Write the overall equation for the electroplating reaction.
6. Justify why the metal to be electroplated onto the object is sometimes used as the anode instead of using an inert electrode such as graphite.
7. Explain why electroplating is used instead of using pure metal. For example, why would a jeweller use silver-plating instead of pure silver?
8. Relate your experimental method to the industrial use of electrolysis in electroplating.

LEARNING CHECK 11.3

DESCRIBING

1 **Define**:
   - **a** electrorefining
   - **b** electroplating.

2 **Identify** which electrode should be the impure metal when electrorefining.

3 **Identify** the electrode that should be the object to be plated when electroplating.

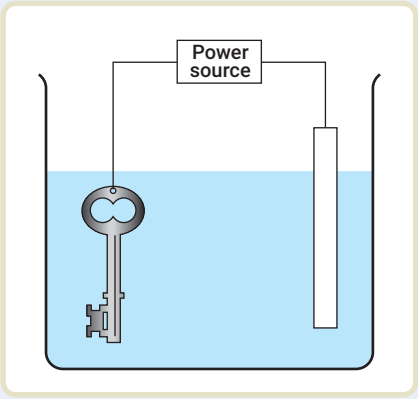
APPLYING

4 **a** **Sketch** a labelled diagram of an electrolytic cell that could be used for electrorefining copper.

   b If the concentration of an electrolyte of copper(II) sulfate was 1 mol L^{-1} before electrolysis, predict the concentration of the electrolyte after electrolysis. **Justify** your answer.

 Modified from SCSA 2019 SA Q31

5 A solution that contains silver cyanide (AgCN(aq)) is used to plate a key with silver.



   - **a** Redraw the diagram in your notebook and label it to show the:
     - cathode and anode
     - direction of electron flow
     - direction of ion flow
     - polarity (positive/negative) of each electrode.
   - **b** **Identify** a metal that could be used for the other electrode (not the key electrode).
   - **c** **Identify** the half-equations for the reactions that are occurring at each electrode.

11.4 Quantitative aspects of electrolysis

Michael Faraday (1791–1867) is well known for his work on electricity and particularly the discovery that an electric current can be caused to flow in a wire if it is moved in a magnetic field. This led to the development of electric generators, motors and coal-fired, gas-fired and hydroelectric power stations.

He also spent considerable time studying electrolysis. In the course of this work, he was the first to discover the quantitative relationships between the amount of electricity passing into an electrochemical cell and the amounts of reactants and products.

These relationships are known as Faraday's laws.

Faraday's first law of electrolysis

Faraday's first law of electrolysis the mass of a substance produced or consumed at an electrode during electrolysis is proportional to the quantity of electricity that passes through the electrolytic cell

According to **Faraday's first law of electrolysis**, the mass of a substance produced or consumed at an electrode during electrolysis is proportional to the quantity of electricity that passes through the electrolytic cell.

Consider the half-equation:

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

One mole of electrons is needed to produce one mole of silver from silver ions. The charge (in coulombs) on one electron is $1.602\,74 \times 10^{-19}$ coulomb (C) so the charge carried by one mole (6.02×10^{23}) electrons is:

$$1.602\,74 \times 10^{-19} \times 6.02 \times 10^{23} = 96\,485\,C$$

This quantity of electricity is called the **Faraday constant**.

FORMULA AND DATA BOOK

The amount of electric charge passing through a cell is calculated by the formula:

$$q = I \times t$$

where q = amount of electric charge in coulombs (C)
I = electrical current in amperes (A)
t = total time the current is passes in seconds (s)

Faraday constant the quantity of electricity, in coulombs, C, carried by 1 mole of electrons; equal to 96 485 coulombs per mole (C mol^{-1})

Once q is known, the following relationship can be used to calculate the number of moles of electrons and hence the number of moles of products at the electrodes:

$$q = n(e^-) \times F$$

where q = amount of electric charge in coulombs (C)
$n(e^-)$ = number of moles of electrons
F = Faraday constant = 96 485 C mol^{-1}

KEY FORMULAS

Charge (q) = number of moles of electrons ($n(e^-)$) × Faraday constant (F)

Charge (q) = current (I) × time (t)

These formulas can be used to determine the relative amounts of product formed at each electrode during electrolysis. This is illustrated in the following two worked examples.

WORKED EXAMPLE 11.4.1

An electrolytic cell is constructed from a piece of copper wire and a piece of silver wire as the electrodes, dipping into a copper(II) sulfate electrolyte solution. The silver wire is connected to the positive terminal and the copper wire to the negative terminal of a battery.

a Write the oxidation and reduction half-reactions occurring.

b Calculate the change in mass of each of the electrodes when a current of 0.82 A flows for 40 min.

ANSWERS

a 1 Identify the anode and cathode.

Silver is connected to the positive terminal, so it is the anode, and copper is connected to the negative terminal, so it is the cathode.

2 Identify the relative electrode reactions.

Anode (oxidation):

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

Cathode (reduction): Cations present in electrolyte solution are $Cu^{2+}(aq)$, so these are reduced.

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

b 1 Calculate number of coulombs (q) that pass through the cell.

$I = 0.82\,A$, $t = 40\,min = 40 \times 60\,s$

$q = I \times t$

$= 0.82 \times (40 \times 60) = 1968\,C$

2 Calculate the number of moles of electrons ($n(e^-)$) that pass through the cell.

$q = n(e^-) \times F$

$q = 1968\,C$ (calculated above), $F = 96\,485\,C\,mol^{-1}$

$$n(e^-) = \frac{q}{F}$$

$$= \frac{1968}{96\,485}$$

$= 0.0204$ mol

3 Calculate the mass change in each electrode.

Anode:

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

Since the relationship between e^- and Ag(s) is 1:1, the amount of Ag(s) lost $= n(e^-) = 0.0204\,mol$

$M(Ag) = 107.87\,g\,mol^{-1}$

$m = n \times M$

$= 0.0204 \times 107.87$

$= 2.18$ g

Cathode:

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

Since the relationship between e^- and Cu(s) is 2:1:

$$n(Cu) = \frac{n(e^-)}{2}$$

$$= \frac{0.0204}{2}$$

$= 0.0102$ mol

$M(Cu) = 63.55\,g\,mol^{-1}$

$m(Cu) = n \times M$

$= 0.0102 \times 63.55$

$= 0.648\,g$

Therefore, the silver electrode decreases in mass by 2.18 g and the copper electrode increases in mass by 0.648 g.

WORKED EXAMPLE 11.4.2

Determine how long a current of 1000 A would need to be passed through water to which an electrolyte has been added to produce 1000 L of hydrogen gas at 20°C and 101.3 kPa.

ANSWER

1 Calculate the number moles of hydrogen gas to be produced.

$PV = nRT$

$V = 1000\,\text{L}$, $T = 20°\text{C} = 293\,\text{K}$, $P = 101.3\,\text{kPa}$

$$n(\text{H}_2) = \frac{PV}{RT}$$

$$= \frac{101.3 \times 1000}{8.31 \times 293}$$

$$= 41.6\ \text{mol}$$

2 Write the relevant half-equation.

$2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{H}_2\text{(g)} + 2\text{OH}^-\text{(aq)}$

3 Calculate the number of moles of electrons required.

From the half-equation, the relationship between e^- and $\text{H}_2\text{(g)}$ is a 2:1:

$n(\text{e}^-) = 2 \times n(\text{H}_2)$

$= 2 \times 41.6$

$= 83.2\,\text{mol}$

4 Calculate the amount of charge required.

$q = n(\text{e}^-) \times F$

$= 83.2 \times 96\,485$

$= 8\,027\,552\,\text{C}$

5 Calculate the time required.

$q = I \times t$

$q = 8\,027\,552$, $I = 1000\,\text{A}$, $t = ?$

$$t = \frac{q}{I}$$

$$= \frac{8\,027\,552}{1000}$$

$= 8028\ \text{s} = 2.23\ \text{h}$

It would require 2.23 hours.

Weblink
Faraday's first law of electrolysis

Worksheet
Calculations involving electrolytic cells

LEARNING CHECK 11.4

DESCRIBING

1 **State** Faraday's first law.

2 **Explain** what the Faraday constant represents.

3 **Explain** how Faraday's first law of electrolysis can be used to find the amount of chlorine (Cl_2) produced when molten potassium chloride (KCl(l)) is electrolysed. Include half-equations and the Faraday constant in your explanation.

APPLYING

4 20 000 coulombs of charge passed through an electrolytic cell containing molten NaCl. **Calculate** the masses of sodium and chlorine produced.

5 **Calculate** the current required to deposit 0.500 g nickel onto an inert cathode if it flowed for 5 min.

6 **Calculate** how long a current of 0.106 A must flow through an electrolytic cell containing a zinc ion solution for 3.5 g zinc to be deposited on an iron electrode.

ANALYSING

7 A certain amount of electricity deposited 50.0 g of silver from a solution of $AgNO_3$. **Calculate** the mass of copper this same amount of current will deposit from a solution of $CuSO_4$.

8 **Calculate** the number of grams of nickel that will be deposited from a solution of $NiCl_2$ by 4.00 A of current flowing for 24.0 hours if the efficiency of the process is 96.0 per cent.

9 A current of 0.200 A was passed through a saturated NaCl solution for a period of 200 s. The only gases evolved were H_2 at the cathode and Cl_2 at the anode. At the conclusion of electrolysis, the volume of the solution was 80.0 mL.

Calculate the:

a volume of H_2 produced at 25°C and 100 kPa

b pH of the solution.

10 Metal X is known to form the fluoride XF_2. When 3300 C of electricity is passed through the molten fluoride, 1.950 g of X is plated out. **Determine** the atomic mass of X.

CHAPTER SUMMARY

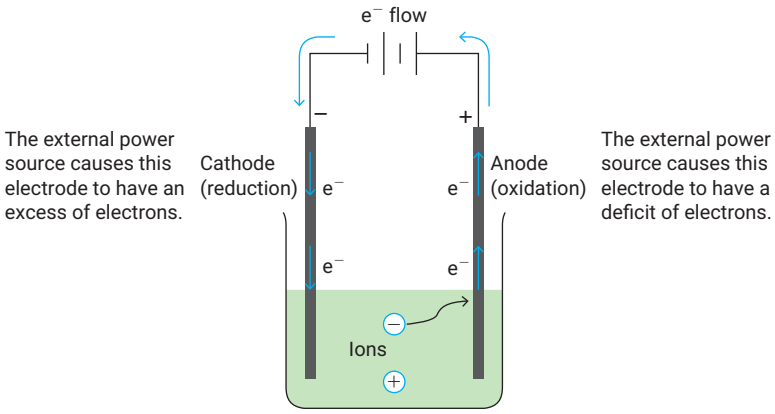
Electrolytic cell processes

- An electrolytic cell is a type of electrochemical cell that transforms electrical energy into chemical potential energy.

  Therefore, electrolytic cells involve non-spontaneous reactions.
- Electrons flow from the negative terminal of a power source to the cathode and from the anode to the positive terminal of the power source.

  Therefore, the polarity of cathode is negative whereas the polarity of the anode is positive.
- Reduction occurs at the cathode and oxidation at the anode.

The processes occurring in the electrolytic cell



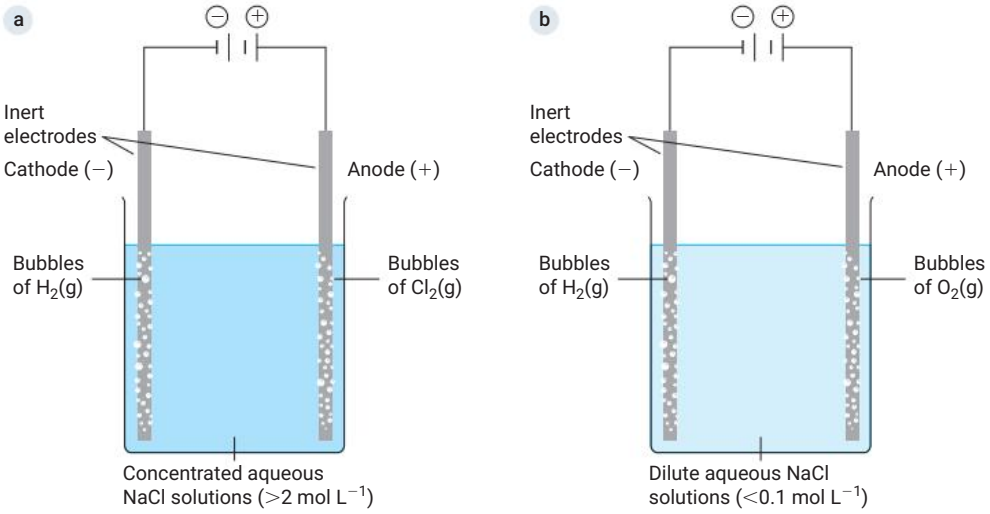
Comparing galvanic and electrolytic cells

	Galvanic cells	Electrolytic cells
Reaction type	Spontaneous	Non-spontaneous
Reactions at each electrode	Oxidation at anode, reduction at cathode	Oxidation at anode, reduction at cathode
Polarity of each electrode	Anode negatively charged; cathode positively charged	Anode positively charged; cathode negatively charged
Electron flow	Electrons flow from anode to cathode	Electrons flow from anode and to cathode
Ion flow	Positive ions flow to cathode half-cell	Positive ions flow towards cathode

Factors affecting the products of electrolysis

- Three factors that can affect the products that are formed are the:
  - nature of the electrolyte
  - concentration of the ions present
  - nature of the electrodes.
- The only factor that affects the electrolysis of molten salts is the nature of the electrode. When inert electrodes are used for electrolysis of a binary molten salt, the products are the elements of the ions present in the salt.
- In the electrolysis of aqueous salt solutions, water may be electrolysed (oxidised or reduced) to produce hydrogen gas and/or oxygen gas.
- The reaction that is more likely to occur is the one that requires the least input of energy; that is, the least negative voltage.

Electrolysis of sodium chloride of different concentrations



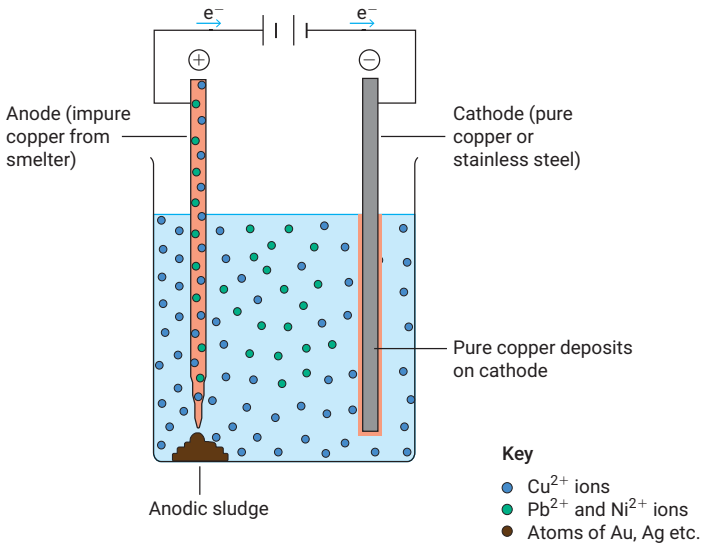
Source: Smith, D. R. et al (2006). Chemistry in use Book 2.

- When the $E°$ values of competing electrode reactions are very similar, the concentration of the solution affects the products.
- When electrodes that are not inert are used, the electrode itself may be oxidised.

Applying electrolysis

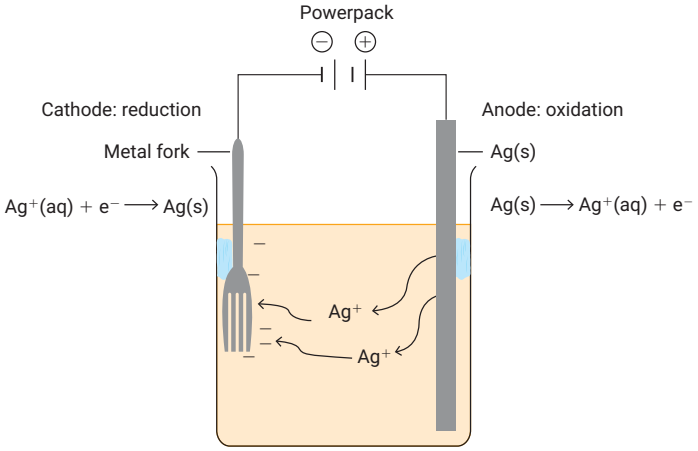
- Electrorefining uses an impure form of a metal as the anode, which is oxidised then reduced onto the cathode.

The electrolytic cell used for electrorefining impure copper from a copper smelter



- Electroplating is an electrolytic process in which a thin coating of a metal is deposited on a metal object. The object to be plated is made the cathode of the electrolytic cell.

Silver-plating a metal fork



Quantitative aspects

- Faraday's first law of electrolysis states that the mass of a substance produced or consumed at an electrode during electrolysis is proportional to the quantity of electricity that passes through the electrolytic cell.
- The Faraday constant is the quantity of electricity, in coulombs C, carried by 1 mol of electrons. It equal to 96 485 coulombs per mole (C mol^{-1}).
  Charge (q) = number of moles of electrons ($n(e^-)$) × Faraday constant (F)
  Charge (q) = current (I) × time (t)

CHAPTER EXAM

MULTIPLE CHOICE

1. In electrolysis, the anode and cathode are determined by the:
- **A** electrode potentials of the ions in the electrolyte.
- **B** connection of the electrodes to the external power supply.
- **C** site of oxidation and reduction.
- **D** movement of ions in the electrolyte.

2. What is the half-reaction that occurs at the anode during the electrolysis of a concentrated potassium bromide solution?
- **A** $Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$
- **B** $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
- **C** $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$
- **D** $K^+(aq) + e^- \rightarrow K(s)$

3. When electroplating a coating of zinc onto a piece of iron, what will the anode and the electrolyte be?
- **A** Zinc and iron(II) nitrate
- **B** Iron and zinc nitrate
- **C** Zinc and zinc nitrate
- **D** Iron and iron(II) nitrate

4. Which of the following statements about the polarity of a cathode is correct?
- **A** It is negative in an electrolytic cell but positive in a galvanic cell.
- **B** It is positive in an electrolytic cell but negative in a galvanic cell.
- **C** It is negative in both electrolytic and galvanic cells.
- **D** It is positive in both electrolytic and galvanic cells.

5. Fluorine gas is prepared by electrolysis of molten salts rather than by electrolysis of aqueous solutions containing a fluoride salt.
The reduction half-equation for fluorine gas is:

$$F_2(g) + 2e^- \rightarrow 2F^-(aq) \qquad E° = +2.89\,V$$

Which of the following statements related to the preparation of fluorine gas is correct?
- **A** Metal fluorides are insoluble in water.
- **B** Fluoride ions are difficult to reduce.
- **C** Fluorine gas reacts violently with water.
- **D** Oxygen gas is produced in preference to fluorine in aqueous solutions.

6. The process used for preparing pure copper in commercial quantities involves electrolysis using copper electrodes and a copper sulfate electrolyte. Which of the following statements about this process is correct?
- **A** Copper metal is deposited on the positive electrode.
- **B** Copper ions migrate towards the anode.
- **C** Hydrogen gas is given off at the negative electrode.
- **D** The mass of the anode decreases.

7. An aqueous solution of $Pb(NO_3)_2$ is electrolysed using copper electrodes. Which of the following cell reactions is most likely to initially occur to the greatest extent?
- **A** $Cu(s) + Pb^{2+}(aq) \rightarrow Cu^{2+}(aq) + Pb(s)$
- **B** $Cu(s) + 2H_2O(l) \rightarrow Cu^{2+}(aq) + H_2(g) + 2OH^-(aq)$
- **C** $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$
- **D** $Pb^{2+}(aq) + 2H_2O(l) \rightarrow 2Pb(s) + O_2(g) + 4H^+(aq)$

Questions 8 and 9 relate to the following information.
The following table shows the formulas of the ions of four different metals and the relative atomic masses of these metals.

Ion in solution	Relative atomic mass
W^{+}	65
X^{2+}	210
Y^{3+}	140
Z^{4+}	120

In an experiment, a fixed amount of electricity was passed between inert electrodes dipping into solutions of each of the metal ions. Metal was deposited on the negative electrode on each solution.

8. For which metal would the greatest number of metal atoms be deposited from solution?
A W
B X
C Y
D Z

9. For which metal would the greatest mass of metal be obtained?
A W
B X
C Y
D Z

10. During electrolysis of a molten ionic compound, the passage of 1930 C produced 1.51 g of element X ($M = 150$) at the cathode. What is the charge on an ion of X?
A 2−
B 1−
C 1+
D 2+

SHORT REPSONSE

11. Galvanic cells and electrolytic cells are both classified as electrochemical cells. **Identify** three similarities and three differences between these two cell types.

12. Some wastewater produced in a school experiment contained a mixture of copper sulfate and silver nitrate. To recover these valuable metals, a recycler electrolysed the solution using a graphite anode and a steel cathode.
a Sketch a diagram of the electrolytic cell set up by the recycler to recover these two metals from the mixture.
b **Predict** the reaction that will initially occur at each electrode. **Justify** your answer.
c **Describe** what you would expect to initially observe at each electrode.
d If the current was allowed to run for some time, **predict** changes would you expect to observe at either of the electrodes. **Justify** your answer.

CROSS-CHAPTER QUESTION

13. An aqueous solution of the soluble salt XSO_4 is electrolysed between inert electrodes until 0.0327 g of metal X are deposited on the negative electrode. To neutralise the solution that was formed in the electrolytic cell required 50 mL of 0.020 mol L^{-1} KOH.

a **Determine** the oxidation and reduction half-equations.

b **Calculate** the number of moles of H^+ produced.

c **Calculate** the atomic weight of metal X.

DATA ANALYSIS

14. Analyse data

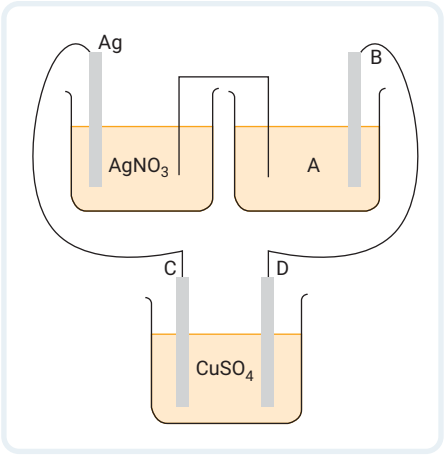
An experiment was carried out according to the diagram under standard conditions.

a Use a table of standard reduction potentials to suggest the identity of metal B and solution A.

b **Determine** what substances will be produced at electrodes C and D.

c **Identify** all electrodes as anodes or cathodes and label each as the site where oxidation or reduction occurs.

d **Justify** your answers with appropriate half-equations.



15. Analyse data

Zinc metal is obtained from zinc ore by first concentrating the ore and converting it zinc oxide. The zinc oxide is then dissolved in dilute sulfuric acid and the solution is electrolysed to produce the pure metal.

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

Anode reaction: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

A current of 12.50 A is passed through a solution containing zinc ions for 7.50 h.

Calculate the theoretical:

a mass of zinc deposited at the cathode

b volume of dry oxygen gas (at 100 kPa and 25°C) produced at the anode.

SCIENCE AS A HUMAN ENDEAVOUR

Syllabus dot point

- Appreciate that the level of alcohol in the body can be measured by testing breath or blood alcohol concentrations.

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Alcohol in the body

When an alcoholic beverage is consumed, the absorbed alcohol dissolves in the watery component of the blood (plasma) and is transported around the body. About 10–20 per cent of the alcohol consumed is directly absorbed through the stomach.

The effect of alcohol depends on its concentration (i.e. the amount of alcohol in the blood) and is referred to as the blood alcohol concentration (BAC). The BAC depends on the amount of alcohol drunk and the volume of blood in a person.

Ethanol interferes with communication between nerve cells and all other cells by suppressing the activities of nerve pathways. The overall effect of the alcohol is to make the person sluggish or slow to react. This is why there are legal limits on blood alcohol levels for drivers of motor vehicles and boats.

Once absorbed into the bloodstream, the ethanol is either broken down in the liver or leaves the body in two ways:

- The kidneys eliminate 5 per cent of the alcohol in the urine.
- The lungs exhale 5 per cent of the alcohol, which can be detected by breath tests.

Alcohol breath-testing devices (breathalysers)

Alcohol breath-testing devices allow police officers to test expelled air from a person to estimate blood alcohol content and hence determine whether the person is in a condition to drive safely. The alcohol moves into the air in the lungs from the blood because it is volatile and evaporates from the blood.

Police officers use portable breath-testing machines like the one shown in **Figure 1** to find out if a driver has a blood alcohol level above the legal limit. It is assumed that there is a direct correlation between the concentration of alcohol in the air from the lungs and the concentration of alcohol in the blood (BAC). The ratio of breath alcohol to blood alcohol is 1:2100. This means that 2100 mL of alveolar air contains the same amount of alcohol as 1 mL of blood.

The State of Queensland/Queensland Police

FIGURE 1 A breathalyser used by Queensland police

Current breathalysers involve oxidation of ethanol to ethanoic (acetic) acid. These breathalysers are mini fuel cells and the electrical current produced is proportional to the alcohol level present. Breathalysers may also use infrared spectroscopy to detect the presence of the hydroxyl (–OH) group of ethanol.

Testing blood for alcohol

When a driver is found to have a high BAC by breathalyser testing, a blood test may be performed. Only certified professionals can conduct blood alcohol analysis.

Blood analysis is a highly accurate method to confirm a person's BAC because it gives a direct determination of the driver's blood alcohol level. It uses advanced technology and rigorous control measures.

Gas chromatography and enzymatic analysis are most widely used. Both methods are selective for ethanol and rely on instrumentation. However, gas chromatography is the most accurate method for determining BAC in blood samples.

A sample of blood is collected. The sample is sealed and placed in a water bath; the alcohol in the blood diffuses into the air in the headspace above the sample. The analyst withdraws a sample of air from the headspace and injects it into a gas chromatography instrument. As the sample passes through the chromatography column, components separate out at different points (similar to paper and thin-layer chromatography). The instrument produces a gas chromatogram **(Figure 2)**, which shows the alcohols present in the blood. The height of the peak is a measure of concentration.

Enzymatic analysis is less commonly used but can provide a quick estimation of BAC. Although this method is much faster, it is less precise than gas chromatography so is mainly used for initial screening.

Artificial intelligence (AI) is beginning to be used for analysis of BAC data to improve the accuracy of roadside breathalyser testing to reduce the possibilities of false negatives and positives. It is thought that AI-driven breathalysers can ensure more reliable results by analysing environmental factors such as temperature and humidity that may affect the reading.

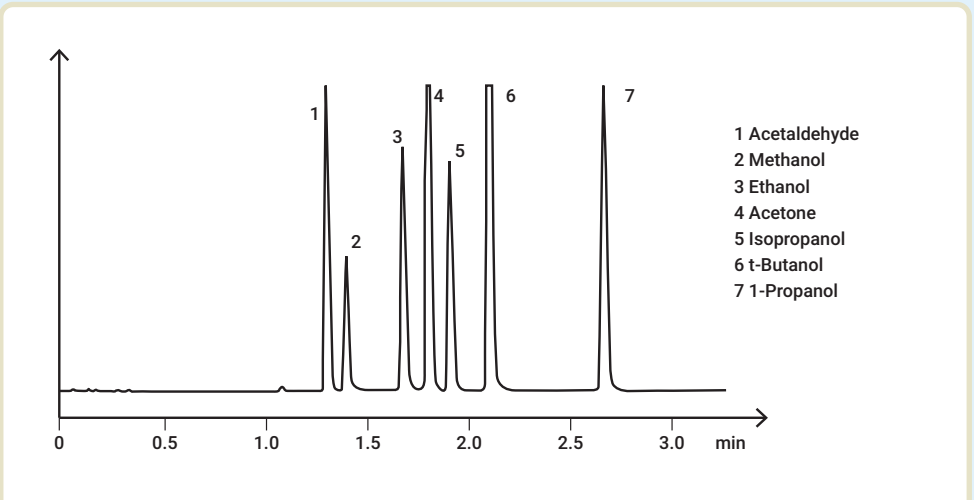

FIGURE 2 A gas chromatogram of a blood analysis for alcohol

Blood Alcohol Analysis System, Shimadzu Corporation. https://www.shimadzu.com/an/industries/clinical-research-forensics/forensic-analysis/blood-alcohol/index.html

UNIT

4

Structure, synthesis and design

Taffpixture/Shutterstock.com

Topic 1: Properties and structure of organic materials

CHAPTERS RELATED TO THIS TOPIC AREA: 12—15

Topic 2: Chemical synthesis and design

CHAPTERS RELATED TO THIS TOPIC AREA: 16—18

9780170483544

Chemical synthesis and the design and production of new materials is one of chemistry's most important uses. Chemistry is also part of the debate about how we use the world's resources. In this unit, you will focus on the principles and applications of chemical synthesis, particularly in organic chemistry, and consider where and how functional groups can be incorporated into existing carbon compounds to generate new substances with properties that can 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.

UNIT OBJECTIVES

By the end of this unit, students should be able to:

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.

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CHAPTER 12

Structure of organic compounds

Scenics & Science/Alamy Stock Photo

SYLLABUS DOT POINTS

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 C_{10}, 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 C_{10}, 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 compounds and the percentage composition of elements in organic compounds.

Introduction

Early chemists knew that chemicals obtained from living things were different from the chemicals obtained from rocks. The term 'organic compound' referred to substances obtained from living things, while 'inorganic compound' describes any substance not obtained from living things.

Because more organic compounds can be made from inorganic sources, we now differentiate organic and inorganic compounds on the basis that organic compounds are carbon based.

In this chapter, you will learn how to determine the structure of an organic compound from its name. You will also learn how to make sense of the vast range of organic molecules by grouping and classifying them.

ASSUMED KNOWLEDGE

- ✓ The periodic table is organised into groups and periods.
- ✓ Electronegativity describes an element's ability to attract electrons to itself.
- ✓ The shape of a covalent compound influences its polarity.
- ✓ Hydrocarbons are organic compounds made up of carbons and hydrogens.
- ✓ Alkanes are saturated, whereas alkenes and alkynes are unsaturated hydrocarbons.
- ✓ Carbon can form a maximum of four covalent bonds.
- ✓ Covalent bonds involve the sharing of electrons between atoms.
- ✓ Covalent bonds occur between non-metals to achieve a full valence shell.
- ✓ There are different types of reactions including combustion, addition etc.
- ✓ The molecular mass of a compound can be calculated from the chemical formula.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ identify and classify organic molecules, including alkanes, alkenes, alkynes, alcohols, aldehydes, ketones, carboxylic acids, haloalkanes, esters, amines and amides, and understand the difference between class and functional groups
- ✓ describe the features of a homologous series and discriminate between saturated and unsaturated molecules
- ✓ discriminate between empirical, molecular and structural formulas, and determine molecular and structural formulas for organic compounds up to C_{10}, including simple branched chains
- ✓ apply IUPAC nomenclature rules for organic compounds and their isomers, including alkanes, alkenes and functional groups
- ✓ identify and deduce the structural formulas of isomers, including *cis*/*trans* and optical isomers, and recognise chiral carbon atoms
- ✓ analyse data to determine the molecular, empirical and structural formulas of organic compounds, as well as their percentage composition.

12.1 Representing organic compounds

carbon skeleton the arrangement of carbon atoms that other atoms join to in an organic molecule

functional group a group of atoms in a molecule that causes the molecule to chemically react in a distinctive way

class a broad category of molecules that share the same functional group

homologous series a series of organic molecules within the same class, with different-length carbon chains

Carbon is able to be the basis of so many compounds because it can form long chains and rings of atoms. These long sequences of atoms form what is known as a **carbon skeleton**. Attached to the carbon skeleton are atoms or groups of atoms called **functional groups**.

Functional groups are particular groups of atoms, which may or may not include carbon, but which determine the name and key chemical properties of the compound. Organic compounds are grouped into families, called **classes**, and within each class are **homologous series**.

The length of the carbon skeleton is represented in the name of the molecule, as shown in Table 12.1.1, which shows the first 10 members of the alkane homologous series, consisting purely of carbon and hydrogen atoms. This name stem is used to identify the number of carbon atoms in the skeleton.

The class of a compound refers to the category of molecules that share the same functional group. Members of a homologous series have the same functional group and therefore similar chemical properties, but differ by the length of their carbon chains, leading to variations in their

physical properties, such as melting and boiling point. Table 12.1.2 shows some commonly occurring functional groups, their names, and classes of compounds that contain that group.

For example, alcohols are the class of compounds containing the hydroxyl (–OH) functional group. Ethanol has two carbons and a hydroxyl group, whereas hexanol contains six carbons and a hydroxyl group (Figure 12.1.1). They are referred to as a homologous series because their only difference is the length of their carbon chain.

Syllabus link
Chapter 7 of *Nelson QCE Chemistry Units 1 and 2* introduced the first 10 alkanes.

TABLE 12.1.1 The names of the first 10 alkanes

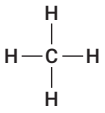
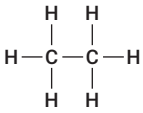
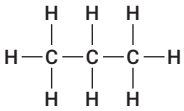
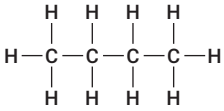
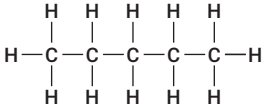
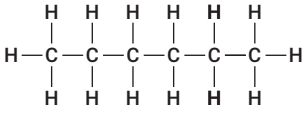
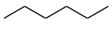
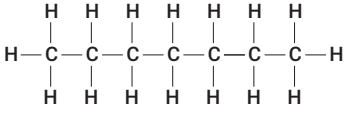
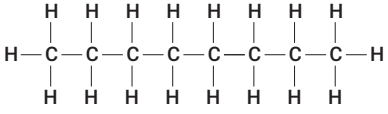
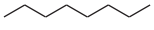
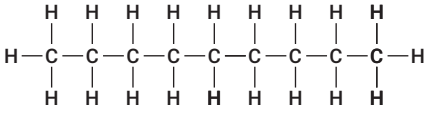
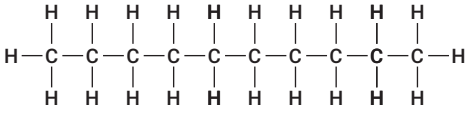
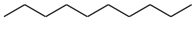
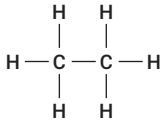
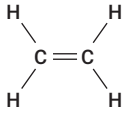
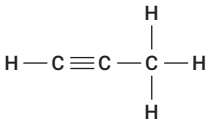
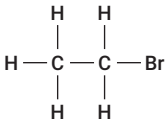
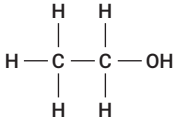
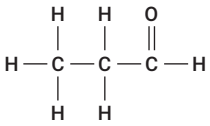
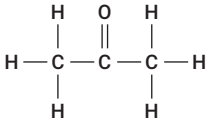
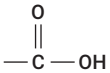
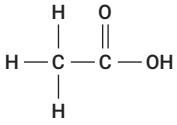
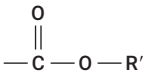
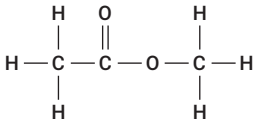
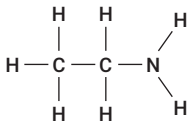
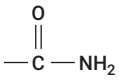
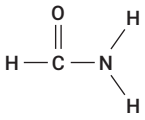
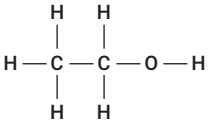
Number of carbon atoms	Name stem	Alkane	Molecular formula	Structural formula	Skeletal diagram
1	Meth-	Methane	CH_4		
2	Eth-	Ethane	C_2H_6		
3	Prop-	Propane	C_3H_8		
4	But-	Butane	C_4H_{10}		
5	Pent-	Pentane	C_5H_{12}		
6	Hex-	Hexane	C_6H_{14}		
7	Hept-	Heptane	C_7H_{16}		
8	Oct-	Octane	C_8H_{18}		
9	Non-	Nonane	C_9H_{20}		
10	Dec-	Decane	$C_{10}H_{22}$		

TABLE 12.1.2 The functional groups of different organic compounds

Name	Functional group	Prefix or suffix	Class	General formula	Example
Alkane	–C–C–	-ane	Alkane	C_nH_{2n+2}	 Ethane
Alkene	—C=C—	-ene	Alkene	C_nH_{2n}	 Ethene
Alkyne	—C≡C—	-yne	Alkyne	C_nH_{2n-2}	 Propyne
Haloalkane	Halogen (–X) –F, –Cl, –Br, –I	fluoro-, chloro-, bromo-, iodo-	Haloalkanes	R–X	 Bromoethane
Hydroxyl	–OH	-ol hydroxyl-	Alcohols	R–OH	 Ethanol
Aldehyde		-al	Aldehydes	R–CHO	 Propanal
Ketone		-one oxo-	Ketones	R–CO–R′	 Propanone
Carboxyl		-oic acid	Carboxylic acids	R–COOH	 Ethanoic acid
Ester		alkyl -oate	Esters	R–COOR′	 Methyl ethanoate

Name	Functional group	Prefix or suffix	Class	General formula	Example
Amine	$-NH_2$	-amine	Amines	$R-NH_2$	 Ethanamine
Amide		-amide	Amides	$R-CONH_2$	 Methanamide


Ethanol

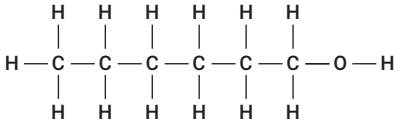
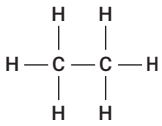

Hexanol

FIGURE 12.1.1 Ethanol and hexanol

A general formula R–OH indicates the structure of alcohols. R signifies an alkyl group of any hydrocarbon attached to the functional group of the molecule.

Molecules are represented by a **structural formula**, which shows all the bonds between the atoms within a molecule and indicates how the atoms are joined together. For example, ethane is represented as two carbons and six hydrogens joined together with single bonds (Figure 12.1.2).

structural formula a displayed arrangement of the atoms in a molecule, showing all bonds


Structural formula

CH_3CH_3
Semistructural formula

C_2H_6
Molecular formula

CH_3
Empirical formula

FIGURE 12.1.2 Structural, semi-structural, molecular and empirical formulas of ethane

Sometimes a condensed structural formula or **semi-structural formula** is used, to be more concise. In a semi-structural formula, no bonds are shown. Each carbon atom in the chain is listed in order. Carbon is listed, followed by the atoms or functional groups that are attached to that carbon and so on. Where multiple atoms (including branched chains) are bonded to a carbon atom in the middle of a chain, brackets are used (see methylpropane in Table 12.1.3). Table 12.1.3 shows the structural and semi-structural formulas of some different molecules. The semi-structural formula of ethane is CH_3CH_3; this indicates that each carbon atom is bonded to three hydrogen atoms.

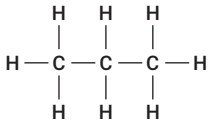
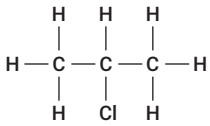
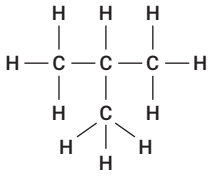
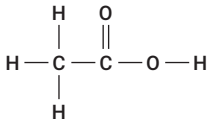
The **molecular formula** shows how many atoms of each type are present in the molecule, but not how they are bonded. The **empirical formula** shows the simplest whole-number ratio of atoms or ions in the substance (Figure 12.1.2).

semi-structural formula a condensed version of the structural formula showing the sequence of atoms listed by carbon atom but not the bonds

molecular formula a representation of the actual number of atoms of each element present in one molecule of a substance

empirical formula the simplest whole-number ratio of atoms or ions in a substance

TABLE 12.1.3 The structural and semi-structural formulas of some different molecules

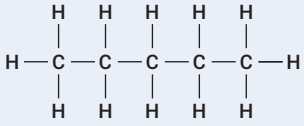
Name	Structural formula	Semi-structural formula	Molecular formula	Empirical formula
Propane		$CH_3CH_2CH_3$	C_3H_8	C_3H_8
2-Chloropropane		$CH_3CHClCH_3$	C_3H_7Cl	C_3H_7Cl
Methylpropane		$CH_3CH(CH_3)CH_3$	C_4H_{10}	C_2H_5
Ethanoic acid		CH_3COOH	$C_2H_4O_2$	CH_2O

LEARNING CHECK 12.1

DESCRIBING

1 **Describe** what is meant by a functional group and provide an example.

2 **Determine** the semi-structural, molecular and empirical formulas for pentane (structural formula shown here).



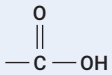
3 **Determine** the names of the following functional groups.

a —OH

b C=C

c 

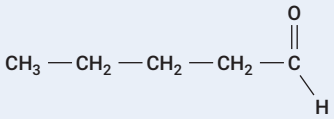
d —Cl

e 

APPLYING

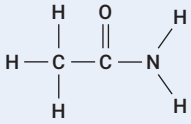
4 **Classify** the following organic molecules according to the class they belong to.

a

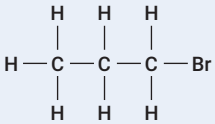


b $CH_3—CH_2—CH_2—COOH$

c

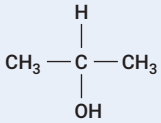


d

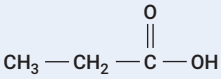


5 **Identify** the functional group in each of the following compounds.

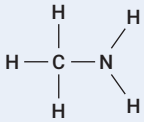
a



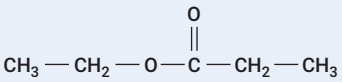
b



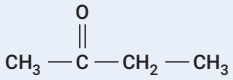
c



d



e



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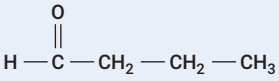
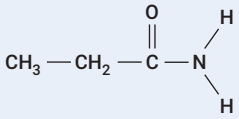


g



12.2 Saturated and unsaturated organic compounds

Syllabus link
Chapter 7 of *Nelson QCE Chemistry Units 1 & 2* introduced hydrocarbons.

Hydrocarbons are compounds made up of only hydrogen and carbon. Almost all other organic compounds can be considered as derivatives of these simple compounds. Because these compounds are primarily composed of carbon, it is important to remember that each carbon atom will almost always form four bonds with its four valence electrons.

One, two or three pairs of the valence electrons from adjoining atoms may be involved in bonding. For example, single bonds (C–C), double bonds (C=C) or triple bonds (C≡C) can form between carbon atoms. Valence electrons not involved in forming carbon–carbon bonds form bonds with other elements, typically hydrogen, oxygen and nitrogen.

When hydrocarbon compounds contain only single bonds between carbon atoms, they are known as **saturated compounds** because the carbon atoms have the maximum number of hydrogen atoms attached. When double or triple bonds are present between carbon atoms, the hydrocarbons are known as **unsaturated compounds** because they contain fewer hydrogen atoms due to the presence of these multiple bonds between carbon atoms (Figure 12.2.1).

saturated compound
an organic compound containing only single bonds between carbon atoms

unsaturated compound
organic compound that has at least one double bond or triple bond between carbon atoms

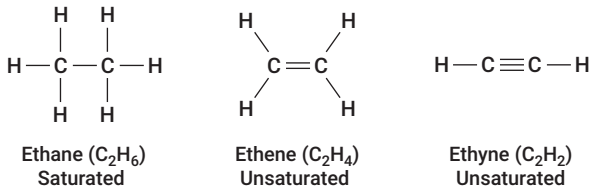


FIGURE 12.2.1 Saturated and unsaturated hydrocarbons containing two carbon atoms

Alkanes, alkenes and alkynes

Alkanes, alkenes and alkynes are hydrocarbons that differ in the presence of single, double or triple bonds between carbons. Each of these classes of organic molecules are named according to the number of carbons in the chain (see Table 12.1.1).

alkane a class of hydrocarbons containing carbon chains with only single bonds between carbons

alkene a class of hydrocarbon with at least one double bond present between two carbons

alkyne a class of hydrocarbon with at least one triple bond present between two carbons

Alkanes are chains of carbon compounds that contain only single bonds between carbon atoms and have the general formula C_nH_{2n+2}. **Alkenes** are chains of carbon compounds that contain at least one carbon–carbon double bond and have the general formula C_nH_{2n}. **Alkynes** are chains of carbon compounds that contain at least one carbon–carbon triple bond and have the general formula C_nH_{2n-2}. The names of alkanes, alkenes and alkynes indicate the number of carbons and the types of bonds within the molecule. Alkanes end in *-ane*, alkenes end in *-ene* and alkynes end in *-yne*. A number at the start of the name indicates the location of the double or triple bond in the carbon chain **(Figure 12.2.2)**.

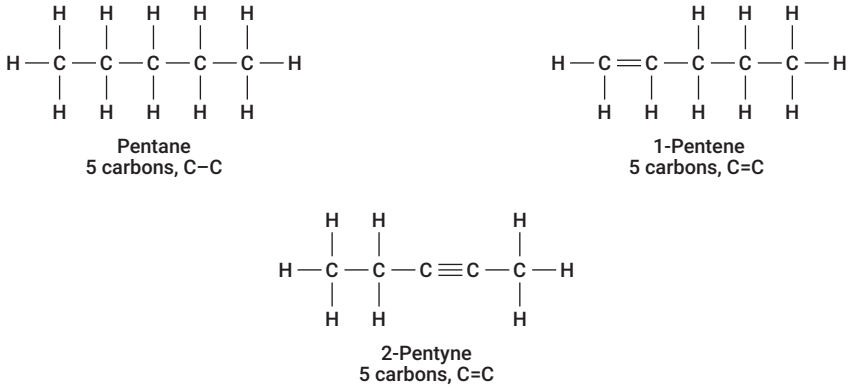


FIGURE 12.2.2 Pentane, 1-pentene and 2-pentyne

branched hydrocarbon a hydrocarbon that has one or more carbon side chains attached

Branched hydrocarbons are formed when one or more carbon-containing branches, or side chains, attach to a straight-chain hydrocarbon to produce a more complex molecular structure with differing properties. Examples of branched chain hydrocarbons (alkyl chains) are shown in **Figure 12.2.3**.

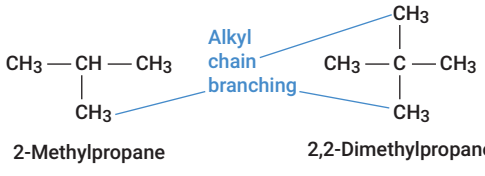


FIGURE 12.2.3 Branched chain hydrocarbons

The name of the branched hydrocarbon reflects the position and size of the alkyl chain. In the example in Figure 12.2.3, the *2-methyl* indicates that there is a one-carbon methyl group (**alkyl group**) attached to carbon number 2 in the propane chain, and *2,2-dimethyl* indicates there are two methyl groups attached to carbon number 2. Note that when writing the name, numbers are separated by commas (2,2) and numbers and words are separated by hyphens (2-methyl). The alkane name is written as one word (2-methylpropane).

alkyl group a group consisting of carbon and hydrogen atoms formed by the replacement of a hydrogen from an alkane

Haloalkanes have the halogens I, F, Cl or Br joined to alkane chains. Haloalkanes are classified as primary (1°), secondary (2°), or tertiary (3°) depending on the number of carbon atoms bonded (represented by R) to the halogen-bearing carbon **(Figure 12.2.4)**.

haloalkane an alkane with a halogen (I, Cl, F or Br) attached to a carbon

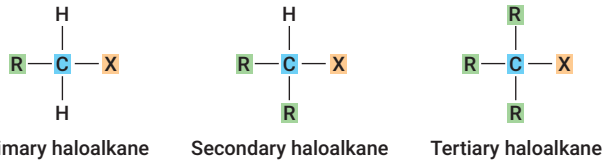


FIGURE 12.2.4 Haloalkanes, where X represents a halogen. The halogen-bearing carbon is highlighted in blue. R represents a carbon chain.

Haloalkanes are named according to the halide functional group and its position. For example, 3-chloropentane has a chlorine attached to the third carbon in a five-carbon chain. 1,2-Dibromopropane has two bromines – one on the first carbon and one on the second carbon of a three-carbon chain. **Figure 12.2.5** shows some examples of haloalkanes.

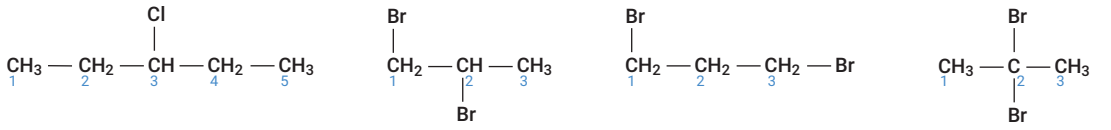


FIGURE 12.2.5 Haloalkanes are named according to the halide and its position.

Alcohols (primary, secondary and tertiary)

Alcohols are any class of organic molecules that contain one or more hydroxyl (–OH) functional groups attached to the carbon atoms in a chain. They are named with the suffix *–ol* at the end of the carbon chain (e.g. butanol). Alcohols are classified as primary (1°), secondary (2°) or tertiary (3°) depending on the number of carbon atoms bonded to the hydroxyl-bearing carbon **(Figure 12.2.6)**. In a primary alcohol, the OH-bearing carbon is bonded to one other carbon in the chain. In a secondary alcohol, the OH-bearing carbon is bonded to two other carbons. In a tertiary alcohol, the OH-bearing carbon is bonded to three other carbons.

alcohol an organic molecule containing one or more hydroxyl functional groups

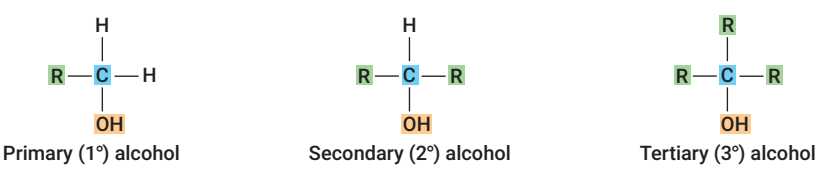


FIGURE 12.2.6 Primary, secondary and tertiary alcohols. The hydroxyl-bearing carbon is highlighted in blue. R represents a carbon chain.

The position of the hydroxyl group is also important when naming the molecule. For example, 1-propanol means that the –OH is joined to the first carbon in the chain, whereas in 2-propanol it is attached to the second carbon in the chain **(Figure 12.2.7)**.

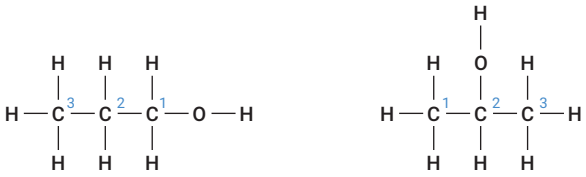


FIGURE 12.2.7 When naming alcohols, the position of the hydroxyl group is important.

Aldehydes, ketones and carboxylic acids

aldehyde an organic molecule containing an aldehyde functional group at the end of the carbon chain

ketone an organic molecule containing a carbonyl functional group within the carbon chain

carboxylic acid an organic molecule containing a carboxyl functional group

Aldehydes, ketones and carboxylic acids each contain a carbonyl (–C=O) group. In an **aldehyde**, the carbonyl group is at the end of the carbon chain with another hydrogen (–CHO). In a **ketone**, the carbonyl group (–C=O) is contained within the carbon chain. In a **carboxylic acid**, a carboxyl group (–COOH) consists of a double-bonded oxygen atom (–C=O) and a hydroxyl group (–OH).

The names of aldehydes end in *-al*, ketones end in *-one*, and carboxylic acids end in *-oic acid*. In the examples in **Figure 12.2.8**, propanal has three carbons with an aldehyde group attached to one of the end carbons, propanone has three carbons with a ketone group attached to the middle carbon, and propanoic acid has three carbons with a carboxylic acid group attached to one of the end carbons.

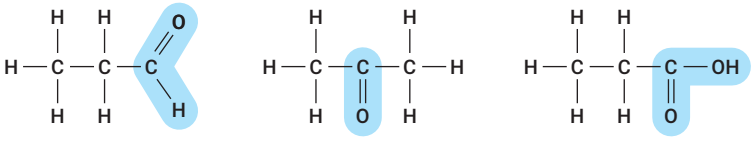


FIGURE 12.2.8 Aldehydes, ketones and carboxylic acids contain a C=O group.

amine an organic molecule containing an amine ($–NH_2$) functional group

amide an organic molecule containing an amide ($–CONH_2$) functional group

Amines and amides

Amines and **amides** contain a nitrogen, which can only bond to three other atoms. Amines have the $–NH_2$ attached to a carbon in a hydrocarbon chain. Amides have a carbonyl (C=O) group attached to the same carbon as the $–NH_2$ in the carbon chain **(Figure 12.2.9)**.

FIGURE 12.2.9 Amines and amides contain nitrogen.

When naming amines, the suffix *-amine* is attached to the end of the carbon chain name (e.g. propanamine). When naming amides, the suffix *-amide* is attached to the end of the carbon chain name (e.g. ethanamide).

Esters

Esters are the product of a reaction between a carboxylic acid and an alcohol. This type of reaction is called an esterification reaction because an ester is formed. The two hydrocarbons are joined by an **ester link**, which has the general structure of R–COO–R′. They are named according to the two molecules from which they are formed.

When naming esters, the first part of the name is indicative of the original alcohol molecule as an *alkyl*, and the second part of the name indicates the original carboxylic acid, ending in *-oate*. For example, the ester ethyl ethanoate is formed from ethanol and ethanoic acid (Figure 12.2.10). Note that when naming esters, the alkyl part of the name is separated from the remainder of the name.

ester an organic molecule containing the ester functional group, –COO–

ester link the –COOC– group that links two alkyl chains in an ester molecule

Weblink
Functional groups

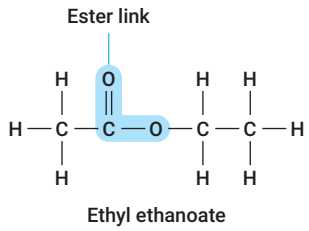


FIGURE 12.2.10 The ester ethyl ethanoate

LEARNING CHECK 12.2

DESCRIBING

1 **Identify** the class of organic molecule that includes the following.
   - **a** Hydroxyl group
   - **b** Halide
   - **c** Carboxyl group
   - **d** Double bond between carbons in the main carbon skeleton
   - **e** NH_2 attached to the carbon chain

2 **Compare** the structure of a ketone, aldehyde and a carboxylic acid.

APPLYING

3 **Determine** the semi-structural formula of:
   - **a** pentane
   - **b** methanol
   - **c** 1-bromobutane
   - **d** 2-pentanol.

12.3 Naming organic compounds

The International Union of Pure and Applied Chemistry (IUPAC) has devised a system of naming organic compounds. This naming system allows scientists to differentiate between molecule types, structure, components and chain length.

The systematic naming of organic compounds means that the structure of the molecule can be directly deduced from the name. Therefore, the name needs to describe the carbon skeleton from which the molecule is formed, together with the functional groups that are present and the specific location of these groups on the carbon skeleton.

According to the IUPAC system, organic molecules are named in three parts: prefix–stem–suffix. The **prefix** and **suffix** describe the functional groups in the molecule. Table 12.1.2 shows some of the prefixes and suffixes that can be used to indicate the functional group present. The **stem** describes the length of the carbon skeleton. Table 12.1.1 shows the first 10 stems that are used, according to the number of carbon atoms in the chain.

prefix a part of the name of an organic molecule that denotes a functional group and its position on the carbon chain; it comes at the start of the name

suffix a part of the name of an organic molecule that denotes a functional group and its position on the carbon chain; it comes at the end of the name

stem the part of the name of an organic molecule that denotes the length of the longest carbon chain

Therefore, to name an organic molecule, we need to follow these steps:

1. Establish the number of carbon atoms in the *longest continuous chain* in the molecule. The stem of the molecule is named accordingly, using the names shown in Table 12.1.1. Note that the way in which molecules can appear to be drawn can be misleading, as shown in Figure 12.3.1.

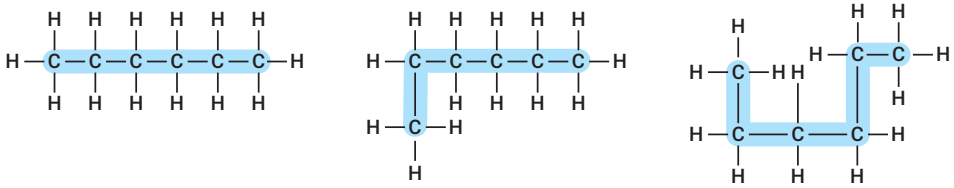


FIGURE 12.3.1 All of these molecules have six carbons in a continuous chain so are different representations of the same molecule, hexane.

2. Identify the functional groups in the molecule, and, using the prefix or suffix listed in Table 12.1.2, name and number them according to their position on the longest chain of carbon atoms. Insert a hyphen between the number and the name of the molecule. Molecules can be represented in a number of different orientations, so by convention we make the numbers associated with each functional group *as low as possible* reading from either direction. For example, Figure 12.3.2 shows two molecules where this convention is important. The first molecule is named 2-chlorobutane, not 3-chlorobutane, and the second molecule is 1-butanol, not 4-butanol.

   For functional groups indicated by a suffix rather than a prefix, the number can be written before the stem or between the stem and the suffix. Therefore, the molecule 1-butanol could also be written as butan-1-ol. Both names are acceptable according to the IUPAC system.

FIGURE 12.3.2 The molecules 2-chlorobutane and 1-butanol. In both molecules, the carbon atoms could either be numbered from left to right or from right to left. The convention is that the numbers are always as small as possible.

3. For alkenes and alkynes, the position of the double or triple bond is indicated by listing the lower of the numbers of the two carbon atoms. **Figure 12.3.3** shows two examples of this.

2-Pentene, *not* 3-pentene

3-Hexyne, *not* 4-hexyne

FIGURE 12.3.3 The numbering should always be as low as possible.

4. If the molecule has a branched carbon chain, then the sections that are not part of the longest chain are known as **alkyl chains** and are named according to **Table 12.3.1**. The alkyl chains are named and numbered according to their position on the longest chain in the same way as a functional group, as seen in **Figure 12.3.4**. Any alkyl groups are named alphabetically, i.e. ethyl comes before methyl irrespective of the numbering.

alkyl chain a carbon group branch attached to a main carbon chain; commonly found as side groups in organic molecules and are often represented by the symbol R in chemical structures

TABLE 12.3.1 The names of the first 10 alkyl chains

Number of carbon atoms in the branch (alkyl group)	Name of alkyl group
1	Methyl
2	Ethyl
3	Propyl
4	Butyl
5	Pentyl
6	Hexyl
7	Heptyl
8	Octyl
9	Nonyl
10	Decyl

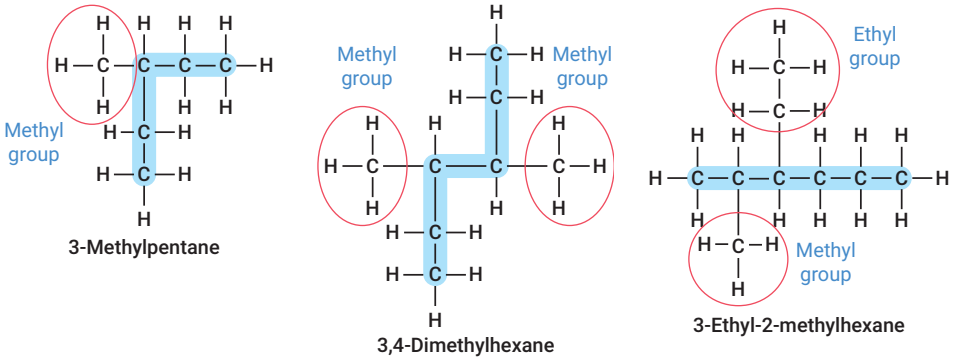


FIGURE 12.3.4 Branched chain alkanes

5. If there is more than one of the same functional group or alkyl chain in the molecule, then the prefixes di-, tri- or tetra- are used. The numbers of each of the groups are indicated first, separated by commas, as seen in **Figure 12.3.5**.

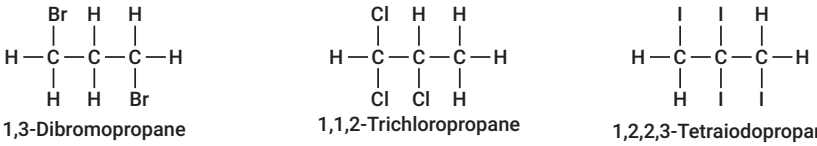


FIGURE 12.3.5 Molecules with more than one of the same functional group

6. If one of the functional groups is a terminal functional group (can only exist at the end of a chain) such as a carboxyl or an aldehyde group, then the carbon atom to which this group is attached is always numbered as 1, as shown in **Figure 12.3.6**.

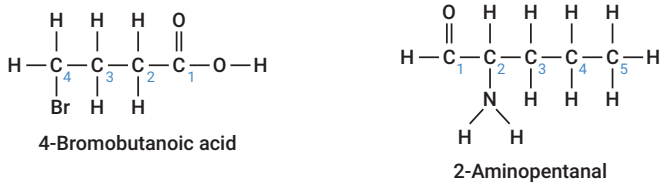


FIGURE 12.3.6 Examples of molecules with terminal functional groups

7. If there are several functional groups, the functional group with the highest priority is the one that gives its suffix to the name of the molecule. The order of priority is shown in **Table 12.3.2**. For example, there is a ketone and an amine present in CH_3–CO–CH_2–NH_2. The substance is priority named as a ketone and the amine as a side chain (i.e. 3-aminopropan-2-one).

TABLE 12.3.2 Order of priority of the different functional groups

Functional group	Priority
Carboxyl group (R–COOH)	Highest priority
Ester (R–COOR')	
Amide (R–$CONH_2$)	
Aldehyde (R–CHO)	
Alcohol (R–OH)	
Ketone (R–CO–R')	
Amine (R–NH_2)	
Alkene (C_nH_{2n})	
Alkyne (C_nH_{2n-2})	
Alkane (C_nH_{2n+2})	
Akyl halide (R–X)	Lowest priority

8. If there is more than one functional group of similar priority, then the functional groups are listed in alphabetical order, each with the number indicating its position on the longest chain. **Figure 12.3.7** shows an example of this naming convention.

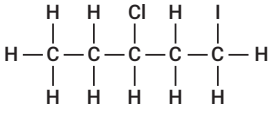


FIGURE 12.3.7 3-Chloro-1-iodopentane

If one of the functional groups can be represented by either a prefix or a suffix, then this is used when the other functional group does not have this option. **Figure 12.3.8** shows the molecule 2-hydroxypropanoic acid (commonly known as lactic acid), where the hydroxyl group is indicated by the prefix and the carboxyl group by the suffix.

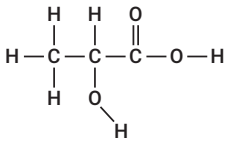


FIGURE 12.3.8 2-Hydroxypropanoic acid

9. The names of esters consist of two words. Esters are formed from the reaction of an alcohol and a carboxylic acid.

- The first part of the name is the alkyl group. This comes from the alcohol from which the ester was formed.
- The second part of the name comes from the carboxylic acid. The end of the acid name is changed from *-oic acid* to *-oate*. **(Figure 12.3.9)**.

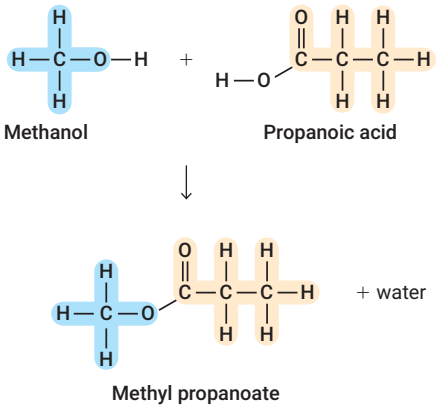


FIGURE 12.3.9 The formation of methyl propanoate, showing the origin of the name

- For amides, the end of the acid name is changed from *-oic acid* to *-anamide*. In addition, the alkyl chain that originated from the amine is written as *N-alkyl-* to emphasise that it is joined directly to the nitrogen atom **(Figure 12.3.10)**.

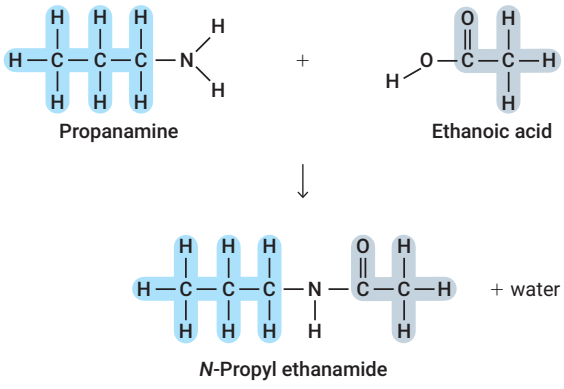


FIGURE 12.3.10 The formation of *N*-propyl ethanamide, showing the origin of the name

Worksheet
Structural formulas and IUPAC rules

Weblink
The basics of organic nomenclature

Although these naming rules may seem complicated, with practice you will understand how the IUPAC naming system is very helpful in revealing the structure of organic compounds. Note that the syllabus does not require you to name amides.

LEARNING CHECK 12.3

DESCRIBING

1 **Determine** the organic structure of:

a propane
b hexane
c octane
d 1-hexyne
e 2-butene
f 1-hexene
g 2-heptene

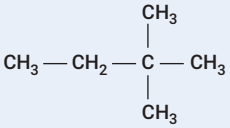
2 **Determine** the semi-structural formula of:

a 1-hexyne
b 3-hexyne
c 3,3-dimethyl-1-butene
d 3-methyl-1-butanol
e butanal
f 3-methyl-2-pentanone
g 2,3-dimethylbutanoic acid
h butyl ethanoate
i 2-methyl-3-octanamine
j *N*-methyl methanamide.

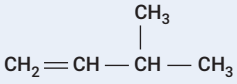
APPLYING

3 Name the following compounds.

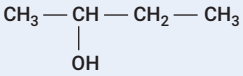
a



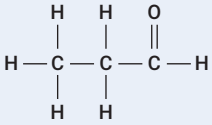
b



c

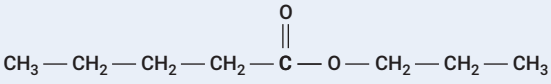


d



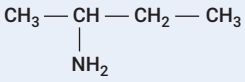
e $HOOCCH_2CH_2CH_2CH_3$

f

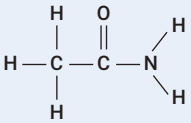


g $CH_3CH_2CH_2CH_2CH_2CH_2OH$

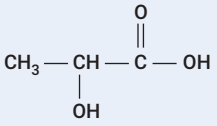
h



i



j



k $ClCH_2CH_2CH_2OH$

4 **Determine** the structural formula of:

a 3-ethyl-3-methylhexane
b 2-methyl-2-pentene
c 2,3-dimethyl-3-pentanol
d 3-methyl-4-octanol
e 4-methylpentanal
f 3-hexanone
g ethanoic acid
h 2-methylpropanoic acid
i propyl ethanoate.

12.4 Structural isomers

Isomers are molecules with the same **molecular formula** (i.e. number of each type of atom) but different arrangements of atoms. **Structural isomers** are molecules in which the number and arrangements of bonds between the atoms, and therefore the arrangement of atoms, is different. For example, Figure 12.4.1 shows three structural isomers with the same molecular formula of C_5H_{12}.

molecular formula the number of atoms of each element in a molecule

structural isomers molecules with the same molecular formula but different arrangements of atoms

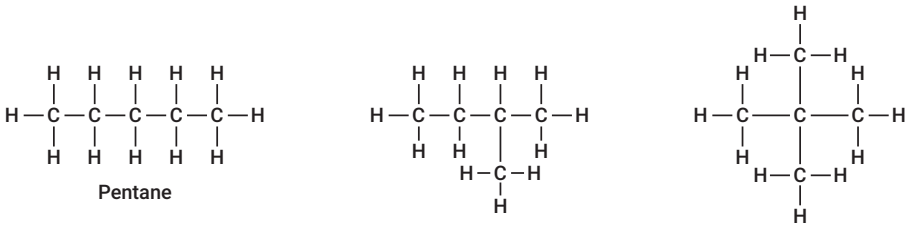


FIGURE 12.4.1 Three structural isomers of C_5H_{12}

The number of possible structural isomers increases with the size of the molecule and the number of different elements present. It is important to name each isomer because there are often many possible representations of the same molecule. By identifying the longest chain of carbon atoms present and the position of each of the different functional groups or branches, we can identify the name and make it clear whether two molecules are in fact the same compound. Figure 12.4.2 shows an example of this.

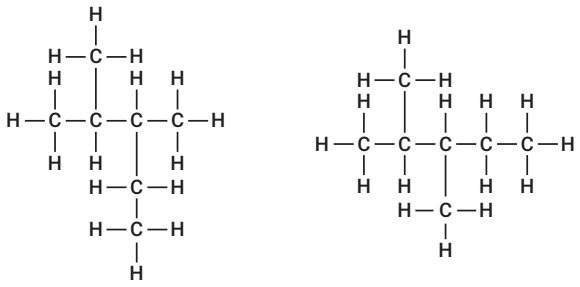


FIGURE 12.4.2 Two different representations of 2,3-dimethylpentane

Most structural isomers have the same functional groups; however, carboxylic acids and esters are usually structural isomers of one another (Figure 12.4.3).

Methyl propanoate and butanoic acid have the same molecular formula of $C_4H_8O_2$ and are therefore structural isomers of one another, with different functional groups

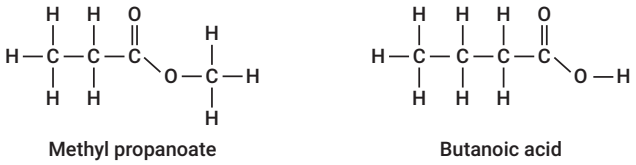


FIGURE 12.4.3 These structural isomers have different functional groups.

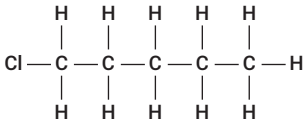
WORKED EXAMPLE 12.4.1

There are eight structural isomers with a molecular formula of $C_5H_{11}Cl$. Draw and name each one.

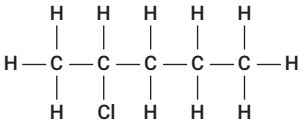
ANSWER

A good strategy is to start with the molecules with the longest continuous chain of carbon atoms and then gradually reduce the length of the chain until all the molecules have been identified.

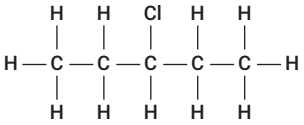
1 Determine the longest chain and its variations.
Molecules with a longest chain of five carbon atoms:



1-Chloropentane

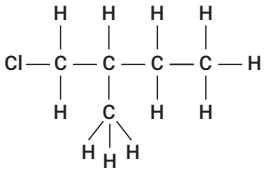


2-Chloropentane

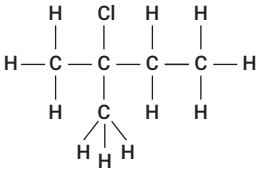


3-Chloropentane

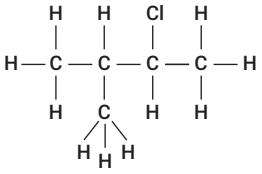
2 Determine the next longest chain and its variations.
Molecules with a longest chain of four carbon atoms:



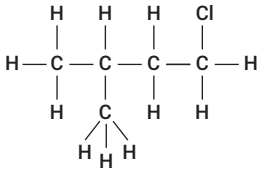
1-Chloro-2-methylbutane



2-Chloro-2-methylbutane

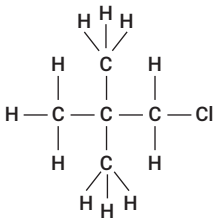


2-Chloro-3-methylbutane



1-Chloro-3-methylbutane

3 Determine the shortest longest chain and its variations.
Molecules with a longest chain of three carbon atoms:



1-Chloro-2,2-methylpropane

LEARNING CHECK 12.4

DESCRIBING

1 **Identify** and draw the semi-structural formulas of two isomers of an alcohol with the molecular formula C_4H_9OH.

2 **Describe** the term 'structural isomer' and give examples to illustrate.

APPLYING

3 **Determine** the semi-structural formulas and name the straight-chain isomers of C_5H_{10}.

4 **Determine** the semi-structural formulas for three esters of molecular formula $C_4H_8O_2$ and name them.

Worksheet
Isomers

12.5 Stereoisomers

Stereoisomers are organic molecules that have the same number of atoms and bonding type as another compound but differ in their spatial arrangement of atoms. Stereoisomers have an important role in organic chemistry and biochemistry because their different spatial arrangements can lead to distinct chemical properties and biological activity.

Geometric isomers and **optical isomers** are two types of isomers that differ in their spatial arrangement, but they have distinct characteristics. Geometrical isomerism is possible in molecules that have a double bond. Double bonds are rigid and do not allow free rotation about them so atoms attached to double bonds are fixed in space. Different spatial arrangements of atoms or groups around the rigid double bond leads to distinct isomers with the same chemical formula but different properties. This allows for *cis–trans* isomers. In contrast, optical isomers, or enantiomers are molecules that are non-superimposable mirror images of one another. Figure 12.5.1 illustrates the different types of isomers.

stereoisomers molecules with the same molecular formula but different spatial arrangements of atoms

geometric isomers molecules with the same structural formula but different arrangements of atoms in space, typically around a rigid central double bond

optical isomers molecules that are non-superimposable mirror images of one another

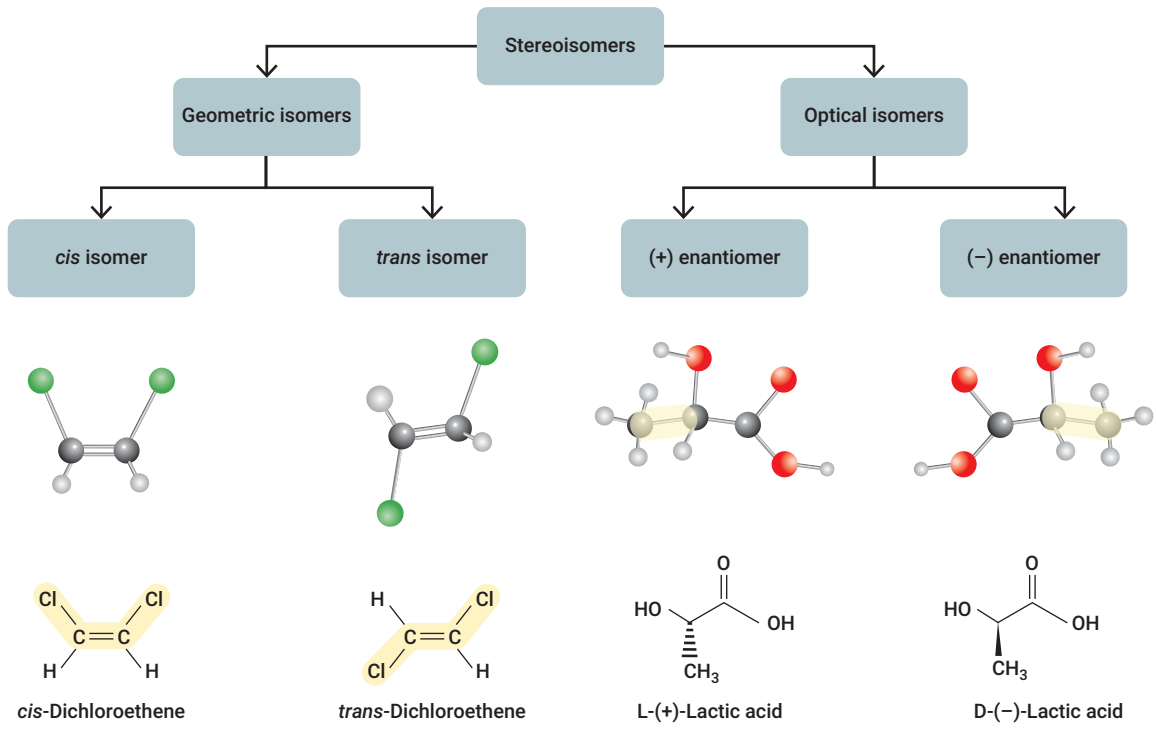


FIGURE 12.5.1 Types of stereoisomers. In *cis*-dichloroethene, the chlorine atoms are on the same side of the double bond; in *trans*-dichloroethene, the chlorine atoms are on opposite sides of the double bond (geometric isomers). L-(+)-Lactic acid and D-(–)-lactic acid are mirror images of each other and cannot be superimposed on each other (optical isomers).

Geometric isomers

The carbon–carbon double bond in alkenes gives rise to geometric isomers. The double bond makes the shape of alkene molecules significantly different from molecules without double bonds. The geometry around the double bond is planar with all the bond angles being 120°. Carbon atoms on either side of the double bond cannot rotate around the bond as can happen with single bonds. The isomerism resulting from the presence of a double bond is typically geometrical isomerism.

2-Butene exhibits stereoisomerism and forming geometric isomers. **Figure 12.5.2** shows the two forms of this molecule.

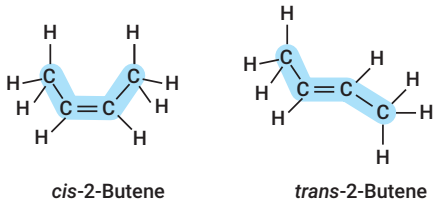


FIGURE 12.5.2 The *cis* and *trans* isomers of 2-butene

In *cis*-2-butene, the two methyl ($-CH_3$) groups are on the same side of the double bond. In *trans*-2-butene, they are on opposite sides. The chemical properties of geometric isomers are very similar, as could be predicted from their identical size and composition. However, their slightly different shapes results in different physical properties.

These two structures represent distinct compounds with different melting points, boiling points and densities, as shown in **Table 12.5.1**.

TABLE 12.5.1 The different properties of *cis*- and *trans*-2-butene

Compound	Melting point (°C)	Boiling point (°C)	Density (g mL^{-1})
cis-2-Butene	–138.9	3.7	0.616
trans-2-Butene	–105.6	0.9	0.599

Optical isomers

Optical isomers, or enantiomers, are pairs of stereoisomers that are non-superimposable mirror images of each other **(Figure 12.5.3)**. They arise from the presence of a chiral centre, usually a **chiral carbon atom** bonded to four different groups or atoms. This results in the different arrangements of the molecule. The two forms of optical isomer are known as **enantiomers**.

chiral carbon atom a carbon atom that is bonded to four different groups or atoms, resulting in two possible arrangements (optical isomers) of the molecule

enantiomers the mirror image forms of optical isomers

The two enantiomers have identical physical properties (e.g. melting and boiling points) except for their interaction with plane-polarised light and some chemical reactions. One enantiomer rotates plane-polarised light in a clockwise direction (+, dextrorotatory), whereas the other rotates it in an anticlockwise direction (–, levorotatory).

Optical isomers can also exhibit significantly different biological activities. For example, in pharmaceuticals one enantiomer may be therapeutically active while the other could be inactive or even harmful. A common example of optical isomers is lactic acid, which exists as two enantiomers **(Figure 12.5.4)**: one that is biologically active (L-lactic acid) and the other that may have different properties and effects.

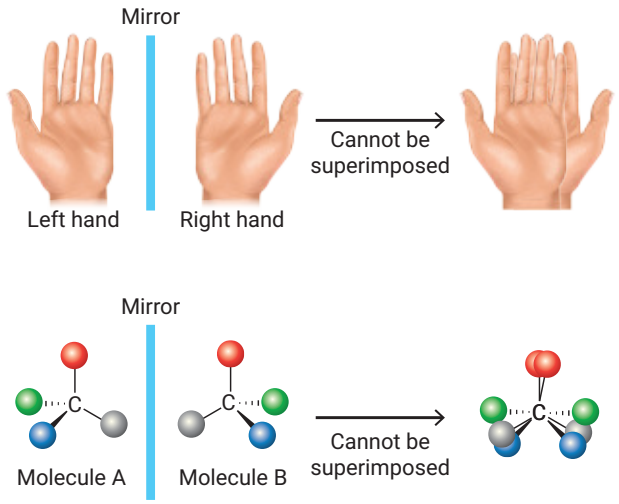


FIGURE 12.5.3 Mirror images are non-superimposable.

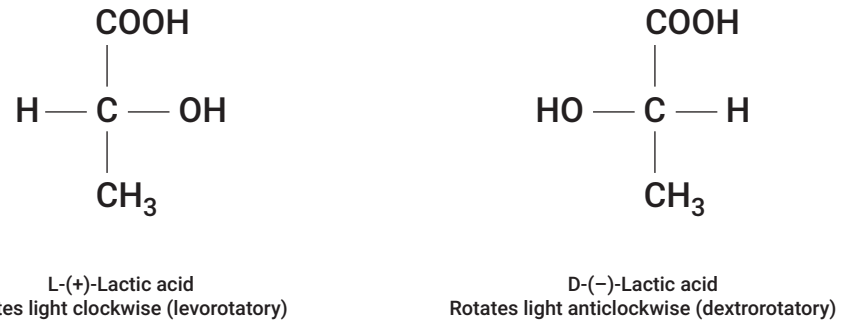


FIGURE 12.5.4 The optical isomers (enantiomers) of L-lactic acid

To identify the chiral carbon atom, look for the carbon atom that is bonded to four different groups or atoms. To draw the enantiomers, you can reflect one arrangement of the groups of atoms to create the two distinct structural representations of the compound (Figure 12.5.5).

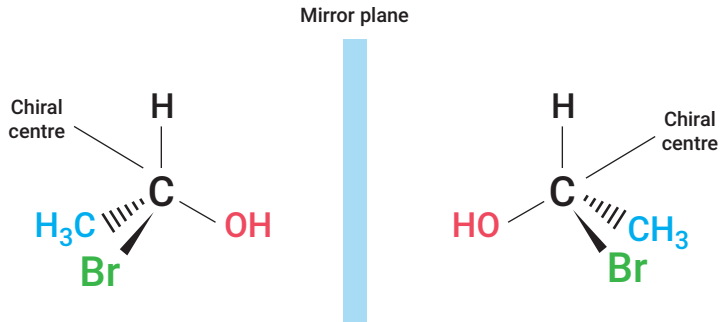


FIGURE 12.5.5 Identifying the chiral centre of two optical isomers

Weblinks
Optical isomers
Geometrical isomers

Worksheet
Interpreting structural representations of molecules

Practical
Constructing 3D models of organic molecules

LEARNING CHECK 12.5

DESCRIBING

1 **Describe** a structural isomer.

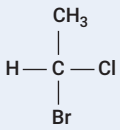
2 **Contrast** a geometric isomer with an optical isomer.

APPLYING

3 Draw and name the *cis* and *trans* isomers of 2-pentene.

4 **Identify** whether the following molecules contain chiral carbons:

a



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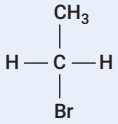
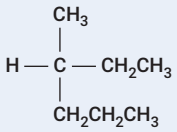
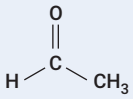


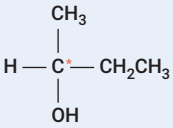
c



d



5 Draw an optical isomer of the following molecule of 2-butanol, using the identified chiral carbon centre.



Syllabus link
Molecular and empirical formulas were introduced in Chapter 9 of *Nelson QCE Chemistry Units 1 and 2*.

12.6 Determining formulas of organic compounds

To fully understand the composition of an organic compound, chemists determine its molecular, empirical and structural formulas by analysing data.

Molecular, empirical and structural formulas

empirical formula the simplest whole-number ratio of elements in a compound

The **empirical formula** of a compound shows the simplest whole-number ratio of elements present. It does not provide information about the actual number of atoms in a molecule but gives insight into the proportion of elements present.

For example, glucose ($C_6H_{12}O_6$) has the empirical formula CH_2O. This represents the simplest ratio (1:2:1) of carbon hydrogen, and oxygen atoms.

molecular formula the chemical formula of a molecule showing the actual number of atoms of each element present

The **molecular formula** shows the actual number of atoms of each element in the molecule. It is always a whole-number multiple of the empirical formula. It can be determined if the molar mass and empirical formula of the compound is known.

$$\text{Molecular formula} = (\text{empirical formula})n$$

where $n = \dfrac{\text{molecular mass}}{\text{empirical mass}}$

Note that n here represents an integer and is different from n 'mol'.

The **structural formula** provides information about how atoms are arranged within a molecule, showing functional groups and bonding patterns. You have practised writing these earlier in the chapter. Condensed structural formulas show how functional groups are arranged within the molecule. For example, ethanol has a condensed structural formula of CH_3CH_2OH, showing that it is a primary alcohol with the –OH group on the end of the molecule.

structural formula a formula that shows how atoms are arranged within a molecule

WORKED EXAMPLE 12.6.1

Determine the molecular formula of a molecule with the empirical formula of CH_2O and molecular mass 180.16 g.

ANSWER

1 Calculate the empirical mass of CH_2O.

Empirical mass $CH_2O = 12.01\text{ g} + (2 \times 1.01\text{ g}) + 16.00\text{ g}$
$= 30.03\text{ g}$

2 Calculate the integer (*n*).

$$n = \frac{180.16}{30.03}$$
$$= 6$$

3 Multiply the empirical formula by the integer, *n*.

Molecular formula $= 6 \times CH_2O$
$= C_6H_{12}O_6$.

Percentage composition of elements in an organic compound

The percentage composition of an element in a compound is the proportion of the element's mass in relation to the total molar mass of the compound:

$$\%\text{ composition} = \frac{\text{mass of element in 1 mol}}{\text{molar mass of compound}} \times 100$$

Worked example 12.6.2 shows how the percentage composition of carbon in ethanol can be calculated.

Syllabus link
Percentage composition was introduced in Chapter 9 of *Nelson QCE Chemistry Units 1 and 2*.

WORKED EXAMPLE 12.6.2

Calculate the percentage composition of carbon in ethanol (C_2H_6O, molar mass = 46.08 g mol^{-1}).

ANSWER

1 Calculate the molar mass of carbon in the ethanol (C_2H_6O).

$m = 2 \times 12.01$
$= 24.02\text{ g}$

2 Calculate the percentage composition of carbon in the ethanol molecule.

$$\%\text{ carbon} = \frac{24.02\text{ g}}{46.08\text{ g}} \times 100$$
$= 52.1\%$ carbon by mass

In some instances, the percentage of each element in a compound is presented. From this, it possible to determine the empirical and molecular formulas of the substance. The percentage can be converted to mass (in grams) if we assume it is a 100 g sample of the substance.

WORKED EXAMPLE 12.6.3

A compound is analysed and found to contain 85.7% carbon and 14.3% hydrogen by mass. Determine its empirical formula.

ANSWER

1 Convert percentages to grams (assuming 100 g sample).

Element	C	H
% (given)	85.7	14.3
Mass (in 100 g)	85.7	14.3

2 Convert grams to moles.

Element	C	H
Mass (in 100 g)	85.7	14.3
Number of moles (n)	$n(\text{C}) = \frac{85.7\text{ g}}{12.01\text{ g mol}^{-1}}$ $= 7.14$	$n(\text{H}) = \frac{14.3\text{ g}}{1.01\text{ g mol}^{-1}}$ $= 14.2$

3 Divide by the number of moles of each element by the smallest calculated mole value.

Element	C	H
Mass (in 100 g)	85.7	14.3
Number of moles (n)	$n(\text{C}) = \frac{85.7\text{ g}}{12.01\text{ g mol}^{-1}}$ $= 7.14$	$n(\text{H}) = \frac{14.3\text{ g}}{1.01\text{ g mol}^{-1}}$ $= 14.2$
Simplest ratio	$\frac{7.14}{7.14} = 1$	$\frac{14.2}{7.14} = 2$

4 Determine the empirical formula.

Empirical formula = CH_2

LEARNING CHECK 12.6

APPLYING

1 A compound with a molar mass of 180 g mol^{-1} contains 40.0% carbon, 6.7% hydrogen and 53.3% oxygen. **Determine** its molecular and empirical formula.

2 An organic compound has the molecular formula C_3H_6O. **Calculate** the percentage composition of each element in the compound.

3 A sample of a compound is found to contain 4.20 g of carbon, 0.70 g of hydrogen and 2.80 g of oxygen. **Determine** its empirical formula.

4 A compound is analysed and found to contain 79.9% carbon and 20.1% hydrogen. **Determine** its empirical formula.

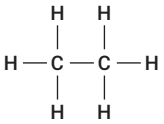
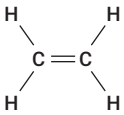
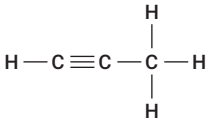
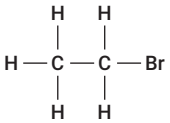
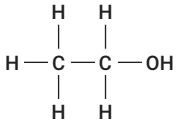
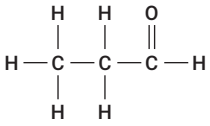
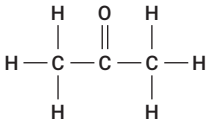
5 Two isomers, compound A and compound B, have the same percentage composition by mass: 54.5% carbon, 9.1% hydrogen and 36.4% oxygen. Their experimentally determined molar masses are 88 and 176 g mol^{-1}, respectively.

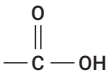
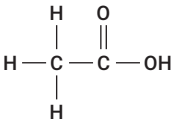
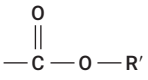
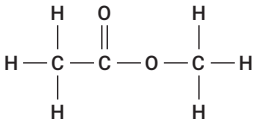
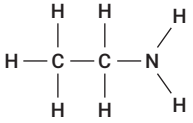
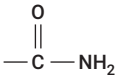
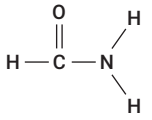
   a **Determine** the empirical formulas of compounds A and B.
   b **Determine** the molecular formulas of compounds A and B.
   c **Determine** possible structural formulas for compound A, if it was a carboxylic acid.

CHAPTER SUMMARY

Types of organic compounds

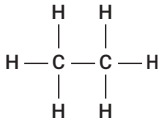
- A homologous series is a group of organic compounds that have the same general formula and exhibit similar chemical properties due to the presence of the same functional group.
- Saturated compounds only have single bonds between carbon atoms.
- Unsaturated compounds have at least one double or triple bond between carbon atoms.

Name	Functional group	Prefix or suffix	Class	General formula	Example
Alkane	–C–C–	-ane	Alkane	C_nH_{2n+2}	 Ethane
Alkene	—C=C—	-ene	Alkene	C_nH_{2n}	 Ethene
Alkyne	—C≡C—	-yne	Alkyne	C_nH_{2n-2}	 Propyne
Haloalkane	Halogen (–X) –F, –Cl, –Br, –I	fluoro-, chloro-, bromo-, iodo-	Haloalkanes	R–X	 Bromoethane
Hydroxyl	–OH	-ol hydroxyl-	Alcohols	R–OH	 Ethanol
Aldehyde		-al	Aldehydes	R–CHO	 Propanal
Ketone		-one oxo-	Ketones	R–CO–R′	 Propanone

Name	Functional group	Prefix or suffix	Class	General formula	Example
Carboxyl		-oic acid	Carboxylic acids	R–COOH	 Ethanoic acid
Ester		alkyl -oate	Esters	R–COOR′	 Methyl ethanoate
Amine	$-NH_2$	-amine	Amines	$R–NH_2$	 Ethanamine
Amide		-amide	Amides	$R–CONH_2$	 Methanamide

Formulas to represent organic compounds

- The structural formula shows all bonds. The semi-structural formula does not show all bonds; the carbons are written in order. The molecular formula shows the number of atoms of each element present in the substance.


Structural formula

CH_3CH_3
Semistructural formula

C_2H_6
Molecular formula

CH_3
Empirical formula

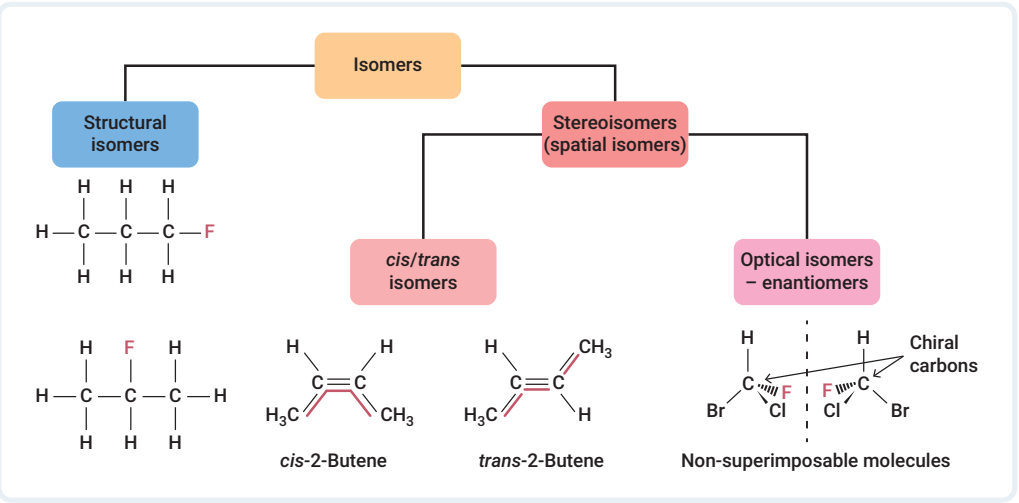
IUPAC naming

1. Identify the longest carbon chain as the base name.
2. Number the chain so that functional groups or substituents have the lowest numbers.
3. List substituents alphabetically; use di-, tri- etc. for multiples.
4. Naming functional groups:

Alkanes	Add prefixes (e.g. methyl, ethyl) and suffix -ane.
Alkenes/alkynes	Add suffix -ene (double bond) or -yne (triple bond).
Alcohols	Add suffix -ol and specify position; classify as primary, secondary or tertiary.
Aldehydes	Add suffix -al (terminal, so no need to indicate position).
Ketones	Add suffix -one and specify position.
Carboxylic acids	Add suffix -oic acid (always on carbon number 1).
Haloalkanes	Add prefix (fluoro-, chloro- etc.); classify as primary, secondary or tertiary.
Esters	Name alcohol part first; acid part ends with -oate.

Isomers

- Isomers have the same molecular formula but different structure.



Determining different formula of organic compounds

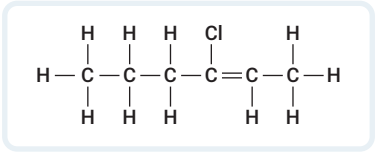
- The empirical formula shows the smallest whole-number ratio of the elements in a compound.
- The molecular formula shows the actual number of atoms of each element in a compound.
- Molecular formula = (empirical formula)n

  where n is an integer and $n = \dfrac{\text{molecular mass}}{\text{empirical mass}}$
- Percentage composition is calculated as:

  $$\%\ \text{composition} = \frac{\text{mass of element in 1 mol}}{\text{molar mass of compound}} \times 100$$

MULTIPLE CHOICE

1. What is the correct name for the following molecule?



A 4-Chloro-5-hexene
B 2-Chloro-2-hexene
C 3-Chloro-3-hexene
D 3-Chloro-2-hexene

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2. How many structural isomers have the molecular formula C_3H_6BrCl?

A 4
B 5
C 6
D 7

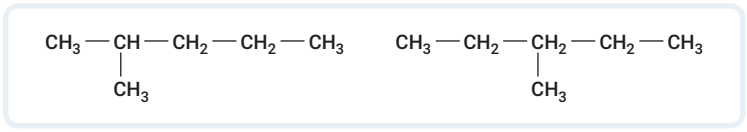
3. For which one of the following molecular formulas is there only one possible structure?

A C_3H_7Cl
B $C_3H_7CH_2OH$
C $C_3H_7NH_2$
D H_2NCH_2COOH

4. Identify which of the following is *not* one of the eight isomers of $C_5H_{11}Br$.

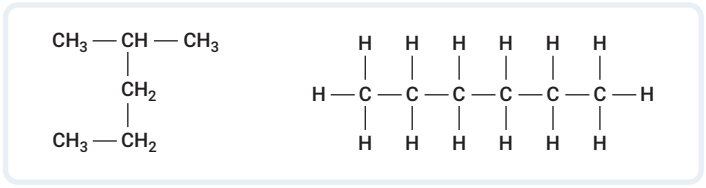
A 4-Bromobutane
B 1-Bromopentane
C 3-Bromopentane
D 2-Methylbutyl bromide

5. Classify the isomer type for the following pair of isomers.



A Structural
B Optical
C Geometric
D Stereoisomer

6. Identify the correct IUPAC names for the following pair of isomers.

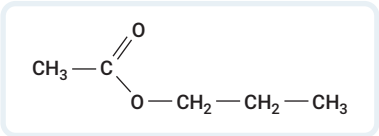


A 4-Methylpentane, hexane
B 1,3-Dimethylbutane, hexane
C 2-Methylpentane, hexane
D 1,3-Dimethylbutane, pentane

7. Identify which of the following molecules is a saturated hydrocarbon.

A C_6H_{10}
B C_6H_{12}
C C_6H_{14}
D C_5H_8

8. What is the correct IUPAC name for the following molecule?



A Ethyl ethanoate
B Propyl ethanoate
C Ethyl propanoate
D Propyl propanoate

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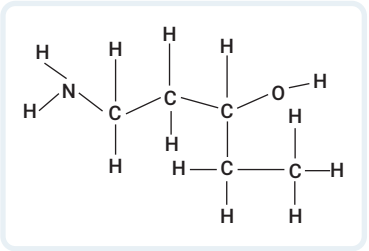
9. What is the IUPAC name of the molecule shown?



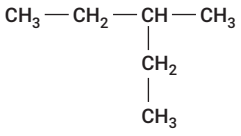
A 3-Hydroxy-3-ethyl-propan-1-amine
B 3-Amino-1-methylpropan-1-ol
C 3-Hydroxypentan-1-amine
D 1-Aminopentan-3-ol

10. Identify the type of isomers that are non-superimposable mirror images of one another.

A Simple isomers
B Optical isomers
C Structural isomers
D Geometric isomers

SHORT RESPONSE

11. **a** **Explain** why classes of organic compounds are based on functional groups.
b **Describe** the difference between the aldehyde and ketone functional groups.
c **Describe** the relationship between an amine and an amide.
d **Determine** the correct names for the following substances:
i C_5H_8
ii C_4H_{10}
iii $CH_3CH_2CH_2COCH_3$
iv



12. The following compounds have been named incorrectly. **Identify** their correct IUPAC names and explain your reasoning.

a 3-Ethylbutane
b 1-Methyl-4-propylhexane
c 3-Methyl-3-butene
d 2-Ethyl-2-methyl-3-butyne

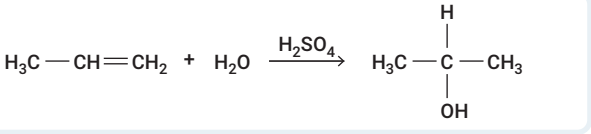
13. A compound is found to contain 72.0% carbon, 12.0% hydrogen and 16.0% oxygen by mass. Its experimentally determined molar mass is 72 g mol^{-1}.

- **a** **Determine** the empirical formula of the compound.
- **b** **Determine** the molecular formula of the compound.
- **c** The compound is known to have two isomers: one an aldehyde and the other a ketone. Draw their possible structures and name them.

CROSS-CHAPTER QUESTION

14. Consider the organic molecule $H_3C—CH=CH_2$.

- **a** **Apply** IUPAC rules to name this compound.
- **b** **Identify** whether the molecule is saturated or unsaturated.
- **c** **Determine** whether this compound could form an optical isomer.
- **d** **Determine** the molecular mass of this molecule.
- **e** If a student weighed out 5 g of this molecule, **calculate** how many moles of this substance were present in the sample.
- **f** The substance reacted with water in the presence of sulfuric acid to form 2-propanol, according to the following equation:

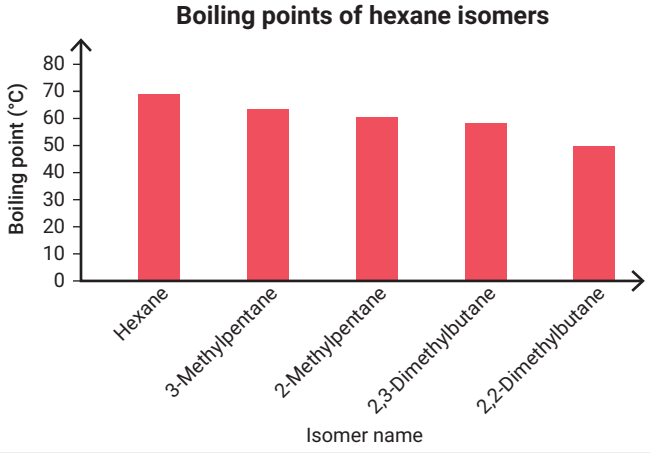


If 5 g of the substance was reacted with the water in the presence of H_2SO_4, **calculate** the mass (in grams) of the 2-propanol formed.

DATA ANALYSIS

15. Analyse data

The following graph illustrates the boiling points of the structural isomers of hexane.



a **Identify** the isomer that has the lowest boiling point.
b **Draw** the structure of the isomer that has a boiling point of 58°C.
c **Contrast** the structure of the isomer with the lowest boiling point, with the isomer that has the highest boiling point.
d **Identify** the effect of increased branching on boiling point, as shown by this data.

16. Analyse data

The following data shows the number of isomers created from simple unbranched alkane chains of varying carbon number.

Name	Molecular formula	Structural formula	Number of isomers
Methane	CH_4	CH_4	1
Ethane	C_2H_4	CH_3CH_3	1
Propane	C_3H_8	$CH_3CH_2CH_3$	1
Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3
Hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
Heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
Octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
Nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
Decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

a **Identify** the trend in the number of isomers created from an increasing number of carbons in the chain.
b **Contrast** the number of isomers formed from butane with the number of isomers formed from decane.
c **Identify** the isomers of pentane by drawing their structures.
d **Determine** the empirical formula of decane.
e **Determine** if any of these alkane isomers will form optical isomers. Give reasons for your answer.

CHAPTER 13

Physical properties and trends of organic molecules

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SYLLABUS DOT POINTS

SCIENCE UNDERSTANDING

- 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 of alkanes, alkenes, alcohols and carboxylic acids.

SCIENCE INQUIRY

- Investigate properties of homologous series* (simulations may be used).

Introduction

Understanding the physical properties of organic molecules is key to understanding their varied uses and applications in society. In addition, as new organic molecules are frequently being developed, it is important that the patterns and trends evident in known molecules are extrapolated so we can accurately predict the properties of new molecules.

Key to our ability to extrapolate this knowledge are two things: understanding how the physical properties of molecules vary within a homologous series, as the carbon chain length increases, and comprehending how molecules are affected by the presence of different functional groups.

ASSUMED KNOWLEDGE

- ✓ Organic compounds have physical properties (melting point, boiling point and solubility) than can be understood in terms of their structure.
- ✓ Different organic structures include alkanes, alkenes, alcohols and carboxylic acids.
- ✓ A homologous series is a class of organic molecules with the same functional group but different chain lengths.
- ✓ Dispersion forces, dipole–dipole interactions and hydrogen bonding are three types of intermolecular forces.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ understand and explain the trends in boiling point, melting point, volatility and solubility of the homologous groups (alkanes, alkenes, alcohols and carboxylic acids) in terms of their intermolecular forces
- ✓ interpret data about boiling point, melting point, volatility and solubility for alkanes, alkenes, alcohols and carboxylic acids
- ✓ investigate the physical properties of homologous series of organic molecules.

13.1 Intermolecular forces

intermolecular force an attractive force that causes molecules to aggregate to form liquids and solids

dispersion force a weak intermolecular force that arises from electrostatic attractions between instantaneous dipoles in neighbouring molecules

dipole–dipole interaction the attraction between molecules with permanent dipoles

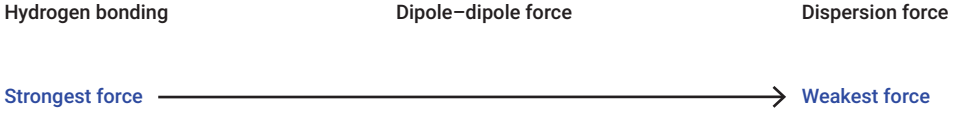
hydrogen bond the attraction of a H atom that is bonded to an O, N or F atom to the lone pair of electrons of N, O or F of an adjacent molecule

polarity a measure of the unequal sharing of electrons in a covalent bond; the result of the difference in electronegativity of the bonded atoms

As for all covalent molecules, the physical properties of organic molecules depend on the nature and strength of the **intermolecular forces** that exist between them. These forces are **dispersion forces**, **dipole–dipole interactions** and **hydrogen bonds** and their origins were discussed in Chapter 11 of *Nelson QCE Chemistry Units 1 & 2*. The stronger the intermolecular force, the greater the energy required to separate the molecules, which means the higher the melting and boiling points will be. In addition, molecules where hydrogen bonding is present are more likely to be soluble in water, because of the formation of hydrogen bonds between these functional groups and water molecules.

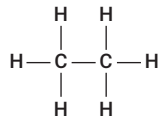
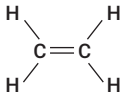
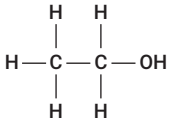
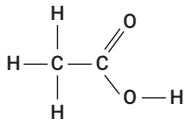
The type of intermolecular force between the different classes of organic molecule depends on the **polarity** of the bonds within the molecules (*intra*molecular bonds) and therefore the nature of the atoms present. Table 13.1.1 provides a summary of the classes of compound and the forces occurring between them.

The strength of the different intermolecular forces in descending order is:



A homologous series is a group of organic compounds with the same functional group, similar chemical properties and structure, only differing by the number of carbons in the chain. This results in a gradual change of physical properties such as melting point, boiling

TABLE 13.1.1 The types of intermolecular forces in the different classes of organic compound

Class of organic molecule	Types of bond present	Polarity	Type of intermolecular force acting	Strongest type of intermolecular force acting between molecules
Alkane 	C–C	Non-polar	Dispersion	Dispersion
	C–H	Non-polar	Dispersion	
Alkene 	C=C	Non-polar	Dispersion	Dispersion
	C–C	Non-polar	Dispersion	
	C–H	Non-polar	Dispersion	
Alcohol 	C–C	Non-polar	Dispersion	Hydrogen bonding
	C–H	Non-polar	Dispersion	
	C–O	Polar	Dipole–dipole	
	O–H	Polar	Hydrogen bonding	
Carboxylic acid 	C–C	Non-polar	Dispersion	Hydrogen bonding
	C–H	Non-polar	Dispersion	
	C–O	Polar	Dipole–dipole	
	C=O	Polar	Dipole–dipole	
	O–H	Polar	Hydrogen bonding	

point and solubility across the series. We can expect organic molecules that have hydrogen bonding, such as alcohols and carboxylic acids, to have higher melting and boiling points than other classes of molecules. These molecules are also more likely to be water soluble. Molecules such as alkanes and alkenes, which are non-polar molecules with only dispersion forces between them, have comparatively low melting and boiling points and are insoluble in water.

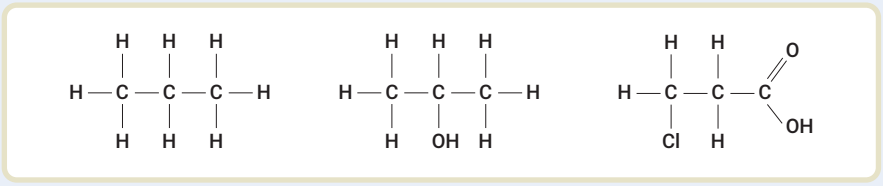
LEARNING CHECK 13.1

DESCRIBING

1 **Describe** the type of intramolecular bonds present within an alkane, and link this to the type of intermolecular forces between molecules.

2 **Sequence** the three types of intermolecular force in order of increasing strength.

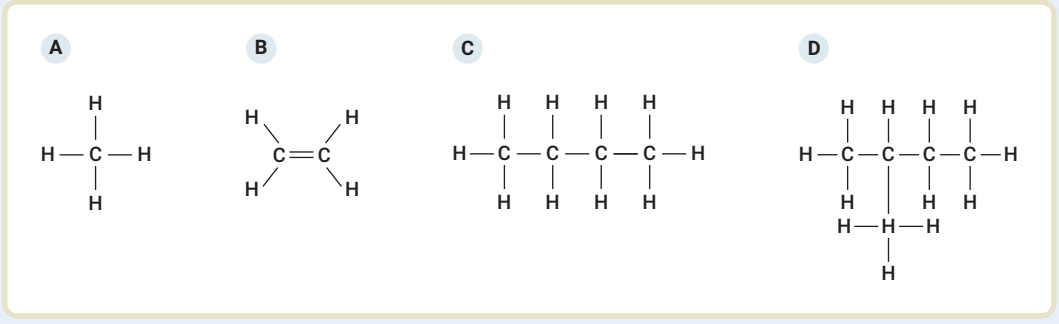
3 The structures of three molecules are shown.



Identify which of the homologous series are *not* represented.

A Alcohols
B Alkanes
C Alkenes
D Carboxylic acids

4 **Identify** which structure shows a different homologous series, and therefore different bonding type, from propane.



5 **Identify** the strongest type of intermolecular forces in the alkene homologous series.

APPLYING

6 **Explain** why carboxylic acids and alcohols have hydrogen bonding between molecules, whereas alkanes and alkenes do not.

13.2 Trends in melting points, boiling points and volatility

We can clearly see evidence of the different intermolecular bonding between organic molecules when we examine the trends in melting and boiling points within and between different homologous series. **Table 13.2.1** and **Figure 13.2.1** show the melting and boiling point data for the first 10 alkanes and alkenes (for 1-alkenes only).

TABLE 13.2.1 The melting and boiling points of the first 10 alkanes and alkenes

Number of carbon atoms	Alkanes		Alkenes	
	Melting point (°C)	Boiling point (°C)	Melting point (°C)	Boiling point (°C)
1	–183	–161		
2	–183	–89	–169	–104
3	–188	–42	–185	–48
4	–138	–0.5	–185	–6
5	–130	36	–165	30
6	–95	69	–140	64
7	–91	98	–119	94
8	–57	126	–102	121
9	–54	151	–81	146
10	–30	174	–66	172

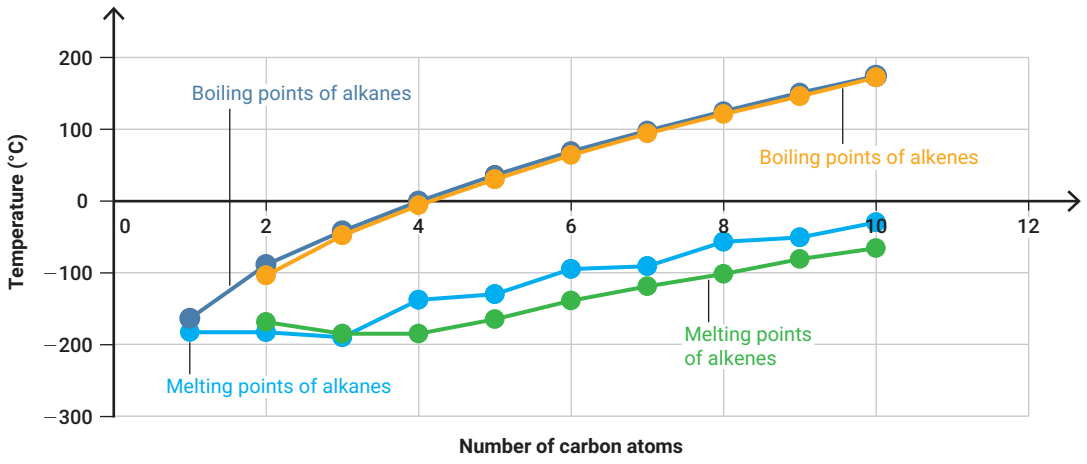


FIGURE 13.2.1 Trends in melting and boiling points of the first 10 alkanes and alkenes

The effect of molecular size

As the chain length of both alkane and alkene molecules increases, the trend in melting and boiling points is clear to see: the larger the molecule, the higher the melting and boiling points (Figure 13.2.1). Because these molecules are all non-polar, this means the larger the molecule the higher the temperatures at which the intermolecular forces (dispersion forces) are overcome sufficiently to allow a change in state.

The larger the molecules, the greater the area of surface overlap between them, where the dispersion forces can act. This means the larger the molecules, the greater the dispersion forces, and the higher the energy required to separate them from one another. This results in higher melting and boiling points. The melting and boiling points for alkanes and alkenes are similar – both increase with molecular size. The presence of the non-polar C=C bond has very little effect because it does not significantly affect the area available for dispersion forces to act between molecules. Figure 13.2.1 shows how melting point and boiling point increase with chain length.

The effect of molecular branching

It is interesting also to compare the boiling points of straight-chain and branched-chain alkanes. **Figure 13.2.2** compares pentane and 2,2-dimethylpropane, two molecules of identical molecular mass. Their different shapes result in different boiling points – the boiling point of pentane is higher because it has a greater surface area, allowing for more dispersion forces (and therefore stronger forces) to form.

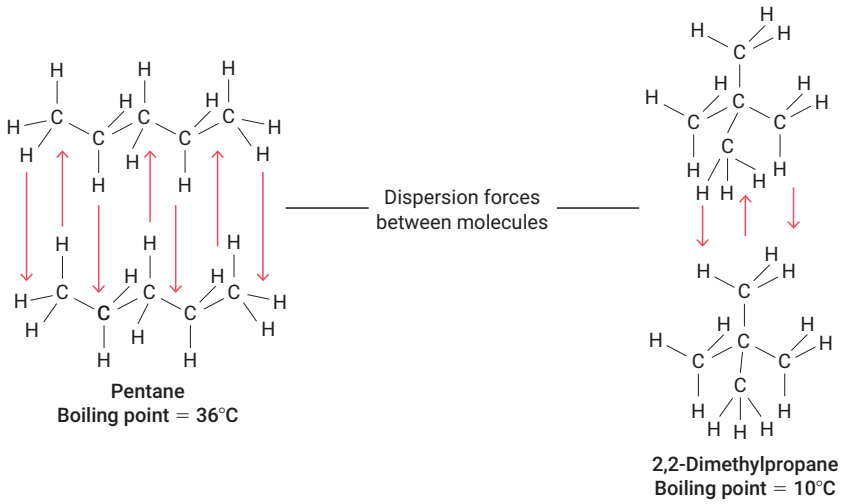


FIGURE 13.2.2 The boiling points of pentane and 2,2-dimethylpropane

The effect of functional groups

Table 13.2.2 and **Figure 13.2.3** show the boiling points for molecules in four different homologous series (alkanes, alkenes, alcohols and carboxylic acids), so we can discern the effect of the different functional groups. Note that the boiling points for alcohols stated are for primary alcohols only.

TABLE 13.2.2 Boiling point trends in different homologous series

Number of carbon atoms	Boiling points (°C)			
	Alkane	Alkene	Alcohol	Carboxylic acid
1	–161		65	101
2	–89	–104	78	118
3	–42	–48	97	141
4	–0.5	–6	118	163
5	36	30	138	186
6	69	64	158	205
7	98	94	176	222
8	126	121	195	240
9	151	146	214	256
10	174	172	229	270

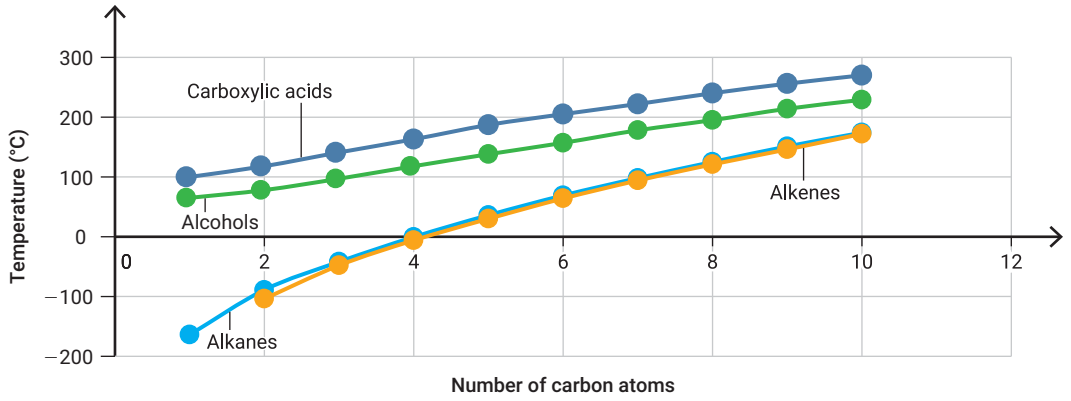


FIGURE 13.2.3 Trends in boiling points in different homologous series

Figure 13.2.3 shows again that increased molecular size results in a higher boiling point and this is evident for all the homologous series shown. However, this graph also shows clearly that the boiling points of alcohols and carboxylic acids are significantly higher than the alkanes and alkenes of equivalent chain length. This is due to hydrogen bonding between molecules, caused by the highly polar O–H bonds they possess, in addition to dispersion forces caused by the C–H bonds **(Figure 13.2.4)**.

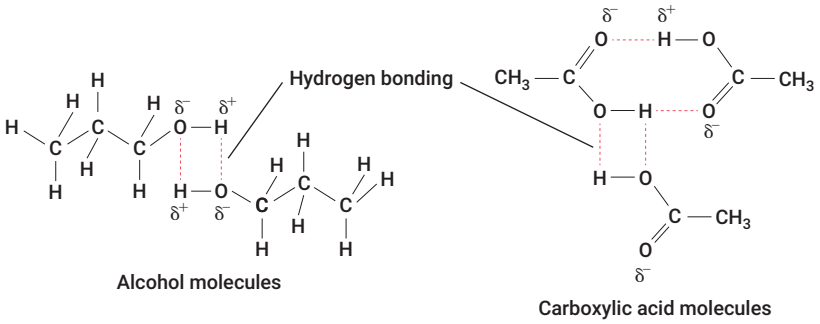


FIGURE 13.2.4 Hydrogen bonding between alcohol and carboxylic acid molecules. There is an unequal distribution of electron density along this bond, represented by the symbols δ+ and δ–.

When two carboxylic acid molecules form a stable pair through hydrogen bonding between their respective –COOH (carboxyl) groups, a **dimer** is formed. For example, in a dimer of ethanoic acid (CH_3COOH), each molecule's hydrogen from the hydroxyl (–OH) group bonds to the oxygen in the carbonyl (C=O) group of the adjacent molecule **(Figure 13.2.5)**. This pairing increases the boiling points because this stable formation requires more energy to break the intermolecular forces present.

dimer a molecular complex consisting of two identical molecules linked together

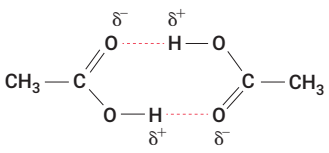
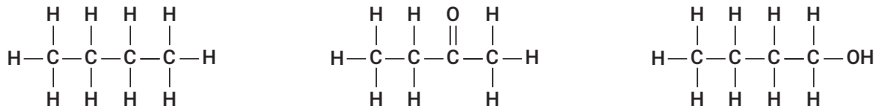


FIGURE 13.2.5 The dimer formed between two identical carboxylic acid molecules.

At a similar size, it is clear that the presence of different types of intermolecular bonds affects the boiling points of molecules (Figure 13.2.6).



Strongest intermolecular force	**Dispersion**	**Dipole–dipole**	**Hydrogen bonding**
Boiling point	**−0.5°C**	**80°C**	**118°C**

FIGURE 13.2.6 The effect of intermolecular forces on boiling points. Stronger intermolecular forces (hydrogen bonding) lead to higher boiling points than weaker dispersion forces do.

The size of the carbon chain also plays a part in the boiling and melting points. As the molecular size of the alcohols or carboxylic acids increases, the number of non-polar carbon and hydrogen atoms increases, and the hydrogen bonding effect of the polar hydroxyl or carboxyl groups does not increase. Hence, the relative effect of the hydrogen bonding is not as great in larger molecules, so the larger the molecule, the smaller the difference in boiling point between the non-polar molecules and their polar counterparts.

volatility how readily a substance vaporises to form a gas at regular temperatures and pressures

The **volatility** of a substance is how readily a substance vaporises to form a gas at regular temperatures and pressures. The term 'volatile' comes from the Latin word *volare*, meaning 'to fly', and it describes the tendency of a substance to vaporise in air. Volatility is not measured directly, but a volatile substance has a high vapour pressure and generally a low boiling point. Perfumes rely on volatility to produce pleasing scents. Volatility generally decreases with molecular size and is also affected by the presence of polar functional groups.

A small alkene with weak intermolecular forces is more volatile than molecules with longer carbon chains and/or polar functional groups, which have higher intermolecular forces (Figure 13.2.7) and low volatility. For example, ethane has a low boiling point, evaporates easily, and is therefore a highly volatile substance compared to heptane, which has a longer carbon chain and more intermolecular forces, making it less volatile. Ethanoic acid, which has a similar length carbon chain to ethane but also has a polar carboxyl group, has more intermolecular forces between molecules, and is also less volatile than ethane.

Weblinks

Three trends that affect boiling points

Volatility in water: compounds vs functional groups

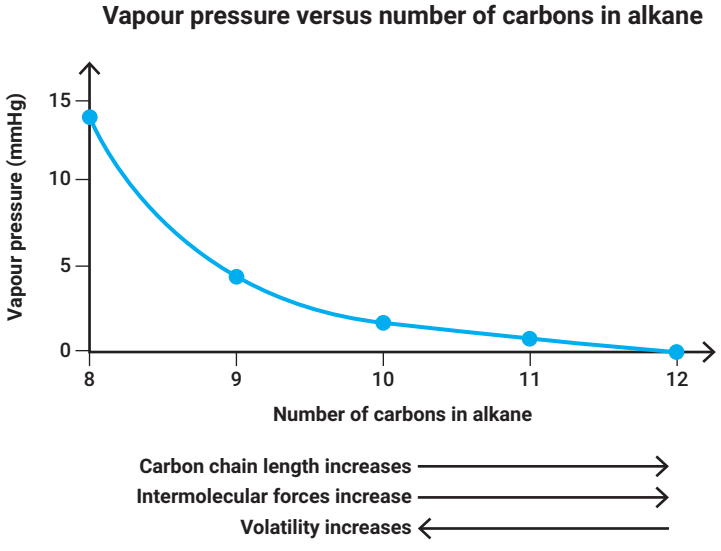


FIGURE 13.2.7 Trends in vapour pressure for alkanes of chain length 8–12, showing trends in volatility

The difference in volatility between two organic molecules in a mixture can be used to separate them. Heating a mixture to a temperature at which one of the substances vaporises leaves the other behind as a liquid. The vapour can then be collected and condensed in a separate container, resulting in the separation of the two liquids. This process of physical separation is known as **distillation**.

distillation a separation technique of a liquid mixture based on boiling point; the mixture is heated and the vapour produced condensed

LEARNING CHECK 13.2

DESCRIBING

1 **Describe** how boiling point changes with increasing molecular size in all homologous series.
2 **Describe** the trends in boiling point for straight-chain organic molecules and their branched-chain isomers.
3 **Identify** the statement that explains why ethene, propene and butene have similar physical properties.
   A They all have the same functional group.
   B They are all gases at room temperature.
   C They are all hydrocarbons.
   D They are all organic.

APPLYING

4 **Explain** why the boiling points of alcohols are higher than those of their equivalent alkanes, and the boiling points of carboxylic acids are higher than those of their equivalent alcohols.
5 **Explain** how and why the volatility of alkanes changes as carbon chain length increases.
6 **Contrast** the volatility of ethane and ethanoic acid.
7 **Determine** whether ethene, propene or pentene is the least volatile. Give reasons for your answer.
8 **Identify** the trends in vapour pressure of propane, butane and pentane and relate this to the volatility.

13.3 Trends in solubility

Solubility in water

The solubility in water of organic molecules varies considerably. For a molecule to be water soluble, it needs to be able to form intermolecular bonds with water molecules. Water molecules are highly polar and therefore bond with other polar molecules. The molecules most likely to dissolve in water are alcohols and carboxylic acids. Both can form hydrogen bonds **(Figure 13.3.1)** and carboxylic acids can also ionise to produce $-COO^-(aq)$ and $H^+(aq)$.

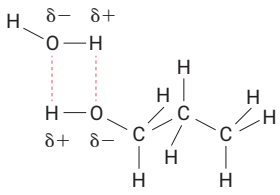


FIGURE 13.3.1 Alcohols form hydrogen bonds with water.

Alkanes and alkenes are non-polar molecules and are therefore insoluble in water. **Table 13.3.1** shows the solubilities of molecules in different homologous series. Alcohols and

carboxylic acids have polar bonds so can form attractive intermolecular interactions with water molecules.

TABLE 13.3.1 Solubilities of different homologous series (g/100 mL) in water. 'Miscible' implies that the substance mixes completely with water and so has no solubility limit.

Number of carbon atoms	Alkanes	Alkenes	Alcohols	Carboxylic acids
1	Insoluble	Insoluble	Miscible	Miscible
2	Insoluble	Insoluble	Miscible	Miscible
3	Insoluble	Insoluble	Miscible	Miscible
4	Insoluble	Insoluble	7.3	Miscible
5	Insoluble	Insoluble	2.2	5
6	Insoluble	Insoluble	0.59	1.1
7	Insoluble	Insoluble	0.1	0.24

hydrophilic having a tendency to attract water

hydrophobic having a tendency to repel water

The solubility of all these molecules decreases as the number of carbon atoms increases. The polar section of these molecules that interacts attractively with water is described as **hydrophilic**. The non-polar hydrocarbon section of these molecules is described as **hydrophobic**. As the carbon chain length increases, the molecule becomes proportionately more hydrophobic and less hydrophilic; hence, its solubility decreases. If the hydrophobic section of the molecule is large enough, then the molecule is insoluble in water, despite the presence of the hydrophilic section. This is shown in **Figure 13.3.2**, which compares the structures of two carboxylic acid molecules.

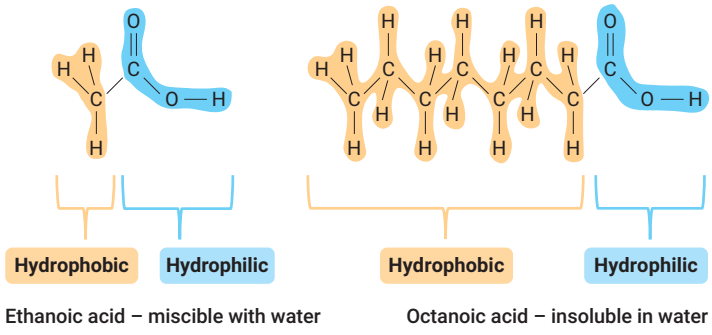


FIGURE 13.3.2 The hydrophobic and hydrophilic sections of two carboxylic acid molecules

Carboxylic acids and alcohols are soluble in water because of the presence of polar hydrogen bonds. These compounds all exhibit hydrogen bonding interactions with water and their solubility varies because of the differing polarities of their C–O and O–H bonds, which therefore affects the strength of their attraction to water.

Solubility in organic solvents

Weblink
Predicting the solubility of organic molecules

Many organic molecules are typically non-polar and are usually soluble in non-polar solvents, following the basic rule of 'like dissolves like'. Organic solvents have a range of polarities, depending on the functional groups that they contain. For example, methanol (CH_3OH) is polar, whereas hexane (C_6H_{14}) is non-polar. Most non-polar organic molecules (alkanes, alkenes) are

insoluble in polar solvents such as water and short-chain alcohols, but soluble or partially soluble in non-polar solvents such as hexane or ethyl ethanoate (ethyl acetate). However, some organic molecules are polar (alcohols and carboxylic acids), so they are less soluble in non-polar solvents than their hydrocarbon counterparts.

Overall, solubility depends on the length of the non-polar carbon chain (the hydrophobic part of the molecule), and the presence of polar functional groups (the hydrophilic part of the molecule). The longer the carbon chain, the less influence a polar functional group may have on the solubility in polar solvents, but the more influence it has on the solubility in non-polar solvents.

Syllabus link
Chapter 16 of *Nelson QCE Chemistry Units 1 & 2* introduces solubility.

PRACTICAL ACTIVITY 13.3.1

INVESTIGATING THE SOLUBILITY OF ORGANIC SUBSTANCES IN WATER

Introduction

The polar nature of the water molecule is largely responsible for its ability to dissolve a range of substances. Polar organic molecules are more able to dissolve in water, due to the intermolecular forces between the polar functional groups and the water molecules. Non-polar organic molecules, or ones of longer chain length, are less likely to dissolve.

Research question

How does the solubility of different organic compounds differ?

Aim

To investigate the solubility of a range of organic substances in water

Materials

- methanol
- ethanol
- 1-propanol
- 1-octanol
- 1-hexene
- distilled water
- ethanoic acid (vinegar)
- 5 mL measuring cylinder
- droppers or dropper bottles of chemicals
- 6 test tubes and stoppers
- test-tube rack
- waste container

RISK ASSESSMENT

What are the risks in doing this investigation?	How can you manage these risks to stay safe?
Alcohols are flammable.	Keep all flammable substances, such as the alcohols, away from flames.
Chemicals may be spilled.	Handle chemicals carefully and use droppers or dropper bottles. Wash your hands after working with organic reagents and solutions.

Copy and complete the risk assessment table in your write-up. Add any more risks you can think of, and ways to manage them. Ask your teacher to check your risk assessment before you proceed.

Procedure

1. Add 2 mL of distilled water to a small test tube.
2. Add 5 drops of ethanol to the water.
3. Stopper the test tube and tap gently to mix.
4. Allow the mixture to settle and record your observations.
5. Dispose of the mixture as directed by your teacher.
6. Repeat steps 1 to 5 for the other organic substances in water.

Analysis of results

1 Classify all substances tested as soluble, partially soluble or insoluble in water.
2 Identify whether there is a relationship between carbon chain length and the solubility of alcohols in water.
3 Identify whether there is a relationship between the type of functional group and the solubility of the substance in water.
4 Ethanol is a small polar molecule. Explain how the structure of ethanol relates to its solubility in water.
5 Octanol has a longer carbon chain attached to a polar hydroxyl group. Explain how the structure of octanol relates to is solubility in water.

Interpretation

6 From your observations of the solubility in water of the substances tested, explain how the structure of organic substances affects their solubility in water.

LEARNING CHECK 13.3

DESCRIBING

1 **Explain** why solubility in water decreases with molecular size in all homologous series.
2 **Describe** how the hydroxyl functional group affects the solubility of short-chain alcohols in water.
3 **Explain** why all alcohols are generally soluble to some degree in water.
4 **Explain** why solubility in water decreases as the alkane chain of the alcohol gets longer.

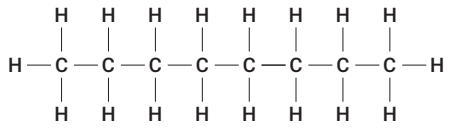
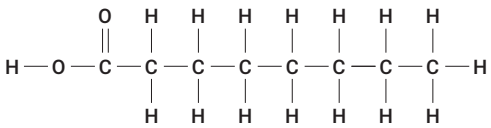
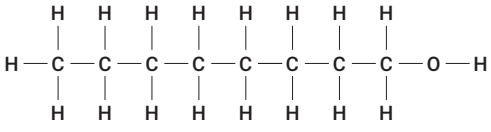
APPLYING

5 **Sequence** the following molecules in decreasing order of solubility in water and explain your reasoning: 1-propanol, propane, propanoic acid.
6 **Explain** why the solubility of 1-octanol is different in water and hexane.

ANALYSING

Questions 7–10 relate to the following information.

A group of students conducted an experiment to observe the solubility of various organic compounds in hexane. Their results are shown below.

Name of substance	Molecular structure	Solubility in water	Solubility in hexane
Octane		Not soluble	Highly soluble
Octanoic acid		Limited solubility	Readily soluble
1-Octanol		Limited solubility	Readily soluble

7 **Identify** whether octane is soluble in water or hexane.

8 **Distinguish** the solubilities of octanoic acid and octane in water and hexane.

9 Draw conclusions about how the presence of a polar functional group affects a molecule's ability to dissolve in water.

10 **Predict** whether the shorter-chain carboxylic acids would be soluble in hexane. Give reasons for your answer.

13.4 Properties of homologous groups

Worksheets
Trends across homologous groups
Trends within homologous groups

Alkanes, alkenes, alcohols and carboxylic acids are fundamental classes of organic compounds, with distinct structures and properties. Understanding how their structure relates to their physical and chemical properties gives us insight into how these molecules behave and react. These groups differ mainly in the types of bonds they possess, and the functional groups attached, influencing how they interact with other substances. A summary of the properties of homologous groups is shown in Table 13.4.1.

TABLE 13.4.1 The properties of homologous groups

Property	Alkanes	Alkenes	Alcohols	Carboxylic acids
Functional group	None (C–C and C–H bonds only)	C=C double bond	–OH (hydroxyl)	–COOH (carboxyl)
Polarity	Non-polar	Non-polar	Polar	Polar
Intermolecular force	Dispersion	Dispersion	Dispersion, dipole–dipole and H-bond	Dispersion, dipole–dipole and H-bond
Solubility in water	Insoluble	Insoluble	Soluble (decreases with chain length)	Soluble (decreases with chain length)
Boiling point	Increases with chain length	Lower than alkanes of similar size	Higher than alkanes/ alkenes of similar size	Highest of the four groups for molecules of similar size
Volatility	Decreases with chain length	Higher than alkanes of similar size	Lower than alkanes/ alkenes of similar size	Lowest of the four groups for molecules of similar size

PRACTICAL ACTIVITY 13.4.1

PROPERTIES OF HOMOLOGOUS STRUCTURES

Introduction

A homologous series is a set of organic compounds with the same functional group that vary only by a CH_2 group. This practical activity allows you to examine the properties of a homologous series safely.

Research question

How do the properties of a homologous series vary?

Aim

To examine the properties of homologous structures in a series

Procedure

1 Choose a homologous series (e.g. alkane, alkene, alcohol or carboxylic acid).
2 Choose a physical property that will be relatively easy to find data for (e.g. melting point, boiling point, solubility in water, solubility in hexane, vapour pressure).
3 Draw the first five members of the homologous series you have chosen. Name each molecule according to IUPAC rules.
4 Research the physical property for each of your five compounds and put the values in a data table.
5 Graph the data.

Analysis of results

1 Identify the trends in the relative values of the physical property.
2 Draw conclusions about the length of the carbon chain and the physical property you have chosen.
3 Explain any similarities and differences between the functional group of your homologous series and the functional groups studied by at least two other students.

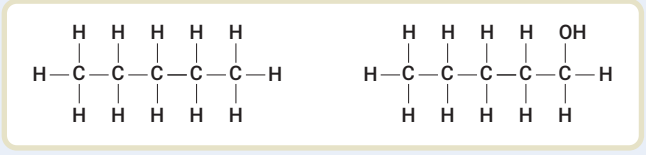
LEARNING CHECK 13.4

DESCRIBING

1 **Compare** the physical properties of alkanes, alkenes, alcohols and carboxylic acids, by considering and explaining the relative strength of the intermolecular forces that exist.

APPLYING

2 Draw conclusions for how functional groups can affect the boiling point of organic molecules of different chain length.
3 Consider the molecules CH_3CH_2COOH, $CH_3CH_2CH_2OH$ and $CH_3CH_2CH_2CH_3$.
   a List the molecules in order of increasing boiling point.
   b **Explain** your answer.
4 Consider the following molecules.



Which molecule would be most soluble in hexane? **Explain** your answer.

ANALYSING

5 The table shows information about four organic compounds.

Formula	Molar mass (g mol^{-1})	Boiling point (°C)
CH_4	16	
CH_3OH	32	
C_4H_{10}	58	
HCOOH	46	

The boiling points of the compounds are –0.5°C, 65°C, –161°C and 101°C. Copy and complete the table with boiling points provided.

CHAPTER SUMMARY

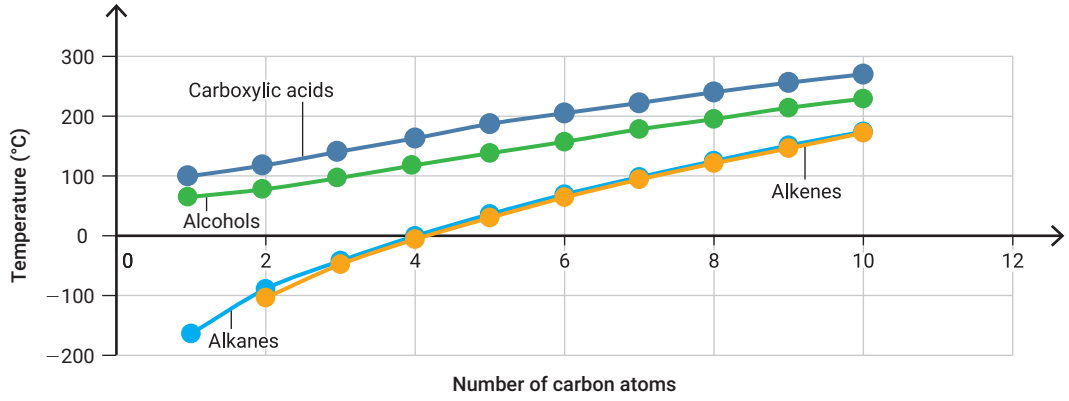
Intermolecular forces

- Intermolecular forces (dispersion, dipole–dipole, hydrogen bonding) are largely responsible for the physical properties of organic substances.
- Homologous series differ in physical properties because of the length of the carbon chain and branching present influencing the intermolecular forces.

Trends in melting and boiling points

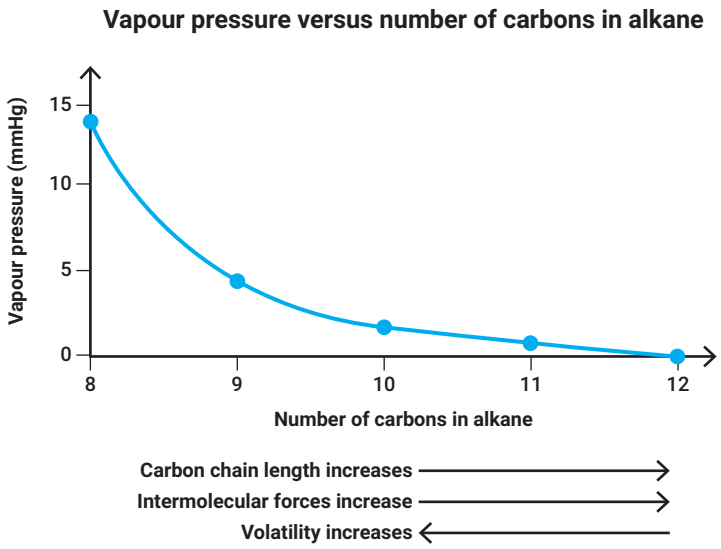
- Melting and boiling points increase with molecular size (carbon chain length) across all homologous series because of the increased intermolecular forces (dispersion) holding molecules together.
- Alkanes and alkenes have lower boiling points because they only have dispersion forces (non-polar).
- Alcohols have higher boiling points because of hydrogen bonding (hydroxyl group).
- Carboxylic acids have the highest boiling points because of dipole–dipole bonding, strong hydrogen bonding and dimer formation.

Trends in boiling points in different homologous series



Trends in volatility

- Volatility decreases with molecular size (carbon chain length) across all homologous series because of increased intermolecular forces (dispersion) holding molecules together.
- Alkanes and alkenes are more volatile because of weaker dispersion forces.
- Alcohols are less volatile because of hydrogen bonding.
- Carboxylic acids are the least volatile because of dimer formation, dipole–dipole bonding and strong hydrogen bonding.



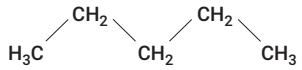
Trends in solubility

- Generally, solubility is 'like dissolves like', i.e. polar substances dissolve in polar solvents and non-polar substances dissolve in non-polar solvents.

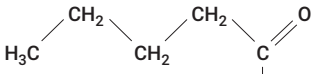
Organic compound	Solvent	
	Water	Organic solvents
Alkanes/alkenes	Insoluble	Soluble
Alcohols	Short-chain alcohols are soluble in water (H-bonding); solubility decreases with chain length	Long-chain alcohols are soluble in non-polar solvents (dispersion forces)
Carboxylic acids	Short-chain carboxylic acids are highly soluble in water (H-bonding); solubility decreases with chain length	Long-chain carboxylic acids are soluble in non-polar solvents (dispersion forces)

MULTIPLE CHOICE

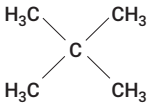
1. Four organic molecules are shown below.



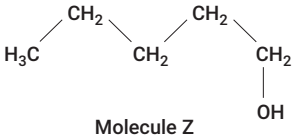
Molecule W



Molecule X



Molecule Y



Molecule Z

What is the correct sequence of molecules in descending order of boiling point (highest to lowest)?

A Z > X > W > Y
B X > Z > W > Y
C Y > W > Z > X
D Y > X > W > Z

2. What is the strongest intermolecular force between molecules of butane?

A Hydrogen bonding
B Dispersion forces
C Dipole–dipole forces
D Ion–dipole forces

3. What is the strongest intermolecular force between molecules of butanol?

A Hydrogen bonding
B Dispersion forces
C Dipole–dipole forces
D Ion–dipole forces

4. Which molecule has the lowest volatility?

A Butanol
B Hexanol
C Pentanol
D Propanol

5. The boiling points of methane, ethane and propane increase with length of carbon chain because more energy is required to overcome the:

A intramolecular hydrogen bonds.
B intermolecular hydrogen bonds.
C intramolecular dispersion forces.
D intermolecular dispersion forces.

 QCAA paper 1 2021 MCQ Q15

6. Identify which organic compound has the highest boiling point.

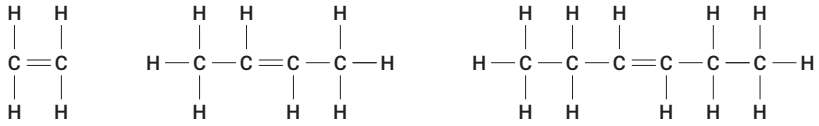
A $CH_3(CH_2)_3CH_3$

B $CH_3(CH_2)_3COOH$

C $CH_2CH(CH_2)_2CH_3$

D $CH_3(CH_2)_3CH_2OH$

7. The structures of three compounds are shown.



These substances all belong to the same homologous series because they all:

A contain an even number of carbon atoms.

B contain the same functional group.

C are hydrocarbons.

D are saturated.

8. What type of forces act between molecules and largely determine their physical properties?

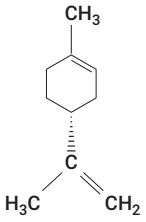
A Strong forces

B Dispersion forces

C Intermolecular forces

D Intramolecular forces

9. Limonene is a non-polar hydrocarbon compound common in the leaves of some Australian native trees.



Limonene

Identify the most suitable solvent to extract limonene from leaves.

A Water

B Ethanol

C Hexane

D Propanone

10. As the amount of branching in alkanes increases:

A volatility increases.
B melting point decreases.
C boiling point decreases.
D all of the above.

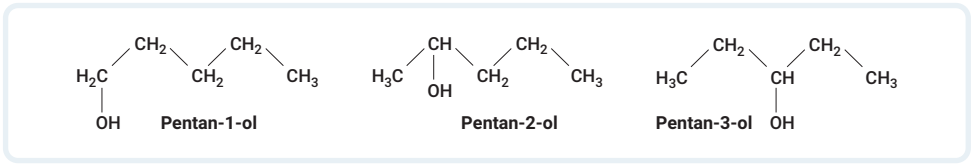
SHORT RESPONSE

11. The following three molecular formulas are for members of the same homologous series.

CH_3COOH C_2H_5COOH $C_5H_{11}COOH$

a **Identify** the homologous series.
b **Explain** how the solubility in water of these compounds varies.
c **Explain** how the volatility of these compounds varies.
d **Predict** which of these compounds would be the most soluble in hexane.

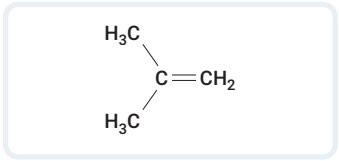
12. The following three organic structures are isomers.



Predict which molecule will have the highest boiling point. Give reasons for your answer.

CROSS-CHAPTER QUESTION

13. Consider the organic molecule shown.

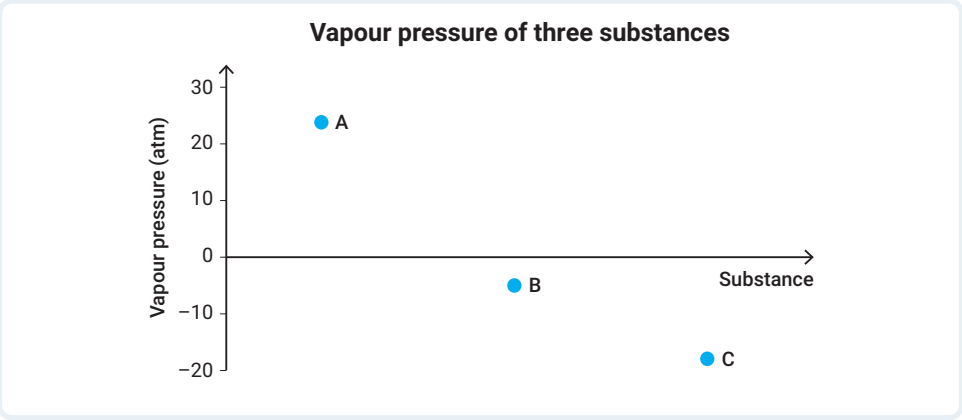


a **Identify** the molecule as saturated or unsaturated.
b **Identify** the homologous series that this molecule belongs to.
c **Apply** IUPAC rules to name this molecule.
d **Predict** whether this molecule would be soluble in water. Give reasons for your answer.
e **Determine** the strongest type of intermolecular forces in this molecule.
f **Contrast** the volatility of this molecule with that of its straight-chain isomer. Give reasons for your answer.

DATA ANALYSIS

14. Analyse data

The following graph shows the vapour pressures of three compounds (A, B and C) with similar carbon chain length but different functional groups – alkane, alcohol and carboxylic acid.



a **Identify** which compound is the most volatile.
b **Identify** which compound is most likely to have the highest boiling point.
c **Classify** each compound as either the alkane, alcohol or carboxylic acid.
d **Identify** the trend in vapour pressure as the strength of the intermolecular forces increases.

15. Analyse data

The following table lists the solubilities of some alcohols and carboxylic acids, measured in grams of solute per 100 mL of water. 'Miscible' means completely soluble in water.

Name	Formula	Solubility in water (g/100 mL)	Solubility in hexane (low, moderate or high)
Methanol	CH_3OH	Miscible	Low
Ethanol	CH_3CH_2OH	Miscible	Moderate
Propanol	$CH_3CH_2CH_2OH$	Miscible	Moderate
Butanol	$CH_3(CH_2)_2CH_2OH$	7.3	Moderate
Pentanol	$CH_3(CH_2)_3CH_2OH$	2.2	Moderate
Hexanol	$CH_3(CH_2)_4CH_2OH$	0.59	High
Heptanol	$CH_3(CH_2)_5CH_2OH$	0.1	High
Methanoic acid	$HCOOH$	Miscible	Low
Ethanoic acid	CH_3COOH	Miscible	Low
Propanoic acid	CH_3CH_2COOH	Miscible	Low
Butanoic acid	$CH_3(CH_2)_2COOH$	Miscible	Moderate
Pentanoic acid	$CH_3(CH_2)_3COOH$	5	Moderate
Hexanoic acid	$CH_3(CH_2)_4COOH$	1.1	High

a **Identify** the solubility of pentanol in water.

b **Identify** the trend in solubilities in hexane for carboxylic acids and alcohols as the carbon chain increases in length.

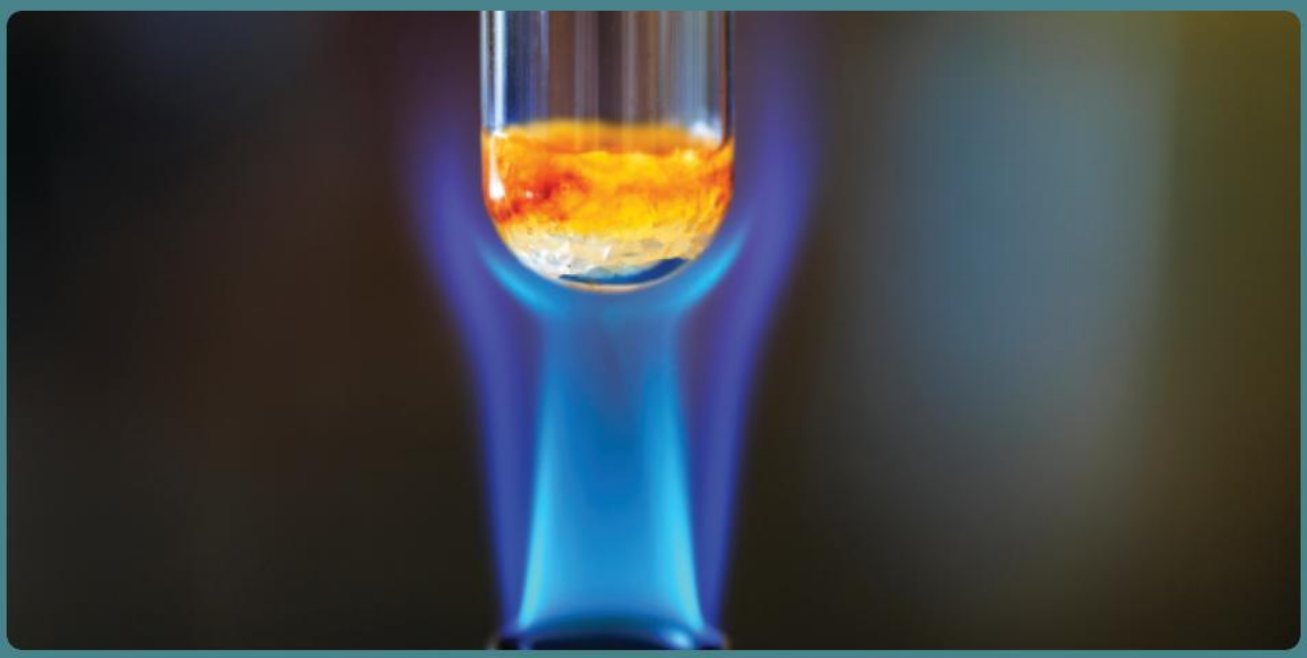
c **Identify** the trend in solubilities in water for alcohols as the carbon chain increases in length.

d **Predict** how the solubilities of the alkanes in hexane would compare to those of the compounds shown in the table.

e **Determine** which of these molecules would have the highest boiling point: octanoic acid, octane, 1-octanol. Give reasons for your answer.

CHAPTER 14

Organic reactions and reaction pathways



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SYLLABUS DOT POINTS

SCIENCE UNDERSTANDING

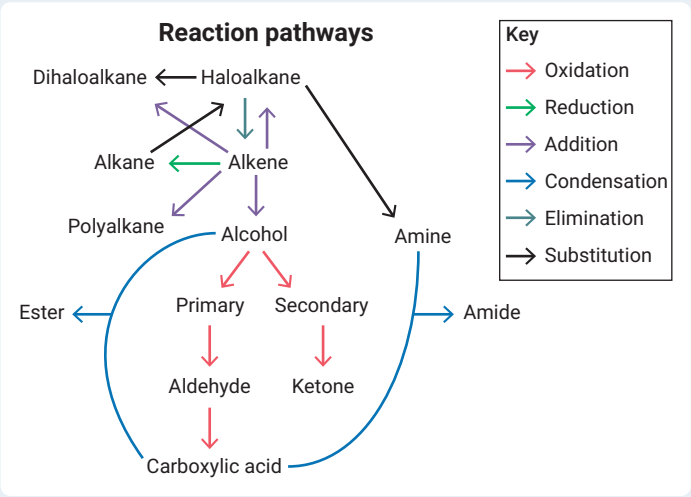
- Identify that an organic compound displays characteristic chemical properties and undergoes specific reactions based on the functional group present.
- Determine, using equations, the reaction of
  - alkanes with halogens (X_2)
  - haloalkanes with halogens (X_2), sodium hydroxide and ammonia
  - alkenes 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.

Introduction

Organic molecules take part in a wide range of chemical reactions, depending on the functional groups that they contain. These reactions are critical when synthesising larger molecules and, hence, are the basis for the entire organic chemical manufacturing industry. In Chapter 12, you learned that the functional groups are groups of atoms within the various classes of organic molecules. These atoms, bonded in specific ways, display characteristic chemical properties and react in specific ways.

A reaction pathway diagram, located in the *Formula and Data Book*, can be used to help determine how these organic compounds react to form new substances.



Adapted from QCAA *Formula and Data Book*, page 1, https://www.qcaa.qld.edu.au/downloads/senior-qce/sciences/snr_chemistry_25_formula_data_book.pdf

In this chapter, you will learn about the types of organic reactions that make up this diagram, and the reagents and reaction conditions that are required for these reactions to occur. These characteristic reactions can help identify organic molecules, and allow chemists to manufacture particular organic molecules for use.

Practicals

- Preparation of some esters (online-only resource)
- Comparing reactivities of alkanes and alkenes (teacher demonstration)
- Distinguishing between primary, secondary and tertiary alcohols (teacher demonstration) (online-only resource)

Worksheets

- Organic reactions
- Organic reactions involving oxygen and nitrogen

ASSUMED KNOWLEDGE

- ✓ Organic molecules are composed of hydrocarbon skeletons (alkanes, alkenes, alkynes) and functional groups (e.g. alcohols, carboxylic acids, haloalkanes).
- ✓ Homologous groups are identified by the functional groups present, which determines their reactivity.
- ✓ IUPAC conventions are used to name organic compounds.
- ✓ Structural formulas of organic molecules can be drawn from their IUPAC names.
- ✓ Balanced chemical equations can be determined from generalised reaction patterns.
- ✓ Acid and base concepts include definitions, pH, and weak versus strong.
- ✓ Acids and bases dissociate in water to form conjugate acids and bases.
- ✓ Typical acid–base reaction patterns include neutralisation and carbonate reactions.
- ✓ Redox processes involve electron transfer, oxidation states and oxidising and reducing agents.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ recognise that the chemical properties and reactivity of organic compounds are determined by the functional group present
- ✓ identify the characteristic reactions associated with each functional group
- ✓ determine and balance chemical equations for reactions involving alkanes, haloalkanes, alkenes, alcohols and carboxylic acids with various reagents, including halogens, sodium hydroxide, ammonia, hydrogen halides and others
- ✓ classify organic reactions as addition, elimination, substitution or redox
- ✓ explain the reaction mechanisms for each organic reaction type, noting that the mechanisms for substitution and elimination are not required
- ✓ determine the primary, secondary and tertiary carbon atoms in haloalkanes and alcohols based on their molecular structure
- ✓ describe the acid–base properties of carboxylic acids and amines and their behaviour in chemical reactions
- ✓ understand that esterification is a reversible reaction (condensation/hydrolysis)
- ✓ explain the process of ester formation from carboxylic acids and alcohols
- ✓ apply Markovnikov's rule to predict the products of addition reactions of alkenes with hydrogen halides and water
- ✓ interpret chemical tests, such as bromine water and acidified potassium dichromate(VI) or potassium manganate(VII), to distinguish between alkanes and alkenes, and primary, secondary and tertiary alcohols.

14.1 Reactions of alkanes

Alkanes are saturated organic compounds that contain unreactive C–C and C–H bonds; therefore, they do not react with most substances. They can only undergo two important reactions: substitution and combustion.

free radical substitution reaction a UV-light-initiated reaction, where a hydrogen atom is replaced with a halogen atom

Substitution reaction with halogens

Alkanes are saturated compounds; therefore, they only undergo substitution reactions. Substitution reactions involve replacing one atom in a molecule with another. In the case of alkanes, **free radical substitution reactions** take place when halogens (X) such as

chlorine (Cl) or bromine (Br) replace one or more hydrogen atoms in the alkane to form a haloalkane. These reactions require a significant amount of energy, in the form of ultraviolet (UV) light. If excess halogen atoms are present, there may be multiple substitutions with hydrogen.

Figure 14.1.1 shows an example of such a reaction between methane and chlorine. You can see that one hydrogen atom in methane has been replaced by one chlorine atom, producing chloromethane. Substitution reactions can continue until all the hydrogen atoms in the compound have been replaced by halogen atoms. This occurs with only one halogen atom being substituted at a time. If four halogen atoms are to be added, then four reactions would need to occur. For example, methane would eventually form tetrachloromethane or tetrabromomethane after four separate substitution reactions.

KEY CONCEPT

A general single substitution reaction between an alkane (C_nH_{2n+2}) and a halogen (X_2) to form a haloalkane (R–X) looks like this:

$$C_nH_{2n+2} + X_2 \xrightarrow{\text{UV light}} R\text{–}X + HX$$

R = carbon chain of any length

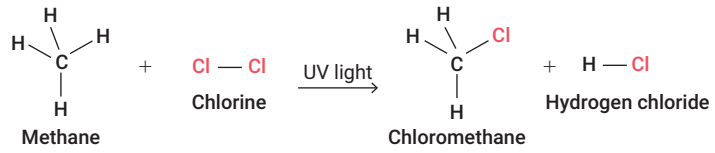


FIGURE 14.1.1 Free radical substitution reaction of methane and chlorine

The UV light provides the energy for the chlorine molecule to break up into highly reactive **intermediate species**, called free radicals. The methane molecule is relatively unreactive and so it requires a highly activated substance, such as a halogen, to initiate the reaction. The reaction is highly exothermic and often results in a violent explosion.

intermediate species species formed during a reaction pathway as precursors to the desired product

Halogen substitution reactions play a useful role in producing intermediates used in polymer production and the production of other industrial and pharmaceutical chemicals. Although halogen substitution of alkanes is versatile and widely used, controlling the selectivity of the reaction and managing risks are key challenges with these organic reactions.

Combustion of alkanes

Combustion is the most significant reaction that alkanes undergo, and their ability to combust is the reason why we primarily use them as fuels. As you know from Year 11, when hydrocarbons such as alkanes are ignited in a plentiful supply of oxygen, they can react readily to produce water, carbon dioxide and a large quantity of heat, according to the general unbalanced reaction equation:

$$C_nH_{2n+2} + O_2(g) \rightarrow CO_2(g) + H_2O(l)$$

$$\text{Alkane} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{water}$$

Balanced equations for the combustion of methane and octane are shown below.

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

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

These reactions represent **complete combustion**, where the alkanes are fully oxidised to form only carbon dioxide and water. We can see that for complete combustion of methane, the ratio of oxygen to methane should be 2:1. For the larger hydrocarbon octane, the ratio is significantly larger, at 25:2.

complete combustion burning of an organic compound in sufficient oxygen to produce only carbon dioxide and water

incomplete combustion burning of an organic compound in limited oxygen to produce carbon monoxide or carbon and water

If there is insufficient oxygen to fully oxidise the methane, then **incomplete combustion** occurs and either carbon monoxide or carbon are formed:

$$2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(l) \quad (1)$$

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

Carbon monoxide is a toxic gas, which can be produced when methane or other hydrocarbons are combusted in poorly ventilated conditions. When larger hydrocarbon molecules, such as octane, present in petrol, are burned in air, it is impossible to achieve complete combustion, as the percentage of oxygen in air is relatively low, about 20 per cent. Therefore, car exhausts always contain toxic carbon monoxide, which is why drivers should never run a car engine in an enclosed space.

The presence of carbon particles in reaction 2 has significance for Bunsen burners because this reaction causes a glowing orange 'safety' flame to occur when the methane is burned in a limited supply of oxygen – a cooler visible flame which occurs when the air hole is closed **(Figure 14.1.2)**. The blue 'roaring' flame of a Bunsen burner occurs when the air hole is open. It has a much higher temperature because there is complete combustion, as the open air hole ensures a plentiful supply of oxygen.

Sciencephotos/Alamy Stock Photo

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FIGURE 14.1.2 The blue and orange flames of a Bunsen burner

Weblink
Reactions of alkanes

LEARNING CHECK 14.1

DESCRIBING

1 **Explain** what is meant by a:
   - **a** substitution reaction with halogen
   - **b** combustion reaction.

2 **Contrast** how the reaction products are different in complete and incomplete combustion reactions.

3 Write an equation to **describe** the complete combustion of pentane.

4 Write an equation to **describe** the incomplete combustion of pentane, forming carbon as a product.

5 **a** Write an equation to **describe** the free radical substitution reaction of pentane with chlorine.
   - **b** Draw the structures and name three possible products.

6 **a** Write an equation to **describe** the complete combustion of hexane.
   - **b** **Explain** why octane is more likely to burn with a sooty flame than pentane.

7 **Identify** the reagents and reaction conditions necessary for hexane to become 2-iodohexane.

APPLYING

8 **Explain** why the free radical substitution reaction of alkanes is not widely used in synthesising useful chemical products.

9 **Explain** why alkanes only undergo substitution reactions.

14.2 Reactions of haloalkanes

Haloalkanes have a **halogen** attached to a hydrocarbon group. This halogen is available to substitute with other atoms or groups of atoms, undergoing substitution to produce further haloalkanes, amines or alcohols.

halogen any of the reactive non-metallic elements from group 17 of the periodic table (fluorine, chlorine, bromine, iodine)

Although alkanes, alkenes and alkynes are non-polar molecules, the introduction of a halogen (F, Cl, Br or I) atom to a molecule means a polar carbon–halogen bond is formed, which significantly changes how the molecule reacts. Additionally, whether the carbon atoms in haloalkanes are primary, secondary or tertiary further influences their chemical behaviour and reactivity. This classification is based on the number of carbon atoms directly bonded to the carbon atom attached to the halogen (Figure 14.2.1).

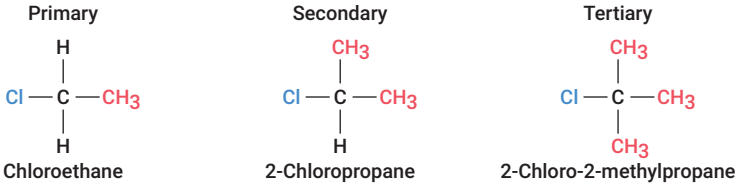


FIGURE 14.2.1 Primary, secondary and tertiary haloalkanes

Substitution with halogens

With haloalkanes, it is possible for more than one of the hydrogen atoms to be further substituted if the halogen is supplied in excess. For example, a di-haloalkane, tri-haloalkane or tetra-haloalkane can be formed when two or more hydrogen atoms are substituted with excess halogens, in the presence of UV light, according to the series of equations shown in Figure 14.2.2.

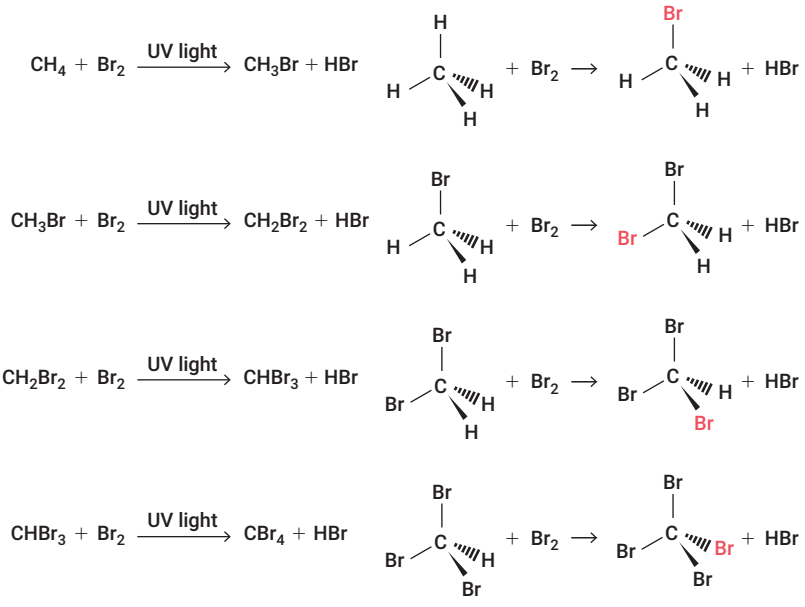


FIGURE 14.2.2 Halogenation of methane with bromine atoms

In this example, the bromine is substituted one at a time, and the haloalkane produced undergoes further substitution. This is one example of how multiple halogen atoms can be substituted onto a hydrocarbon.

Syllabus link
Polar bonds were introduced in Chapter 11.

Nucleophilic substitution

In a halogen–carbon bond, the halogen atom is more electronegative than the carbon atom, so there is an unequal distribution of electron density along this bond. The halogen atom is described as slightly negatively charged and the carbon atom, slightly positively charged. This is represented in **Figure 14.2.3** by the symbols δ+ and δ– that represent a polar bond. Other species, known as **nucleophiles** and which are either negatively charged or possess a lone pair of electrons, are attracted to the slightly positively charged carbon atom and can form bonds with it in preference to the halogen atom. Hence, this is a substitution reaction known as **nucleophilic substitution**, because the halogen atom is substituted for the nucleophile (e.g. OH^-, NH_2^-, CN^-) to form a molecule with a different functional group **(Figure 14.2.4)**.

nucleophile an electron-rich species that donates a pair of electrons to form a covalent bond

nucleophilic substitution a reaction of organic molecules in which a nucleophile replaces a functional group (the leaving group)

The reactions below show examples of different nucleophiles commonly used in reactions with haloalkanes.

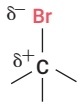


FIGURE 14.2.3 The polar carbon–bromine bond

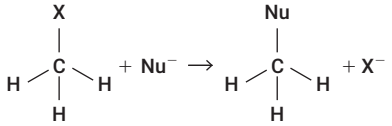


FIGURE 14.2.4 Nucleophilic substitution: X represents a halogen; Nu represents a nucleophile.

Nucleophilic substitution reaction with sodium hydroxide

A nucleophilic substitution occurs when haloalkanes react with an aqueous sodium hydroxide solution to produce alcohols. The nucleophile hydroxide ion (OH^-) replaces the halogen atom in the haloalkane to form an alcohol. A halide ion is produced as a by-product. This occurs according to the general equation shown in **Figure 14.2.5**.

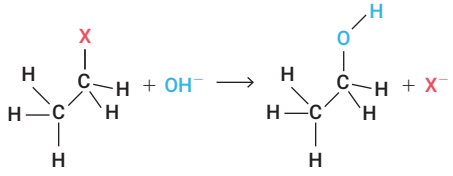


FIGURE 14.2.5 Nucleophilic substitution with sodium hydroxide where X represents a halogen

$$R\text{–}X + NaOH \rightarrow R\text{–}OH + NaX$$

Haloalkane + sodium hydroxide → alcohol + sodium halide

An example of alcohol formation from nucleophilic substitution of the bromine in bromoethane in the presence of sodium hydroxide is shown in **Figure 14.2.6**.

$$CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$$

Bromoethane + sodium hydroxide → ethanol + sodium bromide

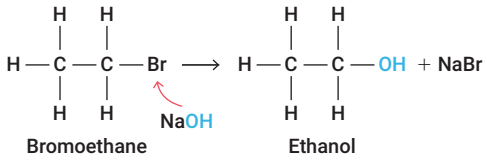


FIGURE 14.2.6 The reaction of bromoethane with sodium hydroxide to form ethanol

Primary haloalkanes can undergo nucleophilic substitution at room temperature, but secondary and tertiary haloalkanes may require reflux conditions. **Reflux** involves heating the mixture to boiling point to form a vapour and then condensing the vapours back into the reaction flask. This allows the reaction mixture to be heated for an extended period, which promotes reaction completion.

reflux a process of heating a reaction mixture to its boiling point and then condensing the vapour back into the reaction vessel

An example of a secondary haloalkane undergoing nucleophilic substitution to produce an alcohol under reflux conditions is shown below and in **Figure 14.2.7**.

$$CH_3CHBrCH_3 + NaOH \xrightarrow{\text{reflux}} CH_3CH(OH)CH_3 + NaBr$$

2-Bromopropane + sodium hydroxide → 2-propanol + sodium bromide

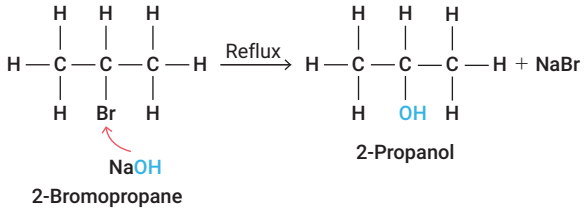


FIGURE 14.2.7 The reaction of 2-bromopropane with sodium hydroxide to form 2-propanol

Weblink
Nucleophilic substitution reactions

Nucleophilic substitution reaction with ammonia

When haloalkanes react with ammonia, nucleophilic substitution occurs. This time, the halogen atom is replaced by an amino group ($-NH_2$) from ammonia (NH_3) to form a primary amine. The nucleophile is the ammonia molecule, NH_3. Note that the by-product is the halogen halide (H–X), as one of the hydrogen atoms from the ammonia molecule combines with the substituted halide ion.

The reaction occurs according to the general equation:

$$R\text{–}X + NH_3 \rightarrow R\text{–}NH_2 + HX$$

Haloalkane + ammonia → amine + hydrogen halide

Although a primary amine is formed initially, a reaction with excess ammonia may also form secondary and tertiary amines. Ethanol is not always required as a solvent but may be used to moderate the reaction rate to prevent multiple substitutions if excess ammonia is present.

An example is bromoethane reacting with ammonia to form the primary amine ethanamine. Hydrogen bromide is also a by-product in the reaction, as shown in **Figure 14.2.8**.

$$CH_3\text{–}CH_2\text{–}Br + NH_3 \rightarrow CH_3\text{–}CH_2\text{–}NH_2 + HBr$$

Bromoethane + ammonia → ethanamine + hydrogen bromide

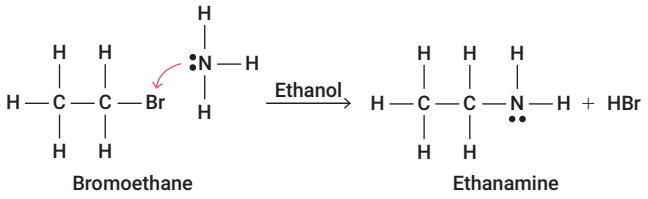


FIGURE 14.2.8 The reaction of bromoethane with ammonia to form ethanamine

Elimination reactions

elimination reaction
a reaction in which a molecule is lost from a larger molecule, producing an unsaturated product

Haloalkanes can also take part in **elimination reactions**, resulting in the loss of a hydrogen and a halide to form a smaller molecule(s) (hydrogen halide or a salt + water) and the formation of C=C double bond to produce an alkene. The reagent used for this reaction is sodium hydroxide dissolved in ethanol, rather than the aqueous solution that is required for substitution.

We have now seen that there are two possible reactions for haloalkanes with the reagent sodium hydroxide, and there are several factors that determine whether substitution or elimination occurs.

- Primary haloalkanes tend to undergo substitution, whereas tertiary haloalkanes tend to undergo elimination (Figure 14.2.9). Secondary haloalkanes can undergo both reactions.
- High concentrations of hydroxide solution favour elimination, whereas low concentrations favour substitution.
- A high proportion of water compared to ethanol in the solvent favours substitution. A greater proportion of ethanol favours elimination.
- A higher temperature favours elimination; a lower temperature favours substitution.

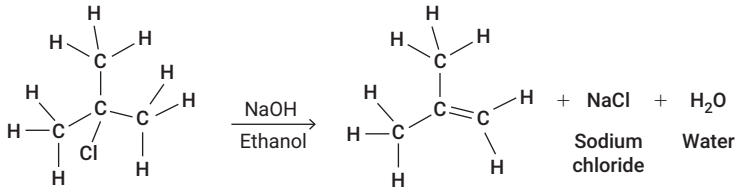


FIGURE 14.2.9 The elimination reaction of 2-chloro-2-methylpropane to form the alkene 2-methylpropene

LEARNING CHECK 14.2

DESCRIBING

1. **Explain** what is meant by nucleophilic substitution reactions.
2. **Explain** what is meant by elimination reactions.
3. **Explain** what is meant by a polar covalent bond.
4. **Contrast** how the reaction conditions can be used to determine whether substitution or elimination reactions occur.

APPLYING

5 Write balanced equations to **describe** the reaction of:
   - **a** 1-bromopropane with aqueous sodium hydroxide
   - **b** 2-chlorobutane with ammonia
   - **c** iodoethane with potassium cyanide (KCN)
   - **d** 2-iodo-2-methylpropane with ethanolic sodium hydroxide.

6 The reaction of hot concentrated aqueous sodium hydroxide with 2-bromopropane can lead to a mixture of products. **Explain** what the products are and how the conditions could be manipulated to produce each of these products in greater amounts.

7 **Identify** the products formed when 3-chlorohexane reacts with sodium hydroxide under reflux conditions.

14.3 Reactions of alkenes

As you have learned, alkenes are unsaturated hydrocarbons that contain at least one carbon–carbon double bond (C=C). The presence of the double bond makes alkenes far more reactive than alkanes. Not only can alkenes take part in combustion reactions, the double bonds in alkenes facilitate **addition reactions**.

addition reaction a reaction in which atoms are added to unsaturated molecules through the breaking of multiple bonds

Addition reactions involve adding more atoms to an unsaturated molecule by breaking the double bond and forming a saturated molecule. A variety of molecules may undergo addition reactions with alkenes.

Combustion of alkenes

Like alkanes, alkenes can take part in combustion reactions to produce carbon dioxide (or carbon monoxide) and water. For example, consider the complete combustion reaction of ethene:

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

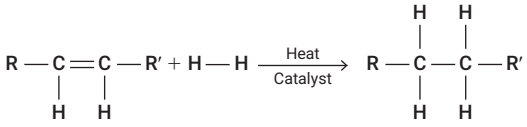
Addition reactions with hydrogen (hydrogenation)

An alkene is converted to an alkane with hydrogen and the aid of a catalyst. The addition of hydrogen atoms removes the double bond and forms a saturated molecule. The catalyst is usually a finely divided metal such as platinum, palladium or rhodium, and reaction conditions include a temperature of 150°C. This reaction is also described as **hydrogenation** (or **reduction**).

hydrogenation an addition reaction in which hydrogen is the molecule added

reduction (hydrogenation) a hydrogenation reaction of alkene, alkynes or amines

The general equation for this reaction is:



Alkene + hydrogen ⟶ alkane

Figure 14.3.1 shows the addition reaction of ethene with hydrogen.

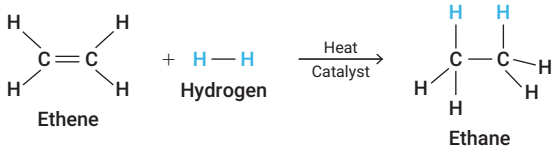
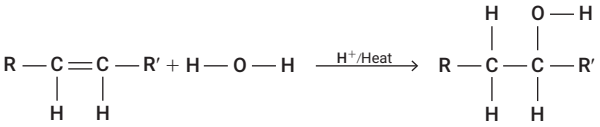


FIGURE 14.3.1 The addition reaction of ethene with hydrogen

Addition reactions with water (hydration)

Water, in the presence of a phosphoric acid catalyst at 350°C, will take part in an addition reaction with an alkene. A –H and –OH are added across the double bond to produce an alcohol. The general equation to show this is:



Alkene + water → alcohol

For example, ethene is converted to ethanol, as seen in **Figure 14.3.2**.

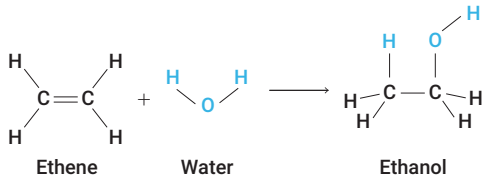
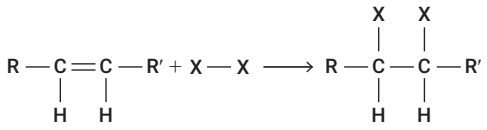


FIGURE 14.3.2 The addition reaction of ethene with water

Addition reactions with a halogen (halogenation)

halogenation an addition reaction involving a halogen molecule

When a halogen such as chlorine or bromine reacts with an alkene in a **halogenation** reaction, the double bonds are broken, allowing halogen atoms to add across the double bond to form a dihaloalkane:



Alkene + halogen → dihaloalkane

The addition reaction of propene with bromine is shown in **Figure 14.3.3**.

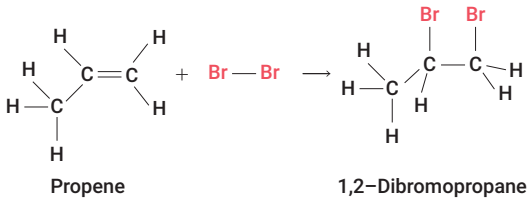


FIGURE 14.3.3 The addition reaction of propene with bromine

Bromine water test

This reaction is commonly used to test for the presence of unsaturated molecules. If brown bromine water is added to an alkene, it will lose its colour because of the addition reaction that takes place (Figure 14.3.4). This reaction does not happen with alkanes, so the solution stays brown in the presence of an alkane. Therefore, it is a useful test to determine whether an alkane or an alkene is present in a solution.

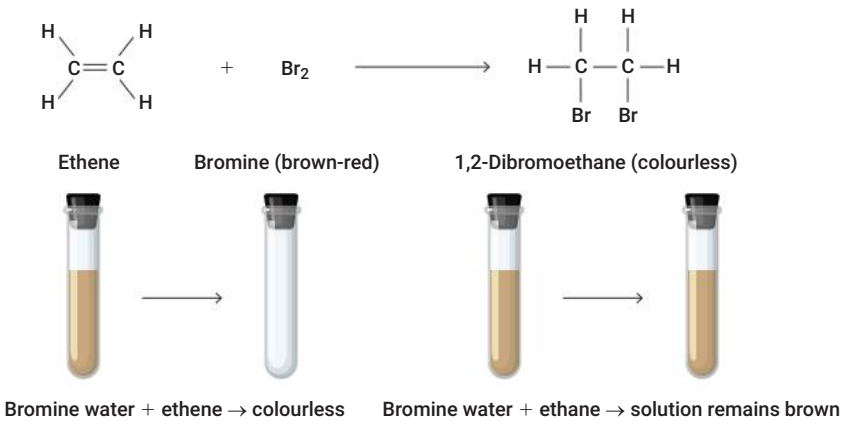
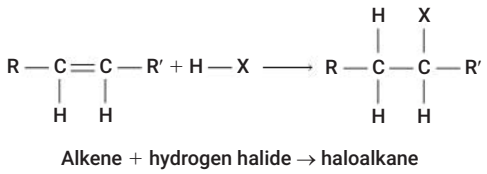


FIGURE 14.3.4 The bromine addition reaction

Addition reactions with hydrogen halides

Hydrogen halides are the hydrides of the group 17 elements (in other words HF, HCl, HBr and HI). These compounds also take part in addition reactions with alkenes to form a haloalkane:



An example of an addition reaction with a hydrogen halide is seen in Figure 14.3.5.

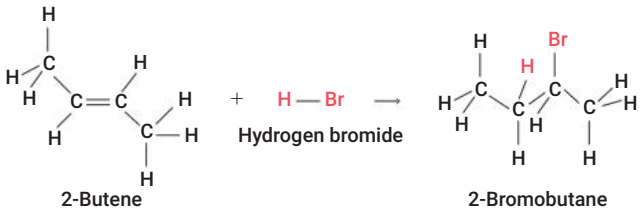


FIGURE 14.3.5 The addition reaction of 2-butene with hydrogen bromide

Markovnikov's rule – addition to unsymmetrical alkenes

Markovnikov's law in reactions involving the addition of a hydrogen atom and another group (e.g. halide, hydroxide), the hydrogen adds to the carbon with the most hydrogen atoms

In the reaction in Figure 14.3.5, adding hydrogen bromide to 2-butene can only lead to one product, 2-bromobutane. However, if 1-butene was used instead, two products would be possible, as shown in **Figure 14.3.6**. **Markovnikov's law** states that in a reaction involving the addition of a hydrogen atom and another group, the hydrogen adds to the carbon with the most hydrogen atoms.

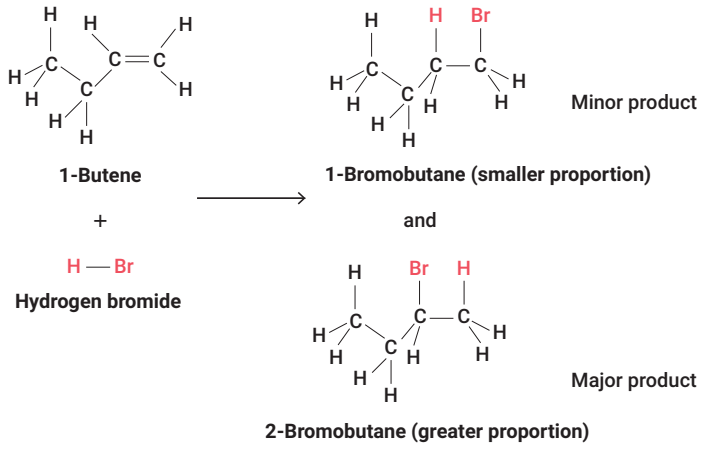


FIGURE 14.3.6 The addition of HBr to 1-butene

KEY LAW

Markovnikov's law

In a reaction involving the addition of a hydrogen atom and another group, the hydrogen atom adds to the carbon already bonded to the most hydrogen atoms, forming the major product.

Weblink
Addition reactions of alkenes explained

It can be thought of this way – *the rich get richer, and the poor get poorer.* The H atoms are more likely to bond to the carbon that already has the most H atoms (and thus get 'richer' in H). This is known as the major product, and forms 75–90% of the time. The alternative atom arrangement formed is known as the minor product. While some minor product is produced, the reaction mainly yields the major product.

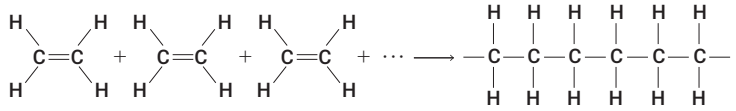
When a hydrogen halide (HX) or water (H_2O) is added to an unsymmetrical alkene, the hydrogen atom is added preferentially to the carbon atom of the C=C bond that is bonded to the most hydrogen atoms, to form the major product.

In the reaction in Figure 14.3.6, a mixture of 2-bromobutane (major product) and 1-bromobutane (minor product) are produced. In 1-butene, carbon 1 has two hydrogen atoms whereas carbon 2 has one hydrogen atom. Therefore, the hydrogen from the HBr is more likely to be added to carbon 1, leading to a greater proportion of 2-bromobutane in the mixture. However, some 1-bromobutane will also be formed. These products can be separated from each other, usually by **fractional distillation** because they have marginally different boiling points.

fractional distillation the separation of a mixture of organic compounds according to their different boiling points

Addition polymerisation of alkenes

In the presence of a suitable catalyst and reaction conditions, ethene molecules will react with each other to form long chains by breaking the double bonds to make **polyalkanes (Figure 14.3.7)**. This type of reaction is called **addition polymerisation** and is discussed in more detail in Chapter 18.



Ethene + ethene + ethene ⋯ → polymer

FIGURE 14.3.7 The addition reaction of ethene to form polyethane

fractional distillation the separation of a mixture of organic compounds according to their different boiling points

polyalkane a long repeating chain of alkane molecules joined together

addition polymerisation the formation of polymer chains by the addition reaction of unsaturated monomers

LEARNING CHECK 14.3

DESCRIBING

1 **Explain** what is meant by:
   - **a** addition reaction
   - **b** addition polymerisation reaction.

2 **Explain** why alkenes can undergo addition reactions, yet alkanes cannot.

3 Write equations to **describe** the reactions of the following chemicals. Where necessary, indicate the required reaction conditions.
   - **a** Propene with liquid bromine (Br_2)
   - **b** 2-Methylpropene with water
   - **c** 2-Butene with hydrogen (H_2)
   - **d** 2-Butene with HBr

APPLYING

4 **Identify** which reactions in Question 3 are likely to produce more than one product. For each of these reactions, **determine** the possible products and indicate which is likely to be the preferred product.

14.4 Reactions of alkynes

Alkynes are a family of hydrocarbons containing at least one triple bond between two carbon atoms (C≡C). Like alkenes, alkynes are unsaturated hydrocarbons. The simplest member, ethyne (C_2H_2) is a linear molecule, as shown in Figure 14.4.1. The triple bond causes the overall molecular shape to become more **planar**, as with alkenes.

The reactions of alkynes are similar to those of alkenes, and they can also take part in combustion and addition reactions, with the same reagents that are used for alkenes.

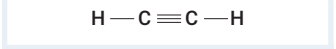


FIGURE 14.4.1 The structure of ethyne is planar.

planar in the same plane

Combustion of alkynes

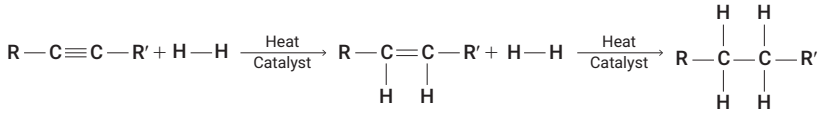
Like alkanes and alkenes, alkynes undergo combustion in a plentiful supply of oxygen to produce carbon dioxide and water. For example:

$$C_3H_4(g) + 4O_2(g) \rightarrow 3CO_2(g) + 2H_2O(l)$$

This highly exothermic reaction is key to the use of ethyne (also known as acetylene) in oxyacetylene torches.

Addition reactions with hydrogen (hydrogenation)

Alkynes undergo addition reactions, but they are less reactive than alkenes. The addition reaction usually takes place in two steps. In the first step, addition of a reagent results in the triple bond being converted to a double bond. In the second addition step, the double bond is broken, resulting in a saturated compound **(Figure 14.4.2)**.



Alkyne + hydrogen → alkene + hydrogen → alkane

FIGURE 14.4.2 Hydrogenation of alkyne → alkene → alkane

The reaction of alkynes with hydrogen gas is known as hydrogenation. Under pressure, hydrogen adds to an alkyne in the presence of a metal catalyst, such as finely divided nickel, palladium or platinum, to form a corresponding alkene or alkane. This is shown in **Figure 14.4.3**.

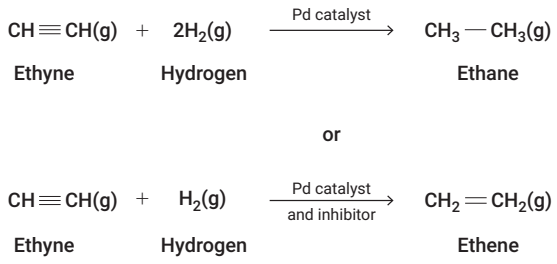


FIGURE 14.4.3 The addition of hydrogen to alkynes

If an inhibitor is added, its presence prevents ethene from being hydrogenated to the saturated alkane, ethane, and it stops at the alkene stage.

Addition reactions with a halogen (halogenation)

Alkynes can react with a halogen (halogenation). When this occurs, the carbon–carbon triple bond is broken and bromine or chlorine is added to each carbon in the triple bond. A haloalkene is formed. A second step then produces a haloalkane. This is shown in **Figure 14.4.4**.

Worksheet
Organic reactions

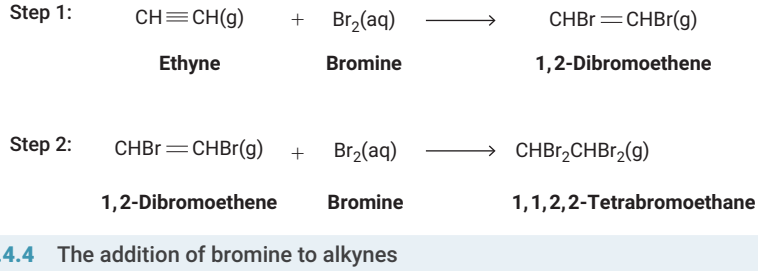


FIGURE 14.4.4 The addition of bromine to alkynes

LEARNING CHECK 14.4

DESCRIBING

1 **Explain** what is meant by an alkyne.

2 **Explain** why alkenes and alkynes are regarded as unsaturated hydrocarbons.

APPLYING

3 Write balanced equations to **describe** the reaction of:

- **a** propyne with liquid bromine (Br_2)
- **b** 1-butyne with hydrogen (H_2) to form butane
- **c** 2-butyne with oxygen.

4 Ethyne is also known as acetylene and is used as the fuel for high-temperature torches that cut and weld metals. **Determine** the properties that ethyne possesses that lead to it being used in these torches.

5 Consider the following reaction sequence for the reduction of an alkyne to an alkane.

Step 1: alkyne + hydrogen → alkene
Step 2: alkene + hydrogen → alkane

- **a** **Determine** the balanced chemical equations for both steps of the reaction sequence when C_5H_8 is the initial alkyne.
- **b** **Identify** the alkene and alkane produced in this reaction sequence.
- **c** **Describe** the type of reaction occurring in each step and **explain** the role of hydrogen in these reactions.
- **d** **Predict** the product if 1-hexyne (C_6H_{10}) were to undergo this sequence of reactions with hydrogen.

14.5 Reactions of alcohols

Ethanol, or ethyl alcohol, is the most well-known member of the alcohol family. It is also one of the most widely used compounds of carbon.

Ethanol is used:

- in beverages such as wine, beer and spirits
- as an additive to petrol or as an alternative fuel for motor vehicles (E10 fuel is 10% ethanol) **(Figure 14.5.1)**
- as a solvent in many products, including medicines, antiseptics and household cleaners
- as a reactant and solvent for product manufacturing, including in plastics, adhesives, pharmaceuticals and perfumes.

Daria Nipot/Shutterstock.com

FIGURE 14.5.1 Ethanol is added to petrol to make E10 fuel, a lower-emissions fuel.

Types of alcohols

Ethanol is only one member of the family of organic compounds called alcohols. The alcohol class has the hydroxyl functional group –OH and alcohols are represented by the general formula ROH.

Alcohols can be classified according to the number of carbon atoms attached to the carbon bearing the –OH group:

- In a **primary alcohol**, the hydroxyl group (–OH) is attached to a carbon atom that is bonded to only one other carbon atom.
- In a **secondary alcohol**, the hydroxyl group (–OH) is attached to a carbon atom that is bonded to two other carbon atoms.

Syllabus link
Chapter 13 describes alcohols and their properties.

primary alcohol an alcohol in which the –C–OH group is joined to one other carbon atom

secondary alcohol an alcohol in which the –C–OH group is joined to two other carbon atoms

tertiary alcohol an alcohol in which the –C–OH group is joined to three other carbon atoms

- A **tertiary alcohol**, the hydroxyl group (–OH) is attached to a carbon atom that is bonded to three other carbon atoms.

Figure 14.5.2 shows primary, secondary and tertiary alcohols with the molecular formula C_4H_9OH.

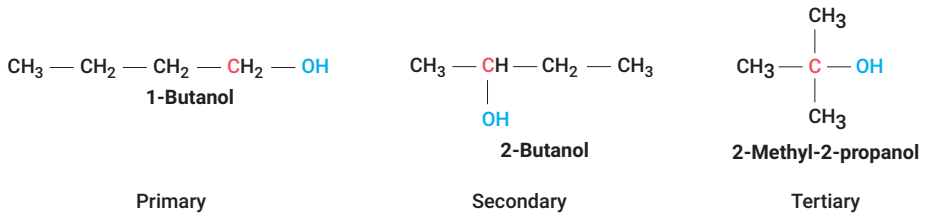


FIGURE 14.5.2 Primary, secondary and tertiary alcohols with the formula C_4H_9OH

The three types of alcohols have different physical properties. This is because the strength of the hydrogen bonding in alcohols depends on the extent to which the –OH group is available for bonding. When the –OH group is on the end of the carbon chain, as in primary alcohols, it is more available for bonding than when it is surrounded by alkyl groups in tertiary alcohols. As described in Chapter 13, this also means that the boiling points decrease from primary to secondary to tertiary alcohols.

The three types of alcohols also vary in their chemical reactivity. The most vigorous reaction with sodium occurs with a primary alcohol and the least vigorous occurs with the tertiary alcohol. Similarly, primary alcohols are more readily oxidised than secondary alcohols are by a strong oxidising agent such as potassium permanganate, whereas tertiary alcohols are not oxidised.

Combustion reactions of alcohols

As with alkanes, alkenes and alkynes, alcohols undergo combustion and can be used as fuels. They burn readily in air to produce carbon dioxide and water according to the general reaction equation:

$$R\text{–}OH + O_2 \rightarrow CO_2 + H_2O$$

$$\text{Alcohol} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{water}$$

An example of this is the combustion of ethanol:

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

The amount of energy released and the efficiency of the combustion of alcohols as fuels varies, depending on their molecular structure.

oxidation (of an organic compound) a reaction in which an organic compound gains oxygen or loses hydrogen (e.g. primary alcohols are converted to aldehydes and carboxylic acids, and secondary alcohols are converted to ketones)

Oxidation reactions of primary, secondary and tertiary alcohols

Alcohols readily undergo **oxidation** with strong oxidising agents such as acidified permanganate (MnO_4^-) or dichromate solutions ($Cr_2O_7^{2-}$). The products of the reaction depend on the structure of the alcohol.

Oxidation of primary alcohols

Primary alcohols are oxidised to form aldehydes, which are then further oxidised to carboxylic acids. These general reactions are shown in **Figure 14.5.3**. The [O] above the arrow in the equation represents the oxidising agent that is reacting with the alcohol. Commonly, either acidified potassium dichromate(VI) ($K_2Cr_2O_7$) or acidified potassium manganate(VII) ($KMnO_4$) is used for this purpose:

First stage of oxidation: $R–CH_2OH + [O] \rightarrow R–CHO + H_2O$

Second stage of oxidation: $R–CHO + [O] \rightarrow R–COOH$

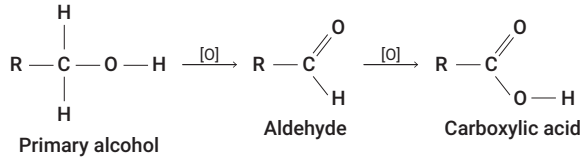


FIGURE 14.5.3 The oxidation of primary alcohols (R indicates the alkyl section of the molecule)

Potassium dichromate(VI) ($K_2Cr_2O_7$) solution has a distinctive orange colour that turns to green when it is reduced by the alcohol ($Cr^{6+} \rightarrow Cr^{3+}$). Potassium manganate(VII) ($KMnO_4$) solution has a purple colour that turns a very pale pink when it is reduced ($Mn^{7+} \rightarrow Mn^{2+}$). This can be used as a simple chemical test to determine which kind of alcohol is present (see **Table 14.10.1** later in this chapter).

The half-equations for the reduction of these reagents can be seen in **Figure 14.5.4** and are available in the *Formula and Data Book*. In both cases, acid is required as the source of the H^+ ions, and sulfuric acid should be used because the sulfate ion that is also present will not be oxidised by the reagent.

FORMULA AND DATA BOOK

Acidified potassium dichromate(VI)

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

orange — green

Acidified potassium manganate(VII)

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

purple — colourless

FIGURE 14.5.4 Half-equations for the reduction of acidified potassium dichromate(VI) and acidified potassium manganate(VII)

Syllabus link
Writing full equations from half-equations is shown in Chapter 8.

The following example shows the oxidation of ethanol to the aldehyde ethanal, then the further oxidation of ethanal to ethanoic acid using acidified potassium dichromate as the oxidising agent. (The oxidation and reduction half-reactions can be derived from the overall reactions given.) The multiple steps in this oxidation reaction of primary alcohols can be represented as the two separate reactions, added together as one final reaction equation.

WORKED EXAMPLE 14.5.1

Write a balanced redox reaction for the oxidation of ethanol to ethanal, and then to ethanoic acid.

ANSWER

1 Write the oxidation and reduction half-equations.

Oxidation of ethanol to ethanal:

$CH_3CH_2OH(l) \rightarrow CH_3CHO(l) + 2H^+(aq) + 2e^-$

Oxidation of ethanal to ethanoic acid:

$CH_3CHO(l) + H_2O(l) \rightarrow CH_3COOH(aq) + 2H^+(aq) + 2e^-$

Reduction of $Cr_2O_7^{2-}$ to Cr^{3+} in acid:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

2 Balance the number of electrons transferred ($6e^-$ for all three equations).

Oxidation of ethanol to ethanal:

$3CH_3CH_2OH(l) \rightarrow 3CH_3CHO(l) + 6H^+(aq) + 6e^-$

Oxidation of ethanal to ethanoic acid:

$3CH_3CHO(l) + 3H_2O(l) \rightarrow\rightarrow 3CH_3COOH(aq) + 6H^+(aq) + 6e^-$

Reduction of $Cr_2O_7^{2-}$ to Cr^{3+} in acid:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

3 Combine the half-equations. These are written as two separate steps that will be added later.

i Ethanol to ethanal reaction

Oxidation of ethanol to ethanal:

$3CH_3CH_2OH(l) \rightarrow 3CH_3CHO(l) + 6H^+(aq) + 6e^-$

Reduction of $Cr_2O_7^{2-}$ to Cr^{3+} in acid:

$3Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

Add the two half-equations, remembering to cancel out electrons and any common species:

$3CH_3CH_2OH(l) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3CH_3CHO(l) + 2Cr^{3+} + 7H_2O(l)$

ii Ethanal to ethanoic acid reaction

Oxidation of ethanal to ethanoic acid:

$3CH_3CHO(l) + 3H_2O(l) \rightarrow 3CH_3COOH(aq) + 6H^+(aq) + 6e^-$

Reduction of $Cr_2O_7^{2-}$ to Cr^{3+} in acid:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

Add the two half-equations, remembering to cancel out electrons and any common species:

$3CH_3CHO(l) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3CH_3COOH(aq) + 2Cr^{3+}(aq) + 4H_2O(l)$

4 Combine both steps for the overall reaction.

Add the two combined equations for the oxidation of ethanol to ethanoic acid.

$3CH_3CH_2OH(l) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$

Aldehydes are easily oxidised to form carboxylic acids, so the final product will not contain any aldehyde; it will contain only the carboxylic acid. To obtain the aldehyde, an excess of the alcohol is used, and the aldehyde is distilled off as soon as it forms, before it can be oxidised.

Oxidation of secondary alcohols

Secondary alcohols are oxidised to form ketones, which cannot be further oxidised. So the final product in the oxidation of a secondary alcohol is a ketone. Again, either acidified potassium manganate(VII) or potassium dichromate(VI) is used as oxidising agents. The general equation for the oxidation of a secondary alcohol is:

$$R\text{–}CH(OH)R' + [O] \rightarrow R\text{–}CO\text{–}R' + H_2O$$

This is also illustrated in **Figure 14.5.5**.

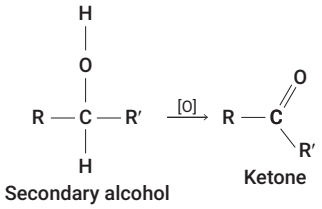


FIGURE 14.5.5 The oxidation of secondary alcohols

Half-equations and overall equations can be written for the oxidation of 2-propanol with acidified potassium manganate(VII). Using the half-equation method (in acidic solution) to balance the oxidation half-equation, two electrons ($2e^-$) and two hydrogen ions ($2H^+$) are released for every molecule of 2-propanol that is oxidised. In the reduction half-equation, five electrons ($5e^-$) are gained for every molecule of MnO_4^- that is reduced. To balance the charges (as $10e^-$) the oxidation half-equation is multiplied by 5, and the reduction half-equation is multiplied by 2:

Oxidation:

$$5CH_3CHOHCH_3(aq) \rightarrow 5CH_3COCH_3(aq) + 10H^+(aq) + 10e^-$$

Reduction:

$$2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$$

Overall:

$$5CH_3CHOHCH_3(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5CH_3COCH_3(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$$

2-Propanol Propanone

As with the oxidation of primary alcohols, the reaction causes the solution to change colour depending on the oxidising agent.

- Potassium dichromate(VI) ($K_2Cr_2O_7$) makes the solution change colour from orange to green.
- Potassium manganate(VII) ($KMnO_4$) makes the solution change from purple to colourless.

Oxidation of tertiary alcohols

Tertiary alcohols are not oxidised in the same way as primary and secondary alcohols because a large amount of energy is required to break a C–C bond. Consequently, there is no change to the colour of either acidified potassium dichromate(VI) or acidified potassium manganate(VII) with a tertiary alcohol, indicating that no reaction has occurred.

Weblink
Oxidation of alcohols

Esterification (condensation) reactions of alcohols

Alcohols react with carboxylic acids to form esters. The general equation for this reaction is shown in **Figure 14.5.6**. These reactions will be discussed later in this chapter.

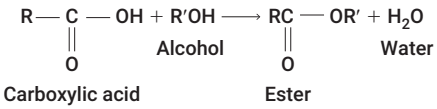


FIGURE 14.5.6 The reaction of an alcohol with a carboxylic acid to produce an ester

Reaction of alcohols with hydrogen halides (H–X)

Alcohols react with hydrogen halides (HX) to undergo substitution reactions, where the hydroxyl group (–OH) is replaced by a halide ion (X^-). It is a nucleophilic substitution reaction, in which the alcohol acts as a nucleophile, and the halide ion (X^-) replaces the –OH group. This reaction typically requires heating and forms an alkyl halide and water, according to the general reaction:

$$R\text{–}OH + HX \rightarrow R\text{–}X + H_2O$$

Alcohol + hydrogen halide → alkyl halide + water

For example, ethanol reacts with hydrogen chloride to form ethyl chloride (an alkyl halide) and water:

$$CH_3CH_2OH(l) + HCl(g) \rightarrow CH_3CH_2Cl(g) + H_2O(l)$$

In this reaction, the chloride (Cl^-) replaces the –OH group to form the alkyl halide chloroethane.

LEARNING CHECK 14.5

DESCRIBING

1 **Explain**, with examples, what is meant by primary, secondary and tertiary alcohols.

2 **Identify** the commonly used oxidising agents in reactions with alcohols.

3 **Describe** and draw the following functional groups.
   - **a** Hydroxyl
   - **b** Aldehyde
   - **c** Ketone

4 **a** Write a balanced equation to describe the reaction of 2-propanol with hydrogen bromide (HBr) to form an alkyl halide and water.
   - **b** **Identify** the IUPAC name of the product of the reaction.
   - **c** **Identify** the type of reaction occurring between alcohols and hydrogen halides and explain the role of hydrogen halide in this reaction.

APPLYING

5 Potassium manganate(VII) ($KMnO_4$) solution has a purple colour and turns colourless when it is reduced to Mn^{2+} ions in acidic solution. It oxidises 1-propanol to propanal, which is further oxidised to propanoic acid. **Determine** the balanced half-equations for these two reaction steps, and the overall chemical equation for this two-step reaction.

6 **Determine** balanced equations to describe the reactions of:
   - **a** 1-pentanol with acidified potassium dichromate(VI)
   - **b** 2-butanol with acidified potassium manganate(VII)
   - **c** 2-methyl-2-pentanol with acidified potassium dichromate(VI)
   - **d** propanal with acidified potassium manganate(VII).

7 Draw conclusions about why sugars containing aldehyde functional groups are known as 'reducing sugars', but those containing ketone groups are not.

8 **Explain** why wine (containing ethanol) can develop an acidic, 'vinegary' taste if left uncorked more than 3 days.

14.6 Reactions of carboxylic acids and esters

Carboxylic acids occur throughout nature. For example, formic (methanoic) acid is a chemical defence for some ants, which they inject when they bite **(Figure 14.6.1)**. Ethanoic acid is found in vinegar, propanoic acid in cheese, butanoic acid in spoiled butter, citric acid in citrus fruits and lactic acid in milk and other dairy products. Many of these carboxylic acids have strong unpleasant odours, but some are quite pleasant and fruity to smell. Synthetic compounds manufactured from carboxylic acids include soap, some plastics, pharmaceuticals and herbicides.

Ploypemuk/Shutterstock.com

FIGURE 14.6.1 Ants inject formic acid when they sting.

Acid–base properties of carboxylic acids

Carboxylic acids, with their –COOH group, are weak acids that donate protons (H^+) in solution, partially dissociating into carboxylate ions ($R–COO^-$) in a reversible reaction. The acidity of carboxylic acids is key to their reactivity in chemical and biological processes, with the dissociation of carboxylic acids represented as:

$$R–COOH \rightleftharpoons R–COO^- + H^+$$

When water is included in the reaction equation, a hydronium ion (H_3O^+) forms, as shown below:

$$R–COOH + H_2O \rightleftharpoons R–COO^- + H_3O^+$$

Carboxylic acids undergo the usual reactions of acids.

As you have learned previously, acids can take part in different types of reactions involving metals, bases and carbonates. Since the carboxylic acid group can only donate one H^+, it is monoprotic **(Figure 14.6.2)**.

Syllabus links
Chapter 4 describes behaviour of acids.
Chapter 17 of *Nelson QCE Chemistry Units 1 & 2* describes different reactions involving acids.

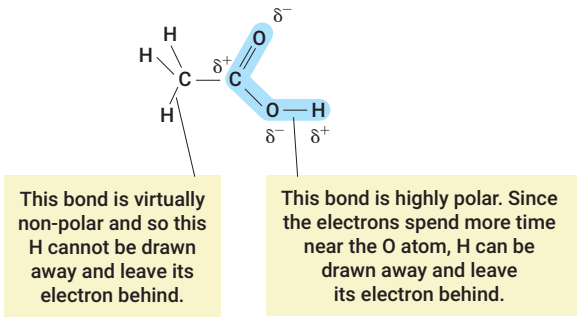


FIGURE 14.6.2 Why ethanoic acid can only act as a monoprotic acid

Reaction with reactive metals

In a manner typical of all acids, carboxylic acids react with reactive metals to produce a salt and hydrogen gas.

For example:

$$Mg(s) + 2CH_3COOH(aq) \rightarrow Mg^{2+}(aq) + 2CH_3COO^-(aq) + H_2(g)$$

Reaction with bases (neutralisation)

Carboxylic acids react with a base to produce a salt and water in a neutralisation reaction.

For example:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq) + H_2O(l)$$

Typically the salt produced is written as one ionic compound (e.g. $NaCH_3COO$), as in the reaction below:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$$

Reaction with carbonates

Carboxylic acids react with carbonates, another form of base, to produce a salt plus carbon dioxide and water. This reaction is commonly used to test for the presence of an acid, by adding carbonate and observing the evolution of bubbles of carbon dioxide.

For example:

$$2CH_3COOH(aq) + Na_2CO_3(aq) \rightarrow 2Na^+(aq) + 2CH_3COO^-(aq) + CO_2(g) + H_2O(l)$$

Amphoteric behaviour of carboxylic acids

amphoteric a substance that can act as an acid or act as a base depending on the reaction conditions

Carboxylic acids are primarily acidic but can exhibit base-like behaviour under certain conditions, especially in reactions with strong acids. This is known as **amphoteric** behaviour, specifically amphiprotic behaviour, as the substance can either accept or donate a proton according to Brønsted–Lowry acid theory. For example, when ethanoic acid (CH_3COOH) reacts with a very strong acid, such as sulfuric acid (H_2SO_4), ethanoic acid acts as a very weak base and accepts an extra proton to form $CH_3COOH_2^+$.

The reaction can be written as:

$$CH_3COOH(aq) + H_2SO_4(aq) \rightarrow CH_3COOH_2^+(aq) + HSO_4^-(aq)$$

Esterification reaction

esterification the condensation reaction in which an ester is formed from an alcohol and a carboxylic acid

Esterification is the reaction of a carboxylic acid with an alcohol to produce an ester. Esters are an important group of organic compounds that occur in a wide range of biological systems. They have pleasant, fruity odours and are responsible for the flavours and fragrances

of many fruit and flowers. Solid animal fats (like the beeswax in **Figure 14.6.3**) and animal and vegetable oils are natural esters. When writing the names of esters, remember that the alcohol component of the name is written first, then the carboxylic acid component.

Lucie Lang/Alamy Stock Photo

FIGURE 14.6.3 Beeswax is a natural ester.

The ester ethyl butanoate **(Figure 14.6.4)** occurs in pineapples, peaches and apricots. The ester group contains an **ester link** because it links the two molecules that reacted to produce it – an alcohol and a carboxylic acid.

ester link the –COO– group that links two alkyl chains in an ester molecule

The esterification reaction between an alcohol and a carboxylic acid is moderately slow at room temperature:

$$R\text{–}COOH + R'\text{–}OH \rightleftharpoons R\text{–}COO\text{–}R' + H_2O$$

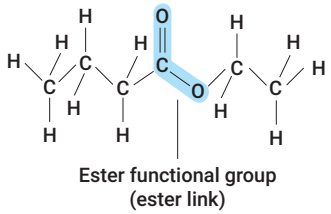


FIGURE 14.6.4 The ester functional group in ethyl butanoate

To speed up the reaction, the mixture is heated in the presence of an acid catalyst, usually concentrated sulfuric acid. The general reaction can be written as shown in **Figure 14.6.5**.

Notice that this reaction is reversible and also produces a water molecule. A reaction in which the functional groups of two molecules join and a small molecule, usually water, is released is called a **condensation reaction**.

Weblink
Esterification reaction

Practical
Preparation of some esters

condensation reaction a reaction in which two molecules combine to produce a larger molecule and a small molecule, usually water

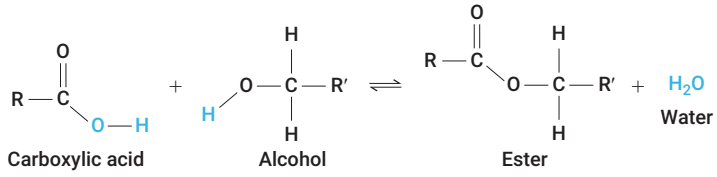


FIGURE 14.6.5 The formation of an ester

Figure 14.6.6 shows the esterification/condensation reaction between ethanoic acid and ethanol to produce ethyl ethanoate and water.

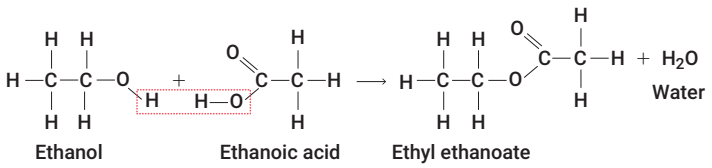


FIGURE 14.6.6 The reaction between ethanoic acid and ethanol

Hydrolysis of esters

hydrolysis a reaction in which a larger molecule is split into two smaller molecules by reacting with water in the presence of an acid or base catalyst

The reaction for forming esters is reversible. So, under certain conditions, esters can react with water in the presence of a catalyst to produce the original acid and alcohol. This reaction with water is called **hydrolysis**. Hydrolysis can occur under both acidic and alkaline conditions. Under acidic conditions (in the presence of heat and sulfuric acid), the reaction is as shown in Figure 14.6.7.

During hydrolysis, the single bond between the carbon and oxygen of the ester functional group breaks and the carboxylic acid and alcohol re-form.

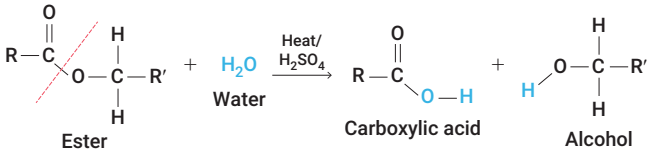


FIGURE 14.6.7 The acid hydrolysis of an ester

For example, ethyl ethanoate is hydrolysed to form ethanoic acid and ethanol (Figure 14.6.8).

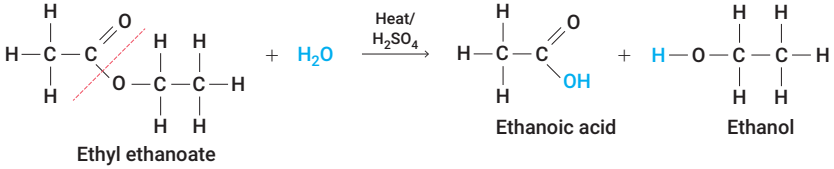


FIGURE 14.6.8 The acid hydrolysis of ester ethyl ethanoate to form ethanoic acid and ethanol

Under alkaline conditions (in the presence of heat and sodium hydroxide), the reaction is as shown in Figure 14.6.9.

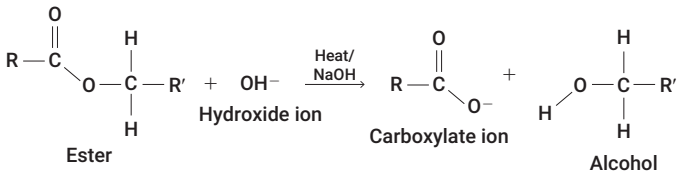


FIGURE 14.6.9 The alkaline hydrolysis of an ester

For example, methyl propanoate is hydrolysed to form the propanoate ion and methanol (Figure 14.6.10).

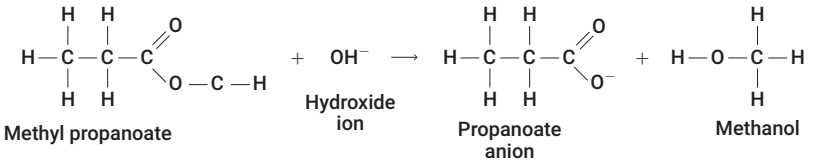


FIGURE 14.6.10 The alkaline hydrolysis of ester methyl propanoate to form the propanoate ion and methanol

The flavours and odours of many confectionary items are esters. A fun way to practise writing the names of esters is to use some commercially produced jellybean flavours and use an ester odour chart to determine the name and structure of the synthetic odour involved.

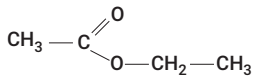
LEARNING CHECK 14.6

DESCRIBING

1 **Explain** why carboxylic acids are described as monoprotic.

2 **Explain** what is meant by a condensation reaction.

3 **Identify** the ester link in the following molecule of ethyl ethanoate.



APPLYING

4 Write balanced equations with named products to **describe** the reaction of:
- **a** methanoic acid with sodium
- **b** 1-butanol with ethanoic acid
- **c** 2-butanol with propanoic acid
- **d** propyl ethanoate in the presence of heat and concentrated sulfuric acid
- **e** methyl butanoate in the presence of heat and aqueous concentrated sodium hydroxide
- **f** 1-pentanol and butanoic acid.

5 The esters methyl butanoate and butyl methanoate are isomers. Draw the two structures and **explain** the key differences in their synthesis.

6 **Construct** a balanced equation to **describe** the neutralisation reaction that occurs between propanoic acid (CH_3CH_2COOH) and sodium hydroxide (NaOH).

7 **Construct** a balanced equation to **identify** the products of the reaction between ethanoic acid (CH_3COOH) and calcium carbonate ($CaCO_3$).

8 **Compare** the esterification reaction with the hydrolysis of esters.

9 **Explain** how the following reactions illustrate the amphoteric nature of carboxylic acids:

$CH_3COOH(aq) + H_2SO_4(aq) \rightarrow CH_3COOH_2^+(aq) + HSO_4^-(aq)$

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

14.7 Reactions of amines and amides

Syllabus link
Chapter 18 discusses amides, amines and polymers in more detail.

Amines have a wide range of uses as catalysts and solvents and in the manufacture of dyes, medicines and polymers, so they are an extremely important family of organic compounds. Amines are also found widely in nature as amino acids, which are the building blocks of proteins.

The amine functional group is $-NH_2$. Amines are compounds in which one or more atoms of hydrogen in ammonia (NH_3) are replaced by a carbon-containing group such as an alkyl group. Alkyl amines are represented by the general formula RNH_2.

As with alcohols and haloalkanes, amines may be classified as primary, secondary or tertiary depending on the number of alkyl groups attached to the nitrogen. A primary amine has one alkyl group, a secondary amine has two alkyl groups, and a tertiary amine has three alkyl groups attached to the nitrogen. **Figure 14.7.1** shows examples of these.

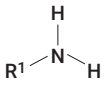
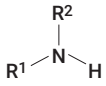
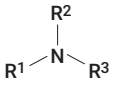
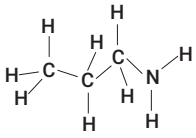
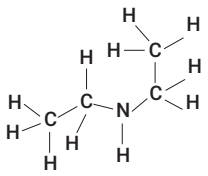
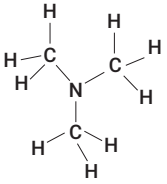
	Primary amine	Secondary amine	Tertiary amine
General structure			
General formula	R^1NH_2	R^1R^2NH	$R^1R^2R^3N$
Example	 **Propanamine**	 **Diethanamine**	 **Trimethanamine**

FIGURE 14.7.1 Primary, secondary and tertiary amines

Acid–base properties of amines

Syllabus link
Chapter 17 of *Nelson QCE Chemistry Units 1 & 2* describes different reactions involving bases.

Amines are generally weak bases, like ammonia from which they are formed. They can accept protons (H^+) due to the lone pair of electrons on the nitrogen atom. The general equation for the reaction of an amine acting as a base by accepting a proton is:

$$RNH_2(aq) + H^+(aq) \rightarrow RNH_3^+(aq)$$

Amine reaction with acids (neutralisation)

Since amines are generally weak bases, they will undergo a neutralisation reaction with acids to form an amine salt, but not water. This can be represented generally as:

$$R\text{–}NH_2(aq) + HCl(aq) \rightarrow R\text{–}NH_3^+Cl^-(aq)$$

For example:

$$\underset{\text{Methanamine}}{CH_3NH_2(aq)} + HCl(aq) \rightarrow \underset{\text{Methylammonium chloride}}{CH_3NH_3^+Cl^-(aq)}$$

Amphoteric behaviour of amines

Although amines are typically weak bases, they can exhibit weak acidic behaviour in certain situations, especially when they react with strong bases or in extremely basic environments. This is because the nitrogen can donate a H^+, thus acting as a weak acid under certain conditions, such as in reactions with super strong bases.

For instance, methanamine (CH_3NH_2) can donate a proton (H^+) from the amine group when it reacts with a very strong base such as sodium hydride (NaH) to form a methylamide ion:

$$CH_3NH_2(aq) + NaH(s) \rightarrow CH_3NH^-(aq) + Na^+(aq) + H_2(g)$$

Amide formation – a condensation reaction

Amines react with carboxylic acids in a similar way to their reaction with an inorganic acid. However, under certain conditions (heat, catalyst, removal of water), amines and carboxylic acids undergo a condensation reaction (eliminating water) to form amides:

$$R^1\text{–}COOH + R^2\text{–}NH_2 \rightarrow R^1\text{–}CONHR^2 + H_2O$$

This is also illustrated in **Figure 14.7.2**.

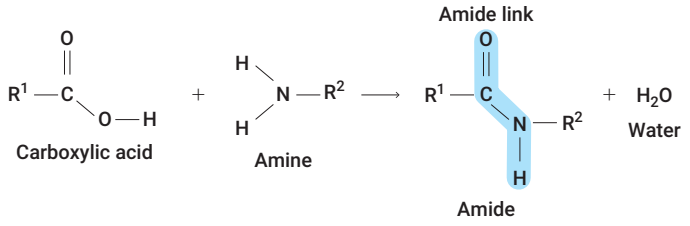


FIGURE 14.7.2 The formation of an amide

amide link the –CONH– group formed when an amine reacts with a carboxylic acid

Figure 14.7.3 shows the reaction to form *N*-ethylethanamide. In secondary amides, the letter N is used to indicate that the alkyl group is attached to the nitrogen.

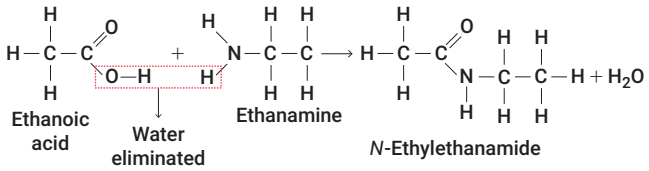


FIGURE 14.7.3 The formation of *N*-ethylethanamide

Weblink
Amines and amides

Worksheet
Organic reactions involving oxygen and nitrogen

Amides are important in industry and living systems. Polyamides are an important group of synthetic plastics. Urea, an important compound in fertiliser production and living systems (as a component of urine), is a carbamide with the formula H_2NCONH_2. It has two NH_2 groups attached to a carbonyl (C=O) group **(Figure 14.7.4)**. Urea was the first organic compound to be synthesised from inorganic starting materials, thus showing organic compounds were part of a chemical system and could be produced outside living things.

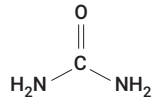


FIGURE 14.7.4 The structure of urea

LEARNING CHECK 14.7

DESCRIBING

1 **Explain** the difference between amine and amide molecules.

2 Write balanced equations with named products to **describe** the reaction of:

- **a** ethanamine with nitric acid
- **b** 2-butanamine with ethanoic acid
- **c** butanoic acid with methanamine
- **d** ethanoic acid with butanamine.

3 **Construct** a balanced equation to **describe** the formation of *N*-propylmethanamide ($C_5H_{11}NO$).

4 **Explain** why the formation of amides is a condensation reaction.

APPLYING

5 **Explain** why amines are described as amphoteric.

6 Compound A reacts with water to produce Compound B and hydroxide ions according to the following equation:

$$\underset{\text{Compound A}}{CH_3CH_2NH_2(aq)} + H_2O(l) \rightleftharpoons \underset{\text{Compound B}}{C_2H_5NH_3^+(aq)} + OH^-(aq)$$

- **a** **Apply** IUPAC rules to name Compound A.
- **b** **Identify** the Brønsted–Lowry acids in the equation.
- **c** A small amount of hydrochloric acid is added to the equilibrium mixture. **Predict** the effect of this on the concentration of Compound A in the mixture. **Explain** your reasoning.

14.8 Organic reaction types

Each class of organic compounds is considered to have its own characteristic molecular structural features that lead to its physical properties and chemical reactions. These properties and reactions can be used to distinguish between and identify different classes of organic compounds. Table 14.8.1 provides a summary of organic reaction types.

TABLE 14.8.1 Organic reaction types

Reaction	Description	Classes of compounds	Reagents and conditions	Example
Combustion	Burning in oxygen to produce carbon dioxide and water	All organic compounds	Oxygen and high temperature or flame to initiate	$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
Substitution (free radical)	Replacement of a hydrogen atom with a halogen atom	All organic compounds	UV light	$C_4H_{10}(g) + Cl_2(g) \rightarrow C_4H_9Cl(g) + HCl(g)$
Substitution (nucleophilic)	Replacement of an electronegative atom (e.g. a halogen) with a nucleophile (e.g. hydroxide ion)	Haloalkanes	Aqueous solution of sodium or potassium hydroxide	$CH_3Cl(aq) + NaOH(aq) \rightarrow CH_3OH(l) + NaCl(aq)$
Addition	Unsaturated molecules combine with other molecules	Alkenes and alkynes	H_2/Pd or halogens or halogen halides	$CH_2{=}CH_2(g) + H_2(g) \rightarrow CH_3CH_3(g)$
Elimination	Larger molecule forms a different structure and releases smaller molecules (i.e. salt, water)	Haloalkanes	NaOH in ethanol solution	$CH_3CH_2Cl(l) + NaOH(aq) \rightarrow CH_2{=}CH_2(g) + NaCl(aq) + H_2O(l)$
Oxidation	Primary alcohols forming aldehydes and carboxylic acids; secondary alcohols forming ketones	Primary and secondary alcohols	Either acidified $KMnO_4$ or acidified K_2CrO_7	$3CH_3CH_2OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$
Reduction	Addition of hydrogen to alkenes to form alkanes	Alkenes	H_2/Pd	$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$
Condensation	Reaction of acid and alcohol to form ester or acid and amine to form amide, with the loss of a water molecule	Carboxylic acid and either alcohol or amine	Concentrated H_2SO_4 catalyst or reflux with NaOH	$CH_3COOH(aq) + CH_3NH_2(aq) \rightarrow CH_3CONHCH_3(aq) + H_2O(l)$ $CH_3COOH(l) + CH_3OH(l) \rightarrow CH_3COOCH_3(l) + H_2O(l)$

LEARNING CHECK 14.8

DESCRIBING

1 **Identify** the reaction type and reaction conditions required for an alkane to form a haloalkane.

2 **Explain** how you would distinguish between two clear liquids, knowing one is propanol and the other is propanoic acid.

3 Carboxylic acids can be produced by the oxidation of primary alcohols. **Identify** the name of the alcohol you would need to oxidise to produce butanoic acid using this process.

14.9 Reaction pathways

So far in this chapter, we have looked at individual reaction types. However, sometimes, to synthesise a compound, we need to use a series of reactions involving different types of compounds. For example, substitution reactions involving alkanes and halogens are used to produce alcohols, which can then be oxidised to carboxylic acids. Together the alcohols and carboxylic acids can take part in esterification reactions to form esters.

FORMULA AND DATA BOOK

Using the reactions listed in this chapter as well as many others, chemists produce a vast range of products from hydrocarbons. The specific issues to consider when synthesising and manufacturing chemicals are covered in Chapter 17; however, it is also important to consider how to combine reactions to produce complex molecules from some simpler origins. **Figure 14.9.1**

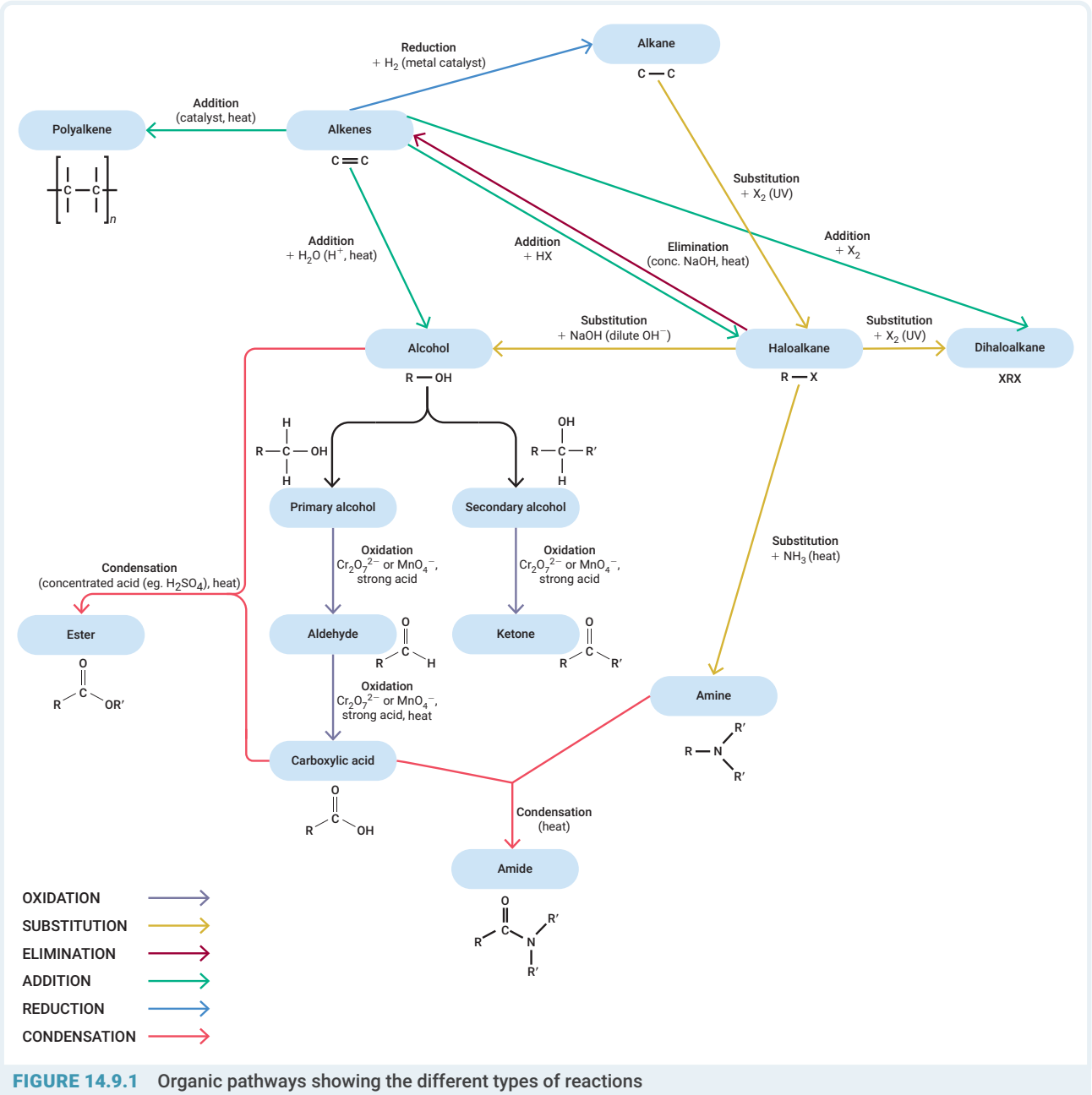


FIGURE 14.9.1 Organic pathways showing the different types of reactions

summarises the organic structures, reaction types and reaction conditions required for a series of reaction pathways as outlined in the reaction pathways diagram in the *Formula and Data Book*. This demonstrates how reaction pathways can be used to chemically manipulate organic molecules to form other desired organic products.

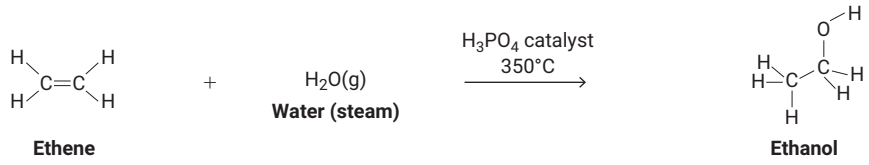
Formation of esters from alkenes

As well as being widespread in nature, esters are commonly used in industry. Esters can be easily synthesised, and they are produced synthetically for use as artificial flavouring and colourings. Several billion kilograms of polyesters are produced annually to make a wide variety of products, including fabrics and bottles. They can be manufactured from alkenes by the reactions discussed in this chapter.

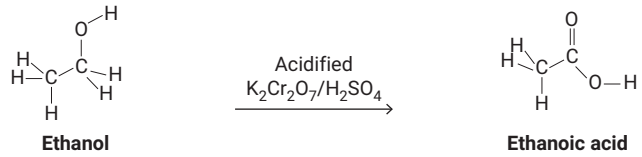
For example, ethyl ethanoate is used in glues and nail polish removers. It is produced in a three-step process from ethene.

- Step 1 involves an addition reaction to form ethanol.
- Step 2 involves oxidation of half of the ethanol molecules to form ethanoic acid.
- Step 3 is the condensation reaction of ethanol and ethanoic acid to produce ethyl ethanoate **(Figure 14.9.2)**.

1 Addition of H_2O to ethene to form ethanol



2 Oxidation of ethanol to form ethanoic acid (retain 50% of the ethanol produced in step 1 for use in step 3)



3 Condensation of ethanol (from step 1) and ethanoic acid to form ethyl ethanoate

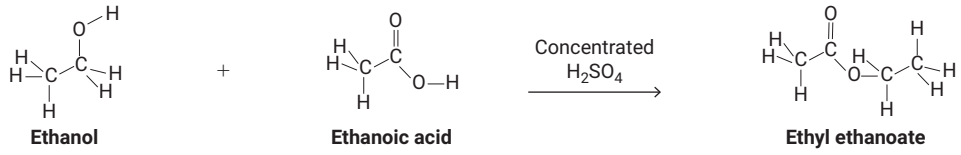


FIGURE 14.9.2 The formation of an ester from an alkene

Weblink
Reactions and reaction pathways

Formation of amides from an alcohol and an amine

Like ester formation, amide synthesis is important. This synthesis reaction can be traced through the reaction pathway diagram. In **Figure 14.9.3**, *N*-ethyl ethanamide is made from ethanol by first oxidising ethanol to ethanoic acid using acidified potassium dichromate ($K_2Cr_2O_7/H^+$). The acid then condenses with ethanamine ($CH_3CH_2NH_2$) to form the amide and water. This condensation usually requires heat or a dehydrating agent to shift the equilibrium. Overall, the pathway (alcohol → carboxylic acid → amide) demonstrates how alcohols can be converted into more complex compounds.

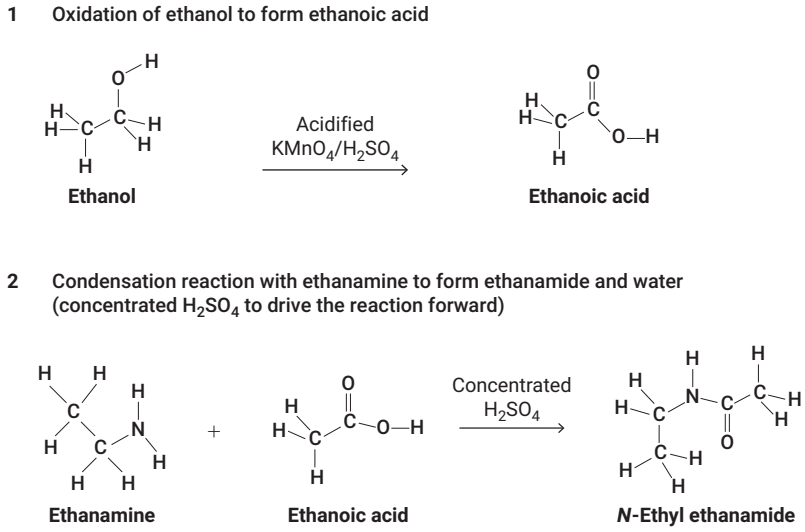


FIGURE 14.9.3 The formation of an amide from an alcohol and amine.

LEARNING CHECK 14.9

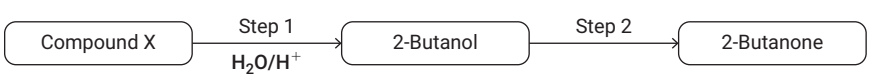
DESCRIBING

1 **Describe** a reaction pathway for the formation of the ester 2-butyl methanoate, using 2-butanol and chloromethane as the raw materials.

2 **Describe** a reaction pathway for the formation of the amide *N*-propyl butanamide from chloropropane and butanoic acid.

APPLYING

3 The flow chart below represents the chemical synthesis of 2-butanone via a two-step process.



a **Identify** Compound X.
b **Deduce** the reagents and reaction conditions required for Step 2.
c **Identify** the types of reactions that take place in Step 1 and Step 2.
d Write balanced chemical equations to **describe** the reactions of Step 2.

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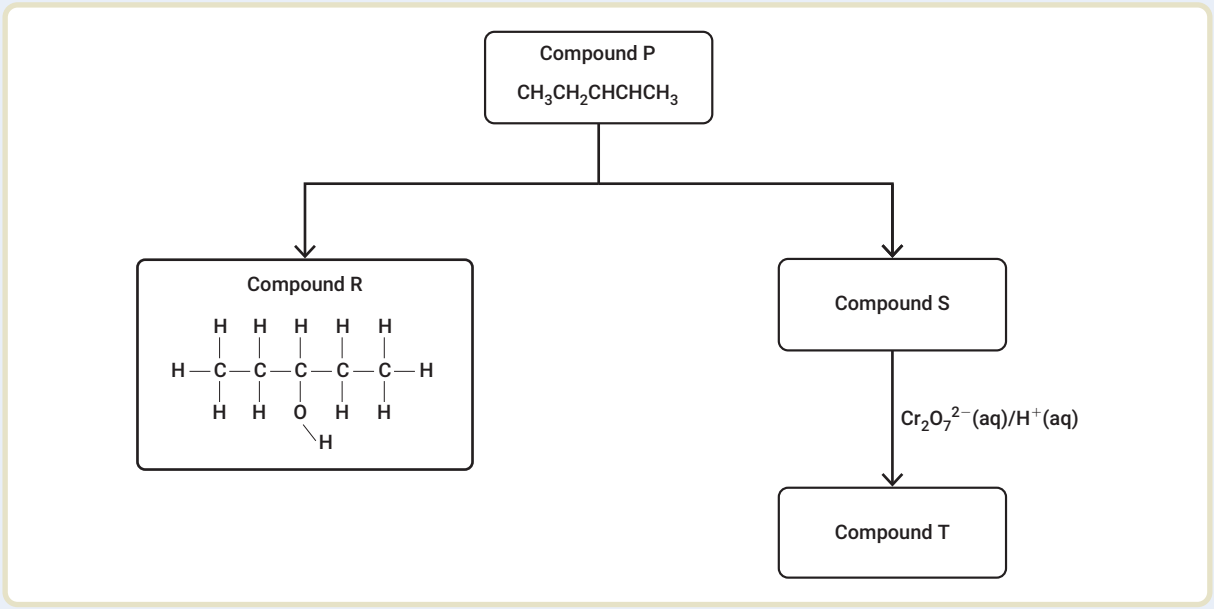
4 Alkenes can be used to manufacture a range of products. The reaction pathway diagram shown represents one example of the use of an alkene.



In this reaction pathway, Compound P is used to produce Compound R and Compound S. Compound S can then be used to produce Compound T.

a **Identify** the IUPAC systematic names for Compound P and Compound R.

b **Identify** the structures and names of Compound S and Compound T.

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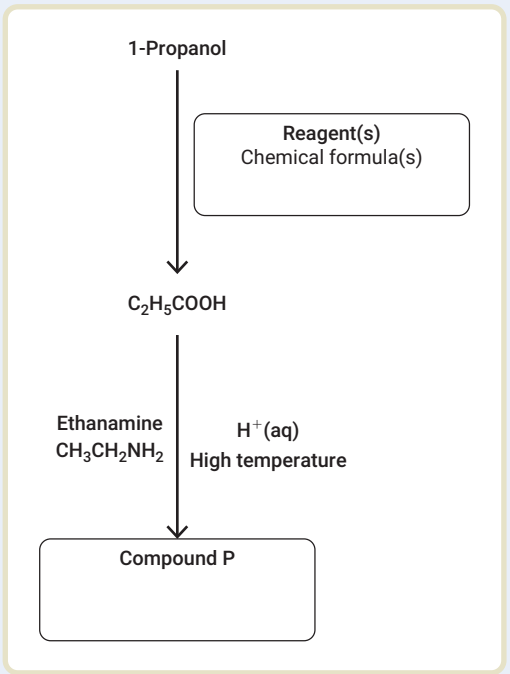
5 The following diagram represents a reaction pathway for the synthesis of Compound P.



a **Identify** the reagent(s) needed to convert 1-propanol to propanoic acid (C_2H_5COOH).
b When C_2H_5COOH is mixed with ethanamine ($CH_3CH_2NH_2$) in an acidified high-temperature environment, Compound P is formed. Give the name of Compound P.

14.10 Testing organic compounds

Weblink
Chemical tests for organic molecules

Organic compounds have characteristic molecular structural features that lead to their physical and chemical properties. Therefore, chemical reactivity can be used to distinguish between different organic compounds. Some tests that can be performed to determine the organic structure of some organic compounds are listed in **Table 14.10.1**.

TABLE 14.10.1 Tests for determining the class of an organic compound

Compound	Chemical test	Test result		Interpretation
Alkanes vs alkenes	Bromine water	Alkanes	No reaction. Solution stays brown.	Saturated molecule, non-reactive.
		Alkenes	Brown → colourless	Double bond allows for halogenation.
Primary, secondary or tertiary alcohols	Acidified potassium permanganate (MnO_4^-)/dichromate ($Cr_2O_7^{2-}$)	1° alcohol	$KMnO_4$: purple → colourless $K_2Cr_2O_7$: orange → green	Oxidises to aldehyde, then carboxylic acid.
		2° alcohol	$KMnO_4$: purple → colourless K_2Cr_2O: orange → green	Oxidises to ketone.
		3° alcohol	No reaction. Solution remains original colour.	Tertiary structure resists oxidation.

PRACTICAL ACTIVITY 14.10.1

COMPARING REACTIVITIES OF ALKANES AND ALKENES (TEACHER DEMONSTRATION)

Introduction

The reactivities of alkanes and alkenes are different. Alkanes react quite slowly by a process of substitution, whereas alkenes react rapidly, usually by the process of addition.

Research question

How does the reactivity of alkanes and alkenes differ?

Aim

To compare the reactivities of alkanes and alkenes

Materials

- 3 mL samples of alkanes and alkenes: hexane, cyclohexane and cyclohexene
- 4 mL of 0.01 mol L^{-1} potassium permanganate ($KMnO_4$) solution
- 5 mL of bromine (Br_2) water
- 2 mL of 2 mol L^{-1} sulfuric (H_2SO_4) acid
- distilled water
- 4 test tubes and test-tube rack
- 6 graduated droppers (one per solution used)
- 5 mL measuring cylinder

RISK ASSESSMENT

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Cyclohexane and cyclohexene are toxic.	Avoid contact with skin; wear gloves and a laboratory coat. Avoid inhaling vapours; use in a fume hood. Wash your hands at the end of the experiment. This activity is a teacher demonstration only.
Bromine water is poisonous and corrosive.	Avoid contact with skin; wear gloves and a laboratory coat. Avoid inhaling vapours; use in a fume hood. Wash your hands at the end of the experiment.
Sulfuric acid is corrosive.	Wear gloves and personal protective equipment to avoid contact with skin. Wash your hands at the end of the experiment.
Hexane, cyclohexane and cyclohexene are highly flammable.	Ensure no flame sources are near these chemicals.

Copy and complete the risk assessment table in your write-up. Ensure you manage these risks appropriately for your particular context. There are also many video demonstrations available if these risks are inappropriate to your context.

Procedure

Part A Oxidation reactions with acidified $KMnO_4$ solution

1. Label three test tubes, one for each hydrocarbon.
2. Place 1 mL of each hydrocarbon into the corresponding test tube.
3. In a clean test tube, mix 4 mL of $KMnO_4$ solution and 2 mL of H_2SO_4.
4. Add 1 mL of the $KMnO_4/H_2SO_4$ solution to each of the test tubes containing the hydrocarbons.
5. Shake the test tubes gently and observe them for 5 minutes.
6. Dispose of the solutions in a chemical waste jar. Do not pour them down the sink.
7. Rinse the test tubes and droppers with distilled water.

Part B Addition and substitution reactions with bromine

1. Place 1 mL of each hydrocarbon into the corresponding test tube.
2. Add 1 mL of Br_2 to each test tube.
3. Shake the test tubes gently and observe them for 5 minutes.
4. If a change is noted, add another 1 mL of Br_2 to that test tube and observe.
5. Dispose of the solutions in a chemical waste jar. Do not pour them down the sink.

Results

Record the results in a table similar to the one below.

Reagent		Hexane	Cyclohexane	Cyclohexene
Acidified $KMnO_4$ solution	After addition			
	After 5 min			
Br_2	After addition			
	After 5 min			

Analysis of results

1 Which of the hydrocarbons were readily oxidised by the acidified $KMnO_4$ solution?

2 Which reacted with the bromine solution?

3 Write the equation for any reaction that occurred with bromine.

Interpretation

4 State in your own words the difference between the reactivities of alkanes and alkenes.

Practical
Distinguishing between primary, secondary and tertiary alcohols (teacher demonstration)

LEARNING CHECK 14.10

DESCRIBING

1 **Describe** two tests you could use to determine whether a clear liquid is a primary or tertiary alcohol.

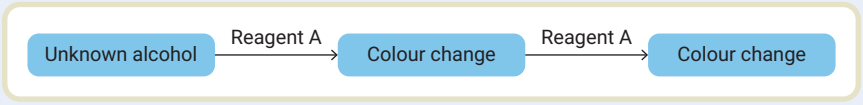
2 **Identify** a test that you could use to determine whether a substance is an alkane or an alkene.

APPLYING

3 You have samples of six organic compounds labelled A–F. You know that they all have a very similar molecular mass, and that they are butanoic acid, butane, butanamine, 1-butene, 1-butanol and butanal. However, you do not know which compound is which. **Describe** a series of tests that you could perform to determine the identity of compounds A–F as efficiently as possible.

4 a **Predict** what would you observe when sodium carbonate powder is added to a solution of propanoic acid.
b Write a balanced equation to **describe** this reaction.

5 A student wanted to identify whether an unknown sample of alcohol was a primary or secondary alcohol. Consider the following flow chart.



a **Identify** Reagent A.
b **Determine** whether the unknown alcohol was a primary or secondary alcohol. **Explain** your answer.

ANALYSING

6 A gaseous hydrocarbon is bubbled through bromine. The bromine is not decolourised. Draw conclusions about the identity of the unknown hydrocarbon.

CHAPTER SUMMARY

Properties and reactions

- Organic compounds display characteristic chemical properties and undergo specific reactions based on the functional group present.

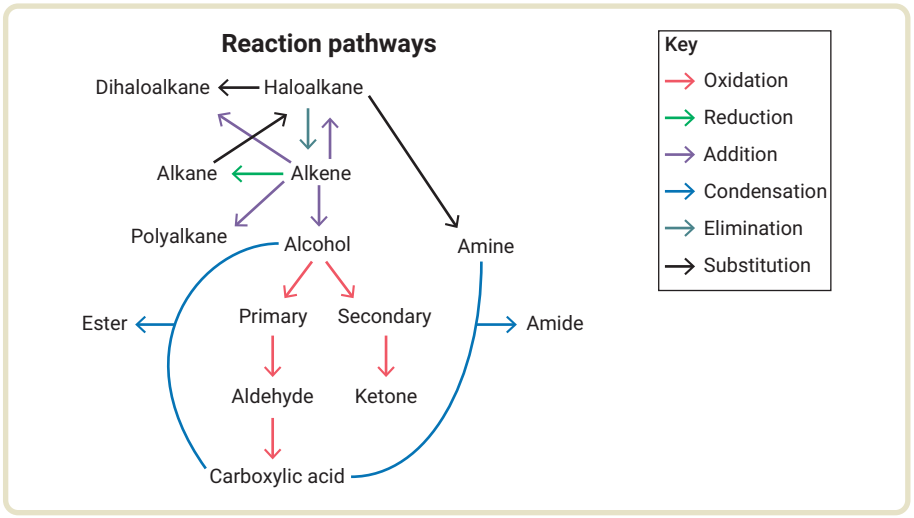
Compound	Reaction type	Examples
Alkanes	Substitution	alkane + halogen (X_2) $\xrightarrow{\text{UV light}}$ haloalkane
	Combustion	alkane + $O_2 \rightarrow CO_2 + H_2O$
Haloalkanes	Substitution	haloalkane + halogens (X_2) $\xrightarrow{\text{UV light}}$ haloalkane
		haloalkane + sodium hydroxide (NaOH) → alcohol
		haloalkane + ammonia (NH_3) → amine
	Elimination	haloalkane + NaOH → alkene + salt + H_2O
Alkenes	Addition	alkene + water $\xrightarrow{\text{acid catalyst}}$ alcohol
		alkene + halogen (X_2) → dihaloalkane
		alkene + hydrogen halide (HX) → haloalkane
		alkene monomer + alkene monomer → polyalkane
	Reduction	alkene + hydrogen (H_2) $\xrightarrow{\text{catalyst}}$ alkane
	Combustion	alkene + $O_2 \rightarrow CO_2 + H_2O$
Alkynes	Reduction	alkyne + hydrogen (H_2) $\xrightarrow{\text{catalyst}}$ alkane
	Combustion	alkyne + $O_2 \rightarrow CO_2 + H_2O$
Alcohols	Substitution	alcohol + hydrogen halide (HX) → haloalkane
	Oxidation	primary alcohol → aldehyde → carboxylic acid
		secondary alcohol → ketone
		Tertiary alcohols resist oxidation.
	Combustion	alcohol + $O_2 \rightarrow CO_2 + H_2O$
Carboxylic acids	Condensation	carboxylic acid + alcohol $\underset{\text{esterification}}{\rightleftharpoons}$ ester
Amines		amine + carboxylic acid → amide + H_2O

Identification and discrimination

- Primary, secondary and tertiary carbon atoms are determined by the number of carbons bonded to the carbon atom attached to the functional group.
- To discriminate between alkanes and alkenes, add bromine water, which decolourises with alkenes but not with alkanes.
- To test for alcohols, add acidified potassium dichromate(VI) or potassium manganate(VII). Primary and secondary alcohols oxidise so colour change is observed. Tertiary alcohols show no reaction.

Reaction pathways

- Reaction pathways are determined from the pathways diagram and involve given reactants and products, considering reagents, conditions and equations.



Adapted from QCAA *Formula and Data Book*, page 1. https://www.qcaa.qld.edu.au/downloads/senior-qce/sciences/snr_chemistry_25_formula_data_book.pdf

Special concepts

- Markovnikov's rule states that in addition reactions with HX or H_2O, the hydrogen adds to the carbon with the most hydrogens already attached.
- Acid–base properties (amphoteric substances):
  - Carboxylic acids act as weak acids, donating protons to form carboxylate ions, but they can also act as weak bases in the presence of strong acids, accepting protons to form protonated carboxylic acids.
  - Amines act as weak bases, accepting protons to form ammonium ions, but they can also act as weak acids, donating protons under certain conditions to form amine anions.

MULTIPLE CHOICE

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1. What is the name of the product formed when chlorine (Cl_2) reacts with 1-butene?

A 1,2-Dichlorobutane
B 1,4-Dichlorobutane
C 2,2-Dichlorobutane
D 2,3-Dichlorobutane

Questions 2 and 3 relate to the following reactions.

$CH_3CH{=}CHCH_3 + H_2O \rightarrow X$
$X + CH_3COOH \rightarrow Y$

2. What is the structure of Y?

A $CH_3CH_2CH(CH_3)COOCH_3$
B $CH_3COOCH(CH_3)CH_2CH_3$
C $CH_3CH_2CH_2COOCH_3$
D $CH_3OOCH_2CH_2CH_2CH_3$

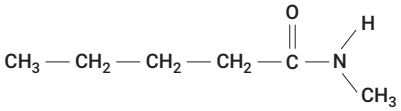
3. The reactions can be described as, respectively:

A reflux and hydrolysis.
B hydrogenation and condensation.
C hydration and esterification.
D reduction and substitution.

4. Which of the following statements about 1-butene is *not* correct?

A It undergoes an addition reaction with hydrogen to form butane.
B It can form two products when reacted with HBr.
C One 1-butene molecule will react with excess oxygen to produce four molecules of carbon dioxide and four molecules of water.
D It will undergo substitution reactions with chlorine in the presence of UV light.

5. Consider the following molecule.

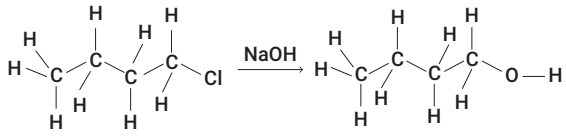


Which of the following compounds would have reacted to form the molecule above?

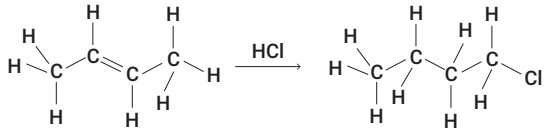
A 1-Pentanol and methanamine
B 2-Pentanone and ethanamine
C 1-Pentanal and ethanamine
D Pentanoic acid and methanamine

6. Which of the following organic reactions does not result in the product shown on the right-hand side of the arrow?

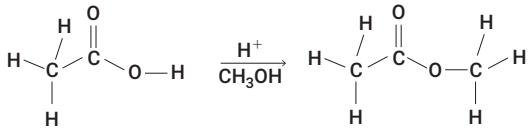
A



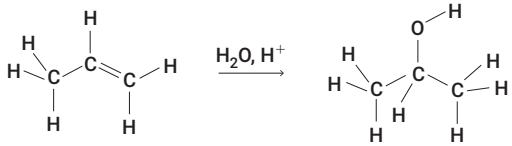
B



C



D



7. A purple solution of acidified potassium permanganate is added to 2-propanol and the mixture is heated. Identify the correct statement about this reaction.

A 2-Propanol is condensed to form propene.
B 2-Propanol is oxidised to form propanone.
C The acidified potassium permanganate solution is a strong reductant.
D The reaction mixture turns from colourless to purple when the reaction occurs.

 QCAA paper 1 2022 MCQ Q7

8. Compound X in these reaction pathways is:

A a ketone.
B an alkene.
C an aldehyde
D a carboxylic acid.

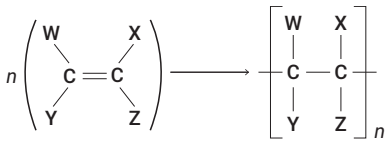
 QCAA paper 1 2021 MCQ Q18

9. Identify the major product when 2-methyl-2-butene reacts with water under acidic conditions.

A $(CH_3)_2CHCOCH_3$
B $(CH_3)_2C(OH)CH_2CH_3$
C $(CH_3)_2CHCH(OH)CH_3$
D $(CH_3)_2C(OH)CH(OH)CH_3$

 QCAA paper 1 2020 MCQ Q3

10.



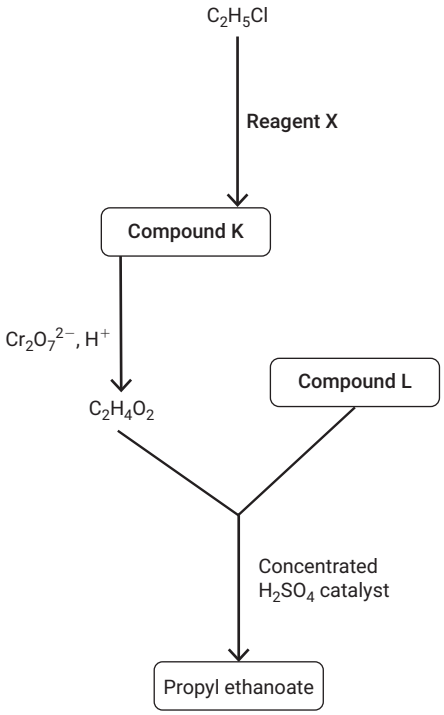
This general chemical equation represents the following type of reaction.

A Addition
B Hydrolysis
C Esterification
D Condensation

SHORT RESPONSE

11. The ester propyl ethanoate has a characteristic odour and has been isolated from many fruits, including pineapple. A sample of this ester is to be prepared in the laboratory in order to develop a synthetic pineapple flavouring. A partially completed reaction pathway for this preparation is shown below. Use this diagram to answer questions a, b and c.

a Write the structural formula for propyl ethanoate.
b Write the structural formulas for compounds K and L.
c Identify the formula of Reagent X.



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12. 2-Chloropropane can be reacted with ammonia to produce an uncharged organic molecule, Compound R.

a Write the equation for the reaction that occurs.

b Give the IUPAC name of Compound R.

c Name the type of reaction that produces Compound R.

CROSS-CHAPTER QUESTION

13. Carboxylic acids are classified as weak acids. Ethanoic acid (CH_3COOH) is an example of a carboxylic acid that ionises in water to form carboxylate ions.

a **Determine** a balanced chemical equation showing the ionisation of ethanoic acid in water.

b **Explain** why carboxylic acids are considered weak acids.

c **Identify** the relationship between a carboxylic acid and its carboxylate ion.

d A solution of ethanoic acid has a concentration of 0.10 M and a K_a value of 1.8×10^{-5}. **Calculate** the concentration of H^+ ions formed.

e **Calculate** the pH of the ethanoic acid solution.

DATA ANALYSIS

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14. Analyse data

Four colourless liquids, A, B, C and D, are known to be butane, 1-butene, 2-butanol and 1-propanol. Reactions are carried out to identify the liquids. The results are shown.

Test 1	A	B	C	D
Bromine (Br_2) water	No reaction	No reaction	No reaction	Decolourised

Test 2	A	B	C
Excess acidified potassium manganate(IV) ($KMnO_4$) solution, heated gently	Decolourised, Compound X formed	Decolourised, Compound Y formed	No reaction

Test 3	Compound X	Compound Y
Ethanol and concentrated sulfuric acid solution, heated gently and refluxed	Fruity smell produced, Compound Z formed	No apparent reaction

a **Identify** Compound D. Explain your reasoning.

b Write a balanced equation to **describe** the decolourisation of the bromine (Br_2) water by Compound D. Apply IUPAC rules to name the product formed.

c **Identify** Compound C. Explain your reasoning.

d **Draw** the structural formula of Compound Y.

e **Identify** Compound B.

f **Draw** the structural formula of Compound Z.

g **Apply** IUPAC rules to name Compound Z.

15. Analyse data

Four bottles containing clear liquids were on the laboratory shelf, but the labels had fallen off. The missing labels found on the floor had the following names: 1-hexene (C_6H_{12}), pentane (C_5H_{12}), water (H_2O) and ethanol (C_2H_6OH).

A group of chemistry students was asked to devise a series of tests to identify the contents of each of the four bottles. The students labelled the bottles A, B, C and D, and conducted their tests. Their results are shown below.

Bottle	Soluble in water	Flammable (combustion)	Decolourises bromine in the absence of UV light
A	Yes	No	No
B	No	Not tested	Yes
C	No	Yes	No
D	Yes	Yes	No

a Using the information from the tests, **identify** which bottle contains each chemical, giving reasons for your decision.

b **Construct** balanced equations for the combustion reactions that occurred.

CHAPTER 15

Organic materials: Structure and function

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SYLLABUS DOT POINTS

SCIENCE UNDERSTANDING

- Describe the structural features of
  - amino acids, tripeptides, monosaccharides and disaccharides
  - polyethene (LDPE and HDPE), polypropene (syntactic, isotactic and atactic) and polytetrafluoroethene (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.

SCIENCE INQUIRY

- Investigate the properties of polymers.

SCIENCE AS A HUMAN ENDEAVOUR

- Appreciate that synthetic polymers often have large 'ecological footprints' as they are synthesised from fossil fuels and do not biodegrade. Therefore, sustainable polymers, produced from renewable sources such as plants, waste products and waste gases are 'greener'.

Introduction

Apart from the inorganic molecules of water and oxygen, we depend more on organic molecules in every aspect of our lives than inorganic ones. The food we eat, the clothes we wear, the plastics we rely on in everyday products and the fuels that power transport vehicles are all mainly composed of organic compounds. The medicines we use to fight microbes and even the microbes themselves are largely made up of organic compounds.

Although inorganic water is the most abundant chemical in the body, most of the other chemicals are carbon-based organic chemicals. All living things are massive chemical machines composed largely of organic compounds interacting in a watery soup. The membranes of our cells, DNA and the enzymes that catalyse the chemical reactions within cells are all organic compounds. Muscles, fat and skin are all based on organic compounds and our bones are formed from a framework of organic compounds in which minerals become embedded.

Most of these useful organic materials are polymers, and in this chapter, you will consider the structures of proteins, carbohydrates and synthetic polymers, and relate the structures to the properties that these substances have.

ASSUMED KNOWLEDGE

- ✓ Organic molecules are built on a skeleton of covalently bonded carbon atoms.
- ✓ The types of atoms present affect the overall shape of a molecule. This can be used to determine the chemical reactivity of the molecule.
- ✓ Classes of organic molecules have characteristic functional groups that affect how they react.
- ✓ The structure and bonding of different organic compounds can affect the properties of these compounds.
- ✓ Organic compounds can contain different functional groups such as alcohols (–OH), carboxylic acids (–COOH), esters (–COO–) and amines ($–NH_2$).
- ✓ Organic structures are named according to IUPAC naming conventions

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ identify and name polymers and monomers from their structures
- ✓ draw structures of monomers and polymers
- ✓ predict the properties of a polymer based on its structure
- ✓ relate the structure, properties and bonding type of a polymer
- ✓ distinguish between a polyester and a polyamide
- ✓ identify the monomers and structure of saccharide and peptide polymers
- ✓ draw the structures of zwitterions formed from 2-amino acids under various pH conditions.

15.1 Polymers

polymer a large molecule made from many thousands of repeating units

monomer an individual unit of a polymer

polymerisation the process by which monomers link together to form a polymer

copolymer a polymer made from more than one type of monomer

homopolymer a polymer made from one type of monomer

Polymers are giant molecules, often called macromolecules, which form when many thousands of smaller molecules (**monomers**) are joined by covalent bonds (Figure 15.1.1). The process of linking monomers together is called **polymerisation**. If the polymer consists of more than one type of monomer, it is known as a **copolymer**. If the polymer consists of only one type of monomer, it is called a **homopolymer**.

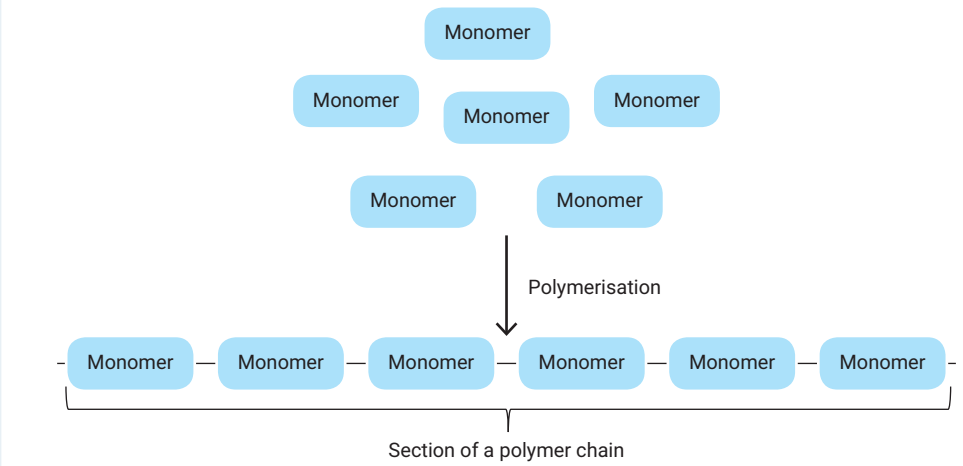


FIGURE 15.1.1 Polymers are formed from monomers.

Polymers can be classified on the basis of how they are formed. The two most common polymerisation reactions to join monomers together are:

- addition polymerisation, which involves an **addition reaction**
- condensation polymerisation, which involves a condensation reaction.

These reactions will be explored in further detail in Chapter 18.

Polymers may be natural or synthetic. Natural polymers such as silk, wool and hair (made of proteins), starch (made of carbohydrates) and DNA are manufactured by living organisms. Synthetic polymers, commonly referred to as plastics, are manufactured in laboratories or on a larger scale in factories.

addition reaction a reaction in which two or more molecules combine to form a single product, without producing any by-products

Don Pablo/Shutterstock.com

FIGURE 15.1.2 Plastic drink bottles are made from a synthetic polymer.

The structure of polymers

Like all chemicals, the properties of polymers depend on their structure. Depending on the type of polymer, the complexity of the structure can vary significantly, leading to a wide range of properties. For synthetic polymers, the structure is typically described in terms of **chain structure**, **crystallinity** or the **monomer arrangement** in the polymer chain.

These concepts will be further discussed throughout the chapter.

The concept of primary, secondary, tertiary and quaternary structures is specifically associated with proteins and other biopolymers, such as DNA. The **primary structure** of a biopolymer is the sequence of its monomers, influencing its properties. The **secondary structure** is the loops or twists in the chain caused by hydrogen bonding within the chain of the primary structure. The **tertiary structure** is the overall three-dimensional shape of the polymer, shaped by intermolecular forces between side chains. The **quaternary structure** occurs when multiple tertiary structures aggregate **(Figure 15.1.3)**.

There is a relationship between structure and properties for both synthetic and natural polymers. Although the properties of synthetic polymers are typically based on chain structure, crystallinity and monomer arrangement, biopolymers such as proteins and DNA are characterised by their more complex arrangement and folding. These structural differences account for the diverse functions and applications of both types of polymers.

chain structure the way in which the polymer chains are organised

crystallinity the degree of order to the polymer structure

monomer arrangement organisation of repeating units in the monomer

primary structure the sequence of monomers in a biopolymer chain

secondary structure the regular folding patterns in a biopolymer chain caused by (mainly) hydrogen bonds

tertiary structure the 3D shape of a single polymer chain held together by interactions from different parts of the molecule

quaternary structure the shape of two or more polymer chains aggregated together, held by intermolecular interactions

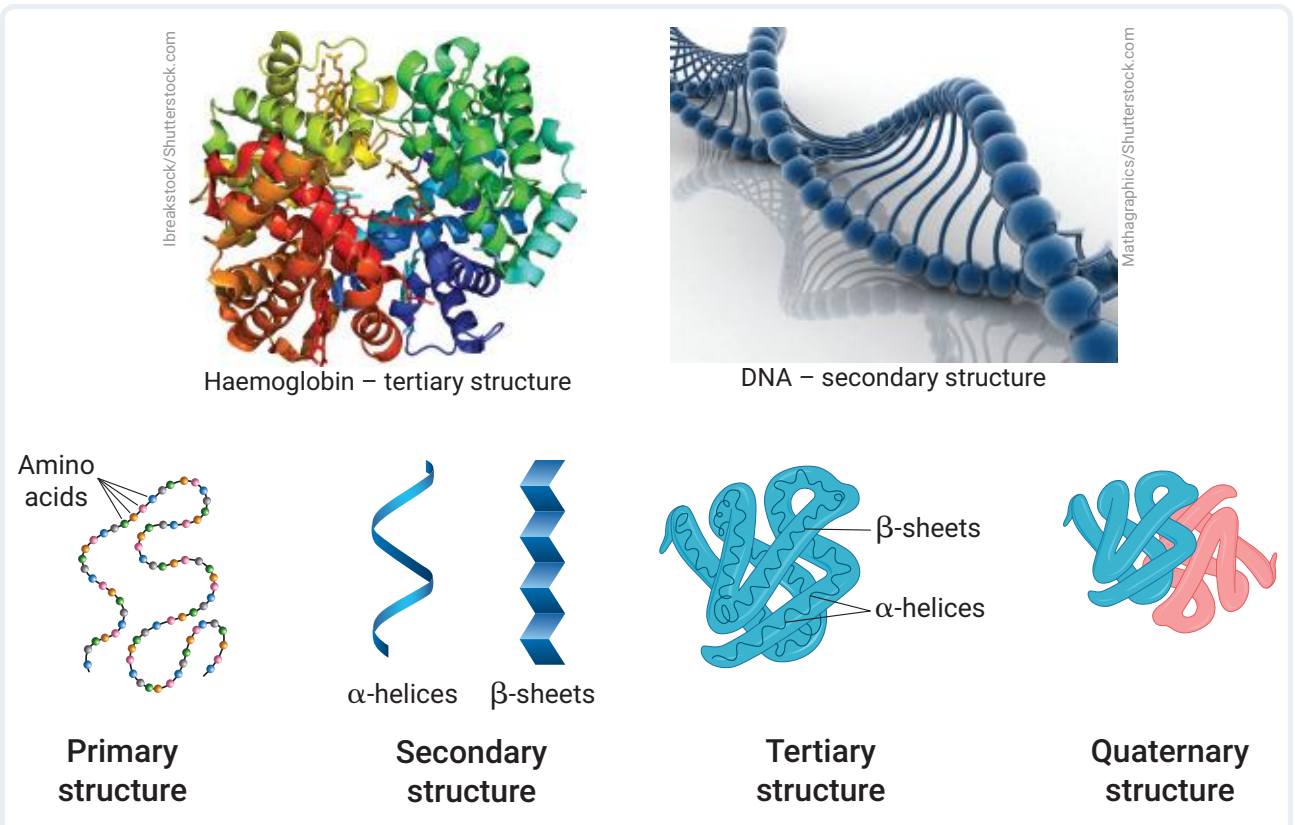


FIGURE 15.1.3 Biopolymers (e.g. proteins and other biopolymers, such as DNA) have a primary, secondary, tertiary and quaternary structure.

Relating properties to structure

Polymers are long complicated molecules held together by covalent bonds. Even though they are composed of long monomer chains, they have different properties. These properties can vary according to the identity of the monomer units and the nature of the covalent bond holding them together.

It is important to match the properties of the polymer for its intended use. The properties depend on the structure of the polymer molecules and the bonding present. These structural features are crystallinity, branching, chain length, side groups and cross-linking **(Table 15.1.1)**.

Crystallinity

crystalline having an ordered arrangement of atoms, ions or molecules in the solid form

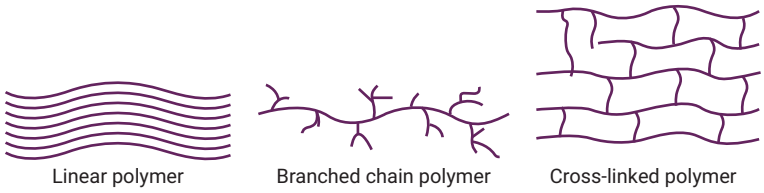
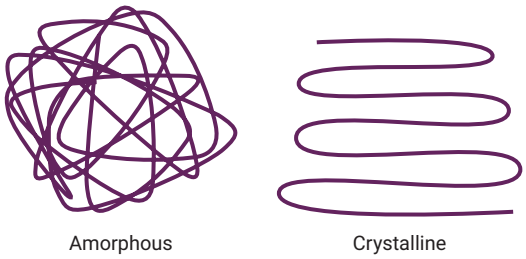
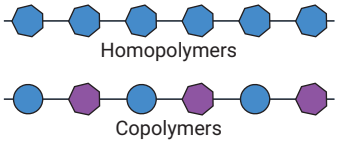
amorphous shapeless; not having an extended ordered arrangement of atoms, ions or molecules

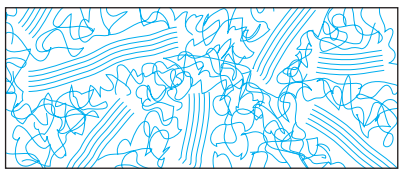
Molecules of linear polymers such as polyethene can flex and twist, resulting in some molecules being tangled. The final polymer has regions that are **crystalline** and regions that are **amorphous (Figure 15.1.4)**.

In crystalline regions, the polymer chains are closer together, so the intermolecular forces are stronger. This leads to greater rigidity and higher density. The more crystalline regions a polymer has, the more rigid and dense it is. Other properties that depend on the degree of crystallinity are opacity, resistance to permeation and higher melting points.

In amorphous regions, the chains are tangled and disordered and have no definite structure. The large gaps between chains means that the intermolecular forces are weaker. This leads to more flexibility and lower density. Other related properties are transparency, permeability and lower melting points.

TABLE 15.1.1 Key structural features of polymers structures

Feature	Description	Examples
Chain structure	Linear, branched or cross-linked Length of chain Side groups present	
Crystallinity	Amorphous or crystalline regions	
Monomer arrangement	Homopolymer or copolymer	



Sharwood et al. 2008 Nelson VCE Chemistry units 3 and 4

FIGURE 15.1.4 Crystalline and amorphous regions in a polymer

When manufacturing plastics in a commercial situation, the percentage of crystalline and amorphous regions can be controlled; therefore, manufacturers can control many of the properties of the resulting polymer.

Branching

Branched polymers differ in structure from linear polymers due to the presence of side chains branching off the main chain. Linear chains with little to no branching can pack together more closely than chains with a high degree of **branching**. Therefore, polymers with low chain branching will tend to be more crystalline, and therefore denser, less flexible and less transparent. Polymers with high chain branching tend to be more amorphous, and therefore less dense, more flexible and more transparent.

branching the presence of side chains on a polymer chain

Chain length

For any given type of polymer, the longer the chain and the more uniform the chain lengths in the overall polymer structure, the higher the melting point and the harder the polymer.

Chain length also affects the flow characteristics of the softened polymer, which affects the manufacturing process. Long chains make the softened polymer more viscous and difficult to extrude, whereas chains that are too short will cause the extruded product to sag or not withstand a high-pressure blow mould process.

Side groups

side group a functional or hydrocarbon group on a polymer chain that is not part of the main chain

The **side groups** attached to the carbon backbone of the polymer affects the properties the polymer exhibits. A bigger side group on a linear chain reduces the flexibility of the polymer, making it stiffer. For example, replacing hydrogen in polyethene with a chlorine atom (to make polyvinyl chloride – PVC) or a benzene ring (to make polystyrene) restricts the ability of the chain to flop around and therefore improves rigidity (Figure 15.1.5).

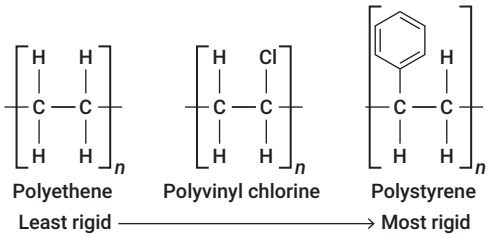


FIGURE 15.1.5 The repeating monomer units of the common polymers polyethene, polyvinyl chloride and polystyrene. The repeating monomer units of the polymer are shown within the square brackets [ ], where *n* represents the number of times the unit is repeated.

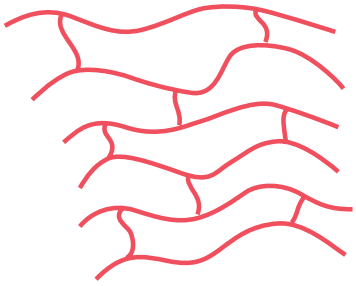


FIGURE 15.1.6 Cross-linking joins chains to each other.

Smith et al. 2010 Chemistry in use. Book 2

Cross-linking

The rigidity and hardness of a polymer can be increased by cross-linking. In this process, linear chains are bonded together to form a more rigid two-dimensional or three-dimensional structure. These **cross-links** are usually formed through strong ionic or covalent bonds between polymer chains (Figure 15.1.6). The more cross-linking there is, the more strongly the polymer chains are bonded and the more rigid the polymer.

cross-link a covalent or ionic bond between polymer chains, holding them together firmly

Polymer stability

The stability of chemical bonds between monomers directly influences polymer resistance to degradation. Strong covalent bonds make the polymer highly durable and resistant to environmental breakdown. Polymers with weaker bonds or bonds that are easily hydrolysed are more prone to degradation and thus exhibit greater biodegradability.

Biodegradability

biodegradable able to decay naturally due to the action of enzymes produced by bacteria

condensation polymer a polymer that forms by the elimination of a small molecule (often water) when monomers join

addition polymer a polymer that forms by monomers joining together without the loss of any atoms

In general, natural polymers are more likely to be **biodegradable** than synthetic polymers. Natural polymers are all **condensation polymers**, and a condensation reaction is more easily reversed than an addition reaction. As you learnt in Chapter 14, ester links, which are formed when an alcohol and a carboxylic acid react, are an example of a reversible bond that may be hydrolysed (by adding water) to separate the monomers. Amide linkages, which are formed when an amine and a carboxylic acid react, are weak and can be broken down. For example, proteins and carbohydrates can all be broken down by the action of enzymes produced by living organisms such as naturally occurring bacteria.

Addition polymers such as polyethene, polypropene and polystyrene will not degrade naturally and so are a significant environmental problem throughout the world. They are generally composed of more stable, covalently bonded carbon backbones that are difficult to degrade. Improvements to the biodegradability of polymers have come about through developing synthetic condensation polymers such as polyamides, polylactic acid, polyesters and polysaccharides, which naturally occurring enzymes find much easier to digest (Figure 15.1.7). We will learn more about these polymers later in the chapter.

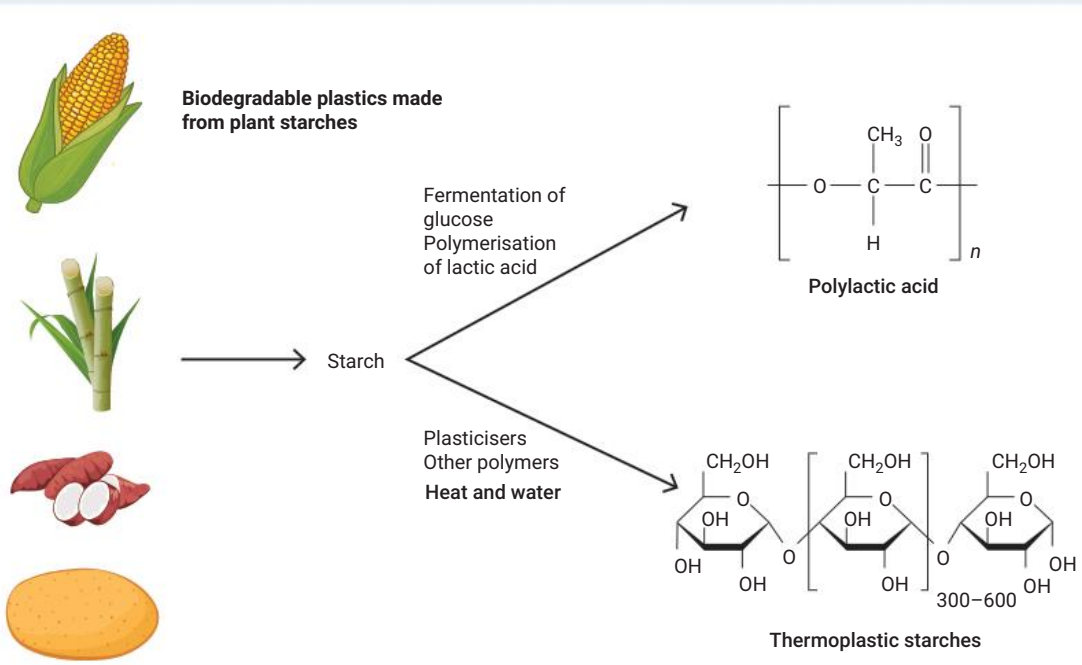


FIGURE 15.1.7 Common biodegradable plastics. Polylactic acid is obtained from starch from plants such as corn, sugar cane, sugar beet and cassava. Thermoplastic starches are made by heating plant starches with water and then adding plasticisers or other polymers.

Biodegradability affects how a plastic will break down naturally in the environment. Non-biodegradable plastics fragment into persistent microplastics that accumulate in ecosystems, posing environmental and health risks for future generations. Recently, governments and manufacturers have attempted to address this issue by banning single-use plastic items and investing in biodegradable alternatives.

Syllabus link

Chapter 14 from *Nelson QCE Chemistry Units 1 & 2* describes intermolecular forces.

Tensile strength

Many polymers are manufactured specifically to obtain high **tensile strength**. This includes synthetic polymers such as nylon, and natural polymers such as the 'silk' that spiders produce to form their webs. Again, this is achieved by synthesising polymers with appropriately strong structures.

tensile strength the resistance of a substance to being pulled or stretched

Cross-linked polymers (e.g. epoxy) form a rigid three-dimensional network, providing exceptional strength and durability as bonds extend throughout the network. Linear polymers (e.g. high-density polyethene (HDPE)) have straight, closely packed polymer chains, resulting in strong intermolecular forces between chains and high strength. Branched polymers (e.g. low-density polyethene (LDPE)) have reduced packing efficiency because of their irregular structure, leading to weaker forces between chains and greater flexibility (Figure 15.1.8).

density the mass per unit volume

Density

The **density** of a polymer varies with structure, and in particular how tightly packed together the polymer chains are. Two factors that can affect this are the branching of the chains and the side groups that can be attached to the chains. Polymer chains with extensive branching and large side groups cannot fit together as tightly, and consequently their overall structure is less dense.

FIGURE 15.1.8 The density and function of plastics depends on the degree of branching.

LDPE and HDPE are examples of plastics that have varying densities relating directly to the branching structure of their polymer molecules.

Table 15.1.2 summarises how the structure of polymers relates to their properties.

TABLE 15.1.2 Summary of the impact of structural differences on the properties of polymers

Property	Structure	Effect on polymer properties
Crystallinity	• Crystalline regions: polymer chains packed closely together. • Amorphous regions: chains are tangled and disordered.	• Crystalline regions: high density, rigidity, opacity and permeability, and higher melting points due to strong intermolecular forces. • Amorphous regions: low density, flexibility, transparency and permeability, and lower melting points due to weaker intermolecular forces.
Branching	• Low branching: chains can pack closely. • High branching: chains are spaced further apart.	• Low branching: more crystalline, denser, less flexible and less transparent. • High branching: more amorphous, less dense, more flexible and more transparent.
Chain length	• Longer chains • Shorter chains	• Longer chains: higher melting points, harder polymers and more viscous when softened. • Shorter chains: lower melting points, softer polymers, prone to sagging during manufacturing.
Side groups	• Side groups attached to main parent chain (e.g. chlorine in PVC, benzene in polystyrene).	• Larger side groups: increased rigidity and reduced flexibility (e.g. polyvinyl chloride (PVC) and polystyrene are stiffer than polyethene).
Cross-linking	• Chains are bonded together by strong ionic or covalent bonds.	• Increased cross-linking leads to greater rigidity, hardness, and resistance to deformation (e.g. melamine, polyurethane).
Polymer stability	• Stability of the structure depending on the type of bonds between monomers.	• Strong covalent bonds: high durability and environmental resistance. • Weak or hydrolysable bonds: less durability, greater biodegradability (e.g. polylactic acid (PLA)).
Tensile strength	• The interactions within polymers that hold polymer chains together.	• Cross-linked (highest strength), linear chains (higher strength), branched chains (lower strength) (e.g. Bakelite (rigid cross-linked), HDPE (strong), LDPE (flexible)).
Density	• The packing of the polymer chains relative to each other.	• Tighter packing (higher density) or loose packing (lower density) due to branching or linearity (e.g. HDPE (high density), LDPE (low density)).
Biodegradability	• Dependent on polymer structure.	• Stable carbon–carbon backbones resist degradation (synthetic polymers). • Natural polymers with bonds that are more easily hydrolysed (reversible ester bonds) promote biodegradability (e.g. polylactic acid (PLA) (biodegradable), polyethylene (non-biodegradable)).

PRACTICAL ACTIVITY 15.1.1

IDENTIFYING PLASTICS BY THEIR DENSITY

Introduction

Plastics are synthetic materials with a wide range of properties. One property that can be used to help identify plastics is density. For this activity, you are to design an experiment to identify unknown samples and to separate and identify the pieces in the mixture.

Research question

Can the densities of different plastics be used to identify unknown samples and separate a mixture of plastic pieces effectively by comparing them to known densities of liquids?

Aim

To design and conduct an experiment that identifies unknown samples of plastics in a mixed plastic sample by comparing them to known densities of liquids

Materials

- liquids of varying densities (See the list below. Note: Not all liquids need to be used.)
- 3 small pieces of different plastic
- 3 test tubes (or as many as required to test with the liquids available)
- forceps

The information in Table 15.1.3 and Table 15.1.4 will help you.

TABLE 15.1.3 Densities of common plastics

Plastic	Density (g mL^{-1})
HDPE	0.95–0.97
LDPE	0.917–0.940
Polyethylene terephthalate (PETE)	1.38–1.39
Polypropylene (PP) Polystyrene (PS) (in solid form)	0.90–0.91 1.04–1.05
PS (in foam form)	Variable, but always less than 1
Polyvinyl chloride (PVC) (rigid)	1.30–1.58
PVC (flexible)	1.16–1.35

TABLE 15.1.4 Densities of nine solutions

Liquid	Density (g mL^{-1})
Methanol	0.79
52% ethanol/water mixture	0.911
38% ethanol/water mixture	0.9408
24% ethanol/water mixture	0.9549
Water	1.00
10% solution of NaCl	1.08
Saturated solution of $MgCl_2$	1.34
40% $CaCl_2$ solution	1.398
Saturated solution of $ZnCl_2$	2.01

RISK ASSESSMENT

What are the risks in doing this practical activity?	How can you manage these risks to stay safe?
Methanol and ethanol are highly flammable.	Ensure no flame sources are present near either of these chemicals.
Zinc chloride is a hazardous material that can cause skin and eye irritation.	Wear gloves and a lab coat when handling this material. Do not dispose of zinc chloride down the sink; collect it as a waste according to your teacher's instructions.

Procedure

1 Consider how you will verify the densities of known samples before testing unknown samples.

2 Take care that no air bubbles adhere to the samples, and shake the tube to check that samples are floating.

Results

Record your observations in an appropriate format. For example, you could draw up a table of liquid densities, matching these to the density of the plastic pieces.

Analysis of results

1 Identify the unknown samples, giving reasons for your decisions.

Interpretation

2 Identify which polymer would be best to use for each of the following and why.

- **a** As a replacement for the lead sinkers used in fishing
- **b** To make a toy boat

3 Determine if there were any plastics difficult to distinguish. Explain your response.

4 Identify other properties that could be used to separate these plastics.

LEARNING CHECK 15.1

DESCRIBING

1 **Explain** what the following terms mean.
   - **a** Polymer
   - **b** Monomer
   - **c** Copolymer

2 **Compare** addition polymerisation and condensation polymerisation and the biodegradability of their products.

3 **Contrast** the primary, secondary, tertiary and quaternary structure of polymers.

4 **Explain** what is meant by the following properties of plastics.
   - **a** Biodegradability
   - **b** Tensile strength
   - **c** Density

5 **Describe** how cross-links, branching and side groups affect the properties of polymers.

6 **Discuss** how the following structures affect the properties of a polymer.
   - **a** Crystallinity
   - **b** Chain length

APPLYING

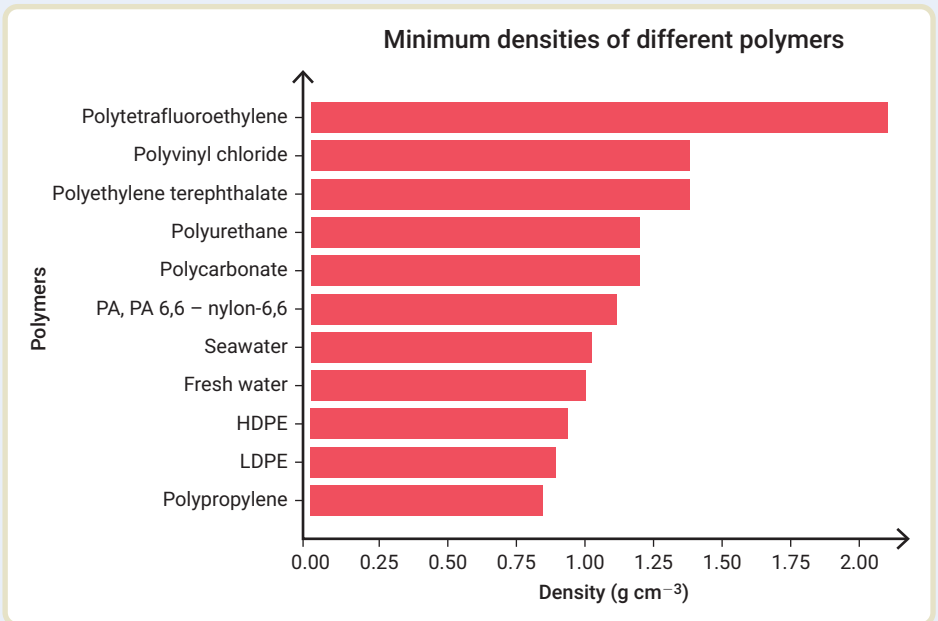
7 **Explain** why synthetic polymers are much less likely to biodegrade than natural polymers.

8 **Compare** the tensile strength of cross-linked and branched polymers, justifying the reasons behind the tensile strength of each type of substance.

9 **Contrast** the intermolecular forces between polymer molecules of LDPE and HDPE, referring to their branching and packing ability.

ANALYSING

10 The following graph shows the minimum densities of different polymers, as compared to seawater and fresh water.



Data attribution: Campanale, C., Savino, I., Pojar, I., Massarelli, C., & Uricchio, V.F. (2020). A practical overview of methodologies for sampling and analysis of microplastics in riverine environments. *Sustainability*, 12(17), 6755. https://doi.org/10.3390/su12176755

a **Identify** the density of polyvinyl chloride.
b **Identify** the density of fresh water.
c **Contrast** the density of polypropylene with HDPE.
d **Determine** whether LDPE would float or sink in fresh water.
e **Predict** whether polytetrafluoroethylene would have a branching structure, similar to low-density polypropylene, based on the respective densities.

15.2 Relating structure and properties of synthetic polymers

plastic a synthetic polymer that is malleable, pliable and capable of being moulded by heat and pressure

thermoplastic a plastic polymer that can be melted and re-formed

thermosetting a plastic polymer that cannot be melted and re-formed

It is important to distinguish between synthetic polymers and **plastic**. Although all plastics are synthetic polymers, not all synthetic polymers are plastics. Synthetic polymers are human-made macromolecules consisting of long chains of monomers joined together. Plastics are a type of synthetic polymer that is malleable and pliable and capable of being moulded by heat and pressure. Chemists distinguish between polymers that can be melted and re-formed and those than cannot by using the terms **thermoplastic** and **thermosetting** (Figure 15.2.1).

Thermoplastic polymers soften on heating and so are easily recycled because they can be melted and remoulded. Thermoplastic polymers are used in plastic bags and plastic wrap (polyethene), garden hoses (polyvinyl chloride (PVC)) and soft-drink bottles (polyethene terephthalate (PET).

Thermosetting polymers do not become soft or change shape on heating, so they are not easily recycled. These polymers are generally stronger, more chemically resistant and more durable than thermoplastic polymers and are used in insulating foams (polyurethane), worktop surfaces, cups and plates (melamine) and some older electrical insulators (Bakelite).

The properties of thermosetting plastics and thermoplastics are based on their molecular structure, as outlined in Table 15.2.1.

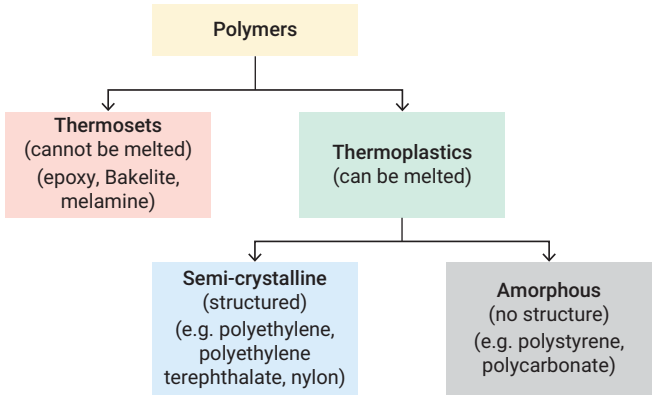


FIGURE 15.2.1 Types of polymers

Weblink
Polymer types

TABLE 15.2.1 Thermosetting and thermoplastic properties

Property	Thermosetting plastics	Thermoplastics
Molecular structure	Cross-linked (rigid)	Linear or slightly branched
Behaviour on heating	Cannot be remelted or reshaped	Can be remelted and reshaped
Durability	High heat and chemical resistance	Varies; generally less resistant
Examples	Epoxy, Bakelite, melamine	Polyethene, nylon, PVC

Synthetic polymers can also be categorised as addition polymers, formed by the addition of monomers without the loss of any small molecules, and condensation polymers, which form through a reaction that produces a by-product such as water. This distinction highlights differences in polymerisation processes and affects properties such as biodegradability and structural stability. You will learn about addition polymerisation and condensation polymerisation reactions in Chapter 18.

Syllabus links
Chapter 14 describes addition reactions involving alkenes.

Chapter 18 describes in further detail the process of addition polymerisation.

The formation of LDPE and HDPE are described in further detail in Chapter 18.

Addition polymers

Addition polymers form when monomers are added together without the loss of any atoms. This is done through addition polymerisation, which is a type of addition reaction.

Polyethene – LDPE and HDPE

One of the most common addition polymers is polyethene. These plastics are thermoplastics because they lack the rigid cross-linking structure of thermosetting plastics **(Figure 15.2.2)**. Instead, the properties of these plastics relate to the intermolecular forces between polymer chains.

As mentioned previously, there are two types of polyethene (low-density polyethene (LDPE) and high-density polyethene (HDPE)) produced by two different processes. Their different properties are a result of differences in their structures.

3d_kot/Shutterstock.com

FIGURE 15.2.2 Addition polymers are used to make everyday items such as food packaging and toys.

LDPE has significant chain branching because some of the hydrogen atoms are replaced by alkyl groups. The branches prevent the polymer chains packing closely together so there is a lot of space in the product and fewer dispersion forces between them. This leads to its low density, low melting point and greater flexibility.

HDPE consists of unbranched polyethene chains that can pack closely together in an orderly way. The tight packing of the chains are leads to the higher density. There is also stronger bonding because there are more dispersion forces between chains, resulting in a higher melting point and less flexibility.

HDPE has a more ordered structure so is said to be more crystalline, whereas LDPE, with its more random structure, is amorphous (non-crystalline). **Figure 15.2.3** shows the difference between the linear chains of HDPE and the branched chains of LDPE, and **Table 15.2.2** summarises their differences.

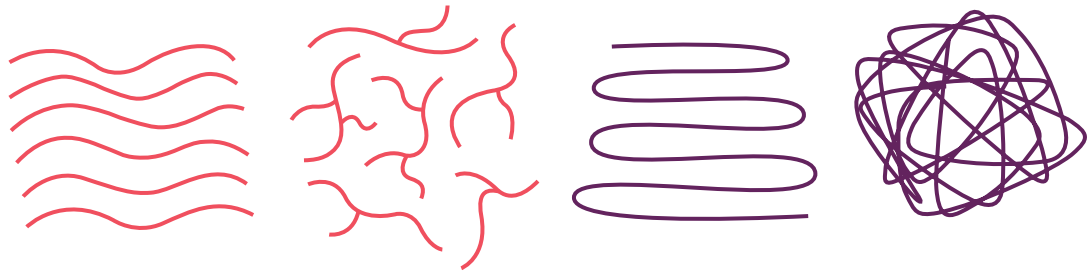


FIGURE 15.2.3 Different arrangements of polymer chains in HDPE and LDPE

Weblink
Differences between LDPE and HDPE

TABLE 15.2.2 Differences in structure, properties and uses of LDPE and HDPE

Polymer	Structure and bonding	Properties	Use
LDPE	• Amorphous (disordered) • Branched chains • Weak bonding due to fewer dispersion forces between chains that are further apart	• Soft, flexible, transparent • Impermeable to water vapour • Unreactive towards acids and bases • Absorbs oils and softens, • Low melting point (80–95°C) • Low tensile strength • Less dense • Not biodegradable	• Plastic bags, toys, plastic food wraps, wire and cable insulation, lamination film for paper and card used in juice and milk cartons, hard disc drives
HDPE	• Crystalline (ordered) • Linear chains • Stronger bonding due to more dispersion forces and closeness of chains	• Denser, tougher, opaque and more rigid • Higher melting point • Greater tensile strength than LDPE • Impermeable to water vapour • Unreactive towards acids and bases • Not biodegradable	• Detergent bottles, milk and water jugs, fuel tanks for vehicles, bottle caps, food storage containers, 3D printer filament, plastic surgery

PRACTICAL ACTIVITY 15.2.1

INVESTIGATING CRYSTALLINE AND AMORPHOUS PACKING OF POLYMER CHAINS

Introduction

The arrangement of polymer chains and the strength of interactions between adjacent chains is the reason some plastics are soft and flexible and others are hard and rigid. If the chains can move easily past each other when the plastic is bent, then it will be flexible, but if the chains are held in place, the plastic will be rigid.

When polymer chains are packed closely together in a regular pattern, they form a crystalline area. The more crystalline areas in the polymer there are, the stronger and less flexible it is. The areas where the chains are randomly arranged, and so further apart, are called amorphous.

Many polymers have both crystalline and amorphous regions. Because polymer chains are so long, any one chain can be involved in both regions along its length.

Resarch question

Does the arrangement of polymer chains, including the balance of crystalline and amorphous regions, influence the flexibility and strength of plastics, as modelled by cold spaghetti?

Aim

To use spaghetti to make a model of polymer structure

Materials

- spaghetti (about 100 g)
- saucepan or large beaker
- hot plate
- strainer
- water
- container with a flat base and straight sides

RISK ASSESSMENT

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Boiling water can cause serious burns.	Wear protective clothing. Use heatproof gloves to handle the container with boiling water.

Copy and complete the risk assessment table in your write-up. Add any more risks you can think of, and ways to manage them. Ask your teacher to check your table before you proceed.

Procedure

1. Cook the spaghetti according to the instructions on the packet.
2. Strain the cooked spaghetti to remove the excess water.
3. Pour the strained spaghetti into the straight-sided container and allow it to cool.
4. Once the spaghetti is cold, turn it out onto a flat surface, making sure it retains its block shape.

Nicholas Stansbie

FIGURE 15.2.4 An upturned spaghetti cake

Results

Draw a diagram or take a photo of the flat bottom of the spaghetti.

Analysis of results

1. Identify crystalline and amorphous regions on your diagram or photo.
2. Estimate the percentage of crystallinity (that is, how much of your polymer is crystalline) in your 'polymer' and compare this with other students' results.

Interpretation

3 Compare how easy it is to lift a piece of spaghetti from an amorphous region and a crystalline region. Discuss this in terms of intermolecular forces between spaghetti 'polymer chains'.

4 Discuss whether your polymer would be more or less rigid than those of other students. Justify your answer.

Evaluation

5 Explain how the properties of the amorphous and crystalline regions relate to the properties of LDPE and HDPE.

Polypropene – atactic, syntactic and isotactic arrangements

Polypropene (sometimes referred to as polypropylene) is an addition polymer of propene, which is formed in a similar process to that of polyethene. As can be seen in **Figure 15.2.5**, the $-CH_3$ group in propene that is not involved in the double bond in the propene monomer exists as a side group to the polymer chain.

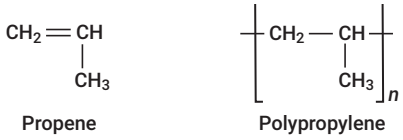


FIGURE 15.2.5 Propene and polypropene

There are three variations of the structure of polypropene, depending on the orientation of the $-CH_3$ group relative to the chain. The spatial arrangement of these side groups makes a difference to the properties of the polymer.

The three possible arrangements are shown in **Figure 15.2.6**, where the coloured ovals represent the $-CH_3$ group and the hydrogen atoms have been omitted for simplicity.

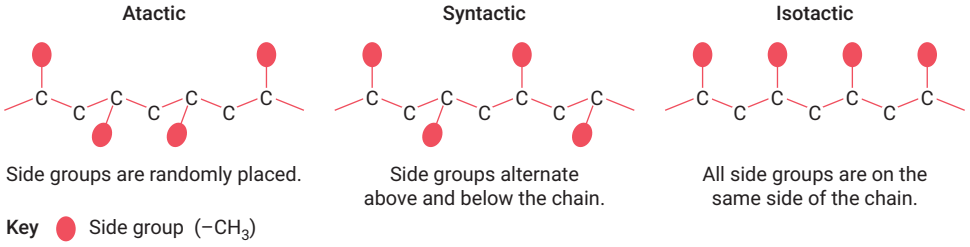


FIGURE 15.2.6 Three possible arrangements of side groups in polypropene

The regular arrangement of the $-CH_3$ groups on the same side of the polymer chain in the **isotactic** (isotactic = isolated to one side) arrangement makes it possible for the chains to pack close together and maximise the dispersion forces between them. This means the polymer is quite strong and hard with excellent resistance to stress, cracking and chemical reactions. It is the common form used to manufacture objects such as crates and ropes.

isotactic a polymer in which the side-chain functional groups are regularly arranged on the same side of the chain

In the random **atactic** (atactic = atypical arrangement) arrangement, the chains cannot lie close together, so the intermolecular forces of attraction are weaker. This results in a softer polymer with a lower melting point. The atactic version formed during the manufacture of the isotactic polymer is considered a waste product and is a soft rubbery polymer, which has limited use mainly as a roofing material and sealant.

atactic a polymer in which the side-chain functional groups are randomly arranged on the polymer chain

Syntactic (syntactic = side groups alternate) polypropene has only recently been made on a large scale. In this version, the $-CH_3$ groups alternate above and below the chain. The regularity means the chains can pack closely, resulting in fairly strong intermolecular forces. However, its attractions are not as strong as in the isotactic version, so it is somewhat softer than the isotactic polymer, but also tough and clear. It is used in packaging and, because it is stable to gamma radiation, it has applications in medicine, such as medical tubing, bags and pouches.

syntactic a polymer in which the side-chain functional groups alternate above and below the chain

The isotactic and syntactic forms of polypropylene are called **stereoregular polymers**. They are semicrystalline. The chains in the crystalline parts are not stretched out in a zigzag way as in polyethene, but curl up into regular spirals, allowing even stronger bonding.

stereoregular polymer a polymers with small, regularly ordered units in a single chain

Table 15.2.3 summaries these characteristics.

TABLE 15.2.3 A summary of the different side group arrangements

Side group arrangement	Description	Impact on properties	Examples
Isotactic	Groups arranged on the same side of the polymer chain allow chains to pack closely together.	Excellent resistance to stress, cracking, and chemical reactions. Higher melting point. Stronger intermolecular forces.	Crates, ropes
Atactic	Groups randomly arranged so chains cannot pack tightly.	Softer and lower melting point due to weaker intermolecular forces from random chain arrangement.	Roofing material, sealant
Syntactic	Side groups alternate above and below the chain. Chains can pack somewhat tightly together.	Softer than isotactic but tough and clear; fairly strong intermolecular forces due to regular chain packing, but not as strong as isotactic.	Packaging, medical tubing, bags, pouches

Polytetrafluoroethene (PTFE)

Polytetrafluoroethene (PTFE) is an addition polymer you are probably more familiar with as Teflon (Figure 15.2.7). It is most commonly known as the non-stick surface on pans (Figure 15.2.8), but it is also used to treat carpets and fabrics to make them stain resistant and has also been used for making artificial body parts. This polymer is also very strong. It is used to make high-grade electrical insulation and pipe thread sealant. The major application, using approximately 50 per cent of PTFE production, is insulation for wiring in aerospace and computer applications.

polytetrafluoroethene (PTFE) addition polymer formed from repeating units of tetrafluoroethene

Practical
How strong is Teflon?

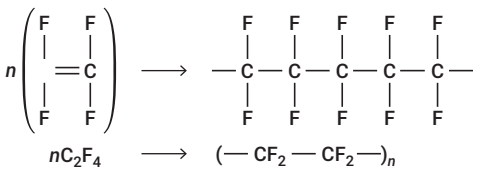


FIGURE 15.2.7 The structure of polytetrafluoroethene (PTFE)

Zoonar GmbH/Alamy Stock Photo

FIGURE 15.2.8 Non-stick frying pans are coated with pigmented Teflon.

PTFE is formed in a very similar reaction to polyethene by addition polymerisation. This polymer has repeating units similar to those of polyethene except all the hydrogen atoms have been replaced with fluorine. Its properties are due to the polar carbon–fluorine bonds and dipole–dipole interaction between polymer chains, which make it strong and tough. It also has the third lowest coefficient of friction of any solid and is resistant to the formation of dispersion forces, which means it is the only known surface geckos cannot stick to.

Syllabus link
Chapter 18 describes how condensation polymers form in more detail.

Condensation polymers

Condensation polymers are formed when two monomer molecules join to eliminate a small molecule (often water). Polyesters and polyamides (nylons) are examples of synthetic condensation polymers, whereas disaccharides and tripeptides are examples of natural condensation polymers.

Polyesters

polyester a polymer formed by a condensation polymerisation reaction between a hydroxyl group and a carboxylic acid group

A **polyester** is a synthetic condensation polymer commonly used in textiles, packaging and various industrial applications **(Figure 15.2.9)**. It is known for its durability, resistance to shrinking, and ease of maintenance, making it a popular material in clothing, home furnishings and plastic.

Polyesters contain an ester group that links repeating units together. The ester bonds (–COO–) formed contribute to the polymer's strength and stability.

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FIGURE 15.2.9 The common uses of polyester

As you learnt in Chapter 14, esters are formed from the reaction between an alcohol and carboxylic acid, so polyesters are formed by the same reaction. They contain an ester group that links repeating units together **(Figure 15.2.10)**. This ester link –COO– contributes to the polymer's stability and strength. To form a repeating unit, a double-sided carboxylic acid (dicarboxylic acid) and double-sided alcohol (diol) link together to make an ester repeating unit. You will learn about the reactants and reactions by which these polymers form in Chapter 18.

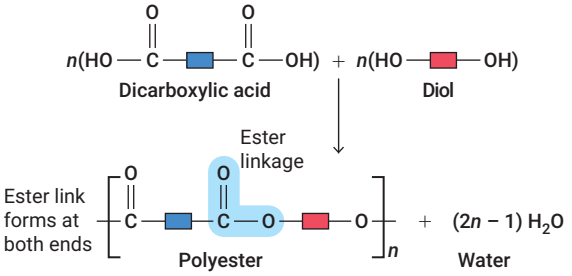


FIGURE 15.2.10 The repeating unit of a polyester. The blue boxes represent the dicarboxylic acid (–COOH) molecules. The red boxes represent the diol (–OH) molecules.

Syllabus link
Chapter 14 describes how esters are formed.

An example of a polyester is polyethene terephthalate (PET), which consists of repeating units of terephthalic acid ($C_8H_6O_4$) and ethylene glycol ($C_2H_6O_2$) **(Figure 15.2.11)**. PET is lightweight and strong, making it suitable for food and beverage containers due to its high tensile strength and resistance to deformation. These properties arise from the polymer's linear structure with strong intermolecular forces between the chains. PET is also impermeable to gases and liquids, which is due to its closely packed molecular structure and partial crystallinity, providing an effective barrier to preserve food and beverages.

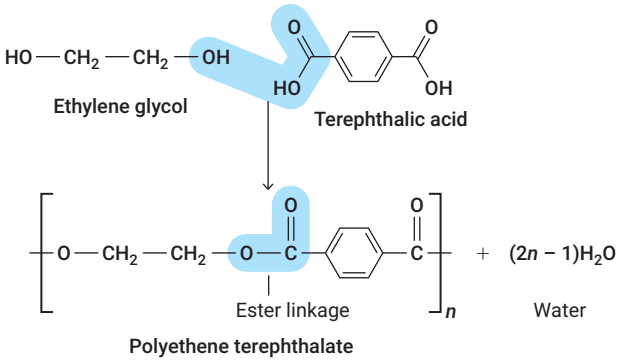


FIGURE 15.2.11 The formation of the polyester PET from terephthalic acid and ethylene glycol

Weblink
Polyesters

The strength of polyesters comes from the dipole–dipole interactions and dispersion forces acting between the polymer chains. The structure can be either crystalline or amorphous, with the crystalline regions offering increased strength, rigidity and thermal resistance.

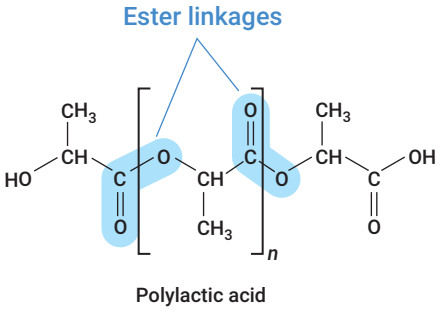
The properties of polyesters make them suitable for a wide range of applications. Their versatility, strength, UV resistance, ability to be dyed and made into fabrics, and relatively low cost, have made polyesters one of the most widely used synthetic materials in the world.

Polylactic acid (PLA)

Polylactic acid (PLA) is a bioactive thermoplastic that is biodegradable and produced from renewable resources, most commonly corn starch or sugarcane. It is also a polyester produced through condensation polymerisation. PLA has gained popularity in Australia because of its environmentally friendly properties, especially in applications such as biodegradable plastics, packaging, disposable cutlery, 3D printing and medical devices.

polylactic acid (PLA)
a biodegradable polymer produced from lactic acid molecules joined by ester links

PLA is synthesised by repeating units of lactic acid molecules ($C_3H_6O_3$) joined by ester linkages **(Figure 15.2.12).** You will learn about this reaction in Chapter 18. These chains can be highly crystalline or amorphous, depending on the processing conditions, which affects the material's properties such as strength, flexibility, and biodegradability.



Polylactic acid

MikeDotta/Shutterstock.com

FIGURE 15.2.12 Polylactic acid (PLA) is a biodegradable plastic that is derived from plant materials. It could help reduce plastic waste.

The ester linkages of PLA that contribute to its relatively low melting point and biodegradability also reduce its tensile strength. Due to the reversibility of ester links (in hydrolysis), PLA breaks down into natural substances such as carbon dioxide and water when exposed to composting environments, making it an attractive alternative to traditional petroleum-based plastics, which persist in the environment for much longer periods. This environmental benefit has led to PLA's increasing use in creating sustainable and eco-friendly products, reducing the long-term impact on waste disposal and pollution.

Polyamide (nylon)

polyamide a polymer formed by a condensation polymerisation reaction between an amine group and a carboxylic acid group

Polyamide, commonly known as nylon, is a synthetic condensation polymer favoured for its strength, durability, and versatility. It is one of the first synthetic fabrics, being created as a replacement for silk, which was expensive and difficult to obtain.

Nylon belongs to a group of polymers called polyamides, which have characteristic amide linkage in the backbone of the polymer chain. As you learned in Chapter 14, amines react with a carboxylic acid to form an amide. A polyamide forms by the same type of reaction. The reactions related to the formation of polyamides will be examined in detail in Chapter 18.

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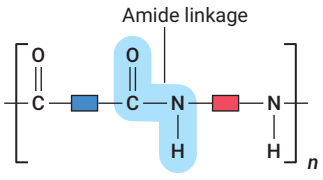
Polyamides

Syllabus links
Chapter 14 describes the formation of the amide functional group.

Chapter 18 describes the formation of polyamides in greater detail.



Polyamide

FIGURE 15.2.13 The repeating unit of a polyamide. The coloured boxes represent different groups of atoms.

Polyamides contain an amide group that links repeating units together. These strong amide linkages (–CONH–) provide excellent resistance to heat, abrasion and wear.

Nylon is an example of a polyamide **(Figure 15.2.14)**.

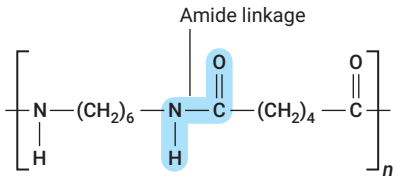


FIGURE 15.2.14 The chemical structure of nylon (a polyamide)

In nylon, the intermolecular forces that contribute to its strength and durability are primarily hydrogen bonding and dispersion forces between polymer chains. Nylon's balance of toughness and flexibility makes it ideal for products like ropes, fabrics and engineering plastics **(Figure 15.2.15)**.

FIGURE 15.2.15 Some common uses of nylon: rope, fishing line and pantyhose

The structure of nylon can be crystalline and amorphous, with crystalline regions offering higher strength. Its durability, resistance to chemicals, and moisture absorption properties further enhance its applications, particularly in demanding environments. However, its hygroscopic (water absorption) properties can make it uncomfortable fabric to wear.

TABLE 15.2.4 A summary of the properties of different condensation polymers

Polymer	Description	Properties	Uses
Polyester	Monomers linked together by ester linkages.	Strength and durability depend on dipole–dipole interactions between the –COO– and dispersion forces, as well as whether the structure is crystalline or amorphous.	Clothing, plastic, packaging
Polylactic acid (PLA)	Lactic acid monomers linked together by ester linkages.	Strength and durability depend on dipole–dipole interactions between the –COO– and dispersion forces, as well as whether the structure is crystalline or amorphous.	Biodegradable plastics, packaging, disposable cutlery
Polyamide (nylon)	Monomers linked together by amide linkages.	Hydrogen bonds (between amide groups) and dispersion forces result in strong intermolecular forces contributing to its strength and durability. Structure can be crystalline and amorphous.	Fabrics, ropes, engineering plastics

LEARNING CHECK 15.2

DESCRIBING

1 a **Describe** the structure of an amorphous polymer and a crystalline polymer.
  b **Explain** how these structural differences affect the properties of a polymer.

2 **Describe** the structure of a copolymer.

APPLYING

3 a Draw the structures of three possible variations of polypropene.
  b **Explain** why each of the different structures would have different properties.

4 **Compare** the density of HDPE and LDPE. Justify your response by referring to the relevant molecular structures and packing ability.

ANALYSING

5 **Explain** why, even though they are both amorphous polymers, polyvinyl chloride (PVC) forms a hard, rigid polymer, while melamine is hard and brittle.

6 **Compare** the links between the monomers of polylactic acid, polyamides and polyesters, and **predict** their biodegradability based on this structure.

15.3 Amino acids and tripeptides

amino acid an organic compound containing a carboxyl (–COOH) and an amino group ($–NH_2$)

protein an organic compound made from long chains of amino acids; an essential food group

polypeptide long chains of amino acids joined together with peptide bonds

tripeptide a short chain of three amino acids linked by peptide bonds

peptide bond an amide-type bond form by joining the carboxyl group of one amino acid to the amino group of another

Amino acids are the fundamental building blocks of proteins, which are essential molecules in every living cell. They are responsible for a wide range of biological functions, including structural roles in hair, skin, and muscles. **Proteins** are large polymer molecules (**polypeptides**), formed by linking many smaller amino acid monomers through condensation polymerisation. This process releases water molecules when amino acids bond together:

Amino acid + amino acid + amino acid + … → peptide polymer (protein) + water

A **tripeptide** is a short chain of three amino acids linked by **peptide bonds**, which is the same as the amide link found in synthetic polyamides. Although much smaller than full proteins, tripeptides still exhibit some of the functional properties of proteins and can act as signalling molecules or building blocks for larger proteins.

Most polypeptides are made from a combination of 20 different amino acids. The different combinations lead to hundreds of thousands of unique proteins, each with a specific sequence of amino acids. The sequence and the way the polymer chain folds into secondary structures (such as alpha helices or beta sheets), and the final three-dimensional arrangement of the protein (tertiary and quaternary structures) determine the protein's unique function from enzymes that catalyse biochemical reactions to structural proteins like collagen and keratin that provide structural support to cells and tissues (Figure 15.3.1).

Syllabus link
Chapter 18 describes the formation of polypeptides in more detail.

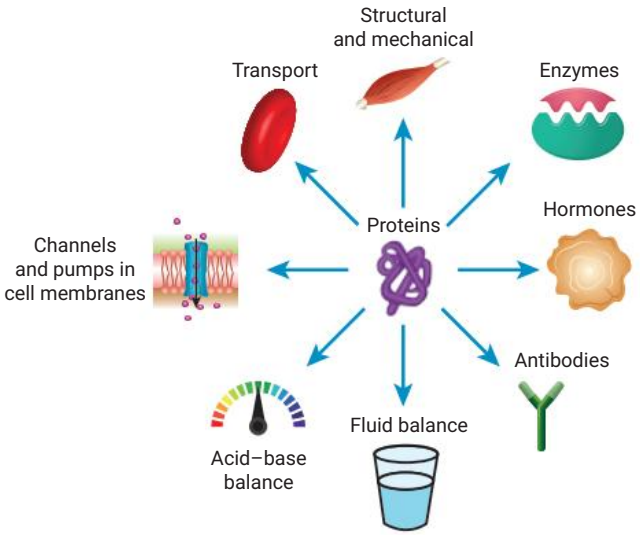


FIGURE 15.3.1 Proteins have many important functions in the body.

Weblink
Polymers

Amino acids

Amino acids are molecules that contain the amino ($-NH_2$) functional group and the carboxyl ($-COOH$) functional group (Figure 15.3.2).

Amino acids are interesting organic molecules because they exhibit both acid and base properties, due to the presence of the carboxylic acid and amine functional groups.

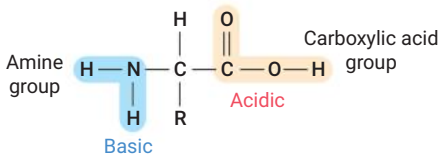


FIGURE 15.3.2 The structure of an amino acid, showing the acidic and basic groups

2-amino acid (or alpha-amino acid) an amino acid with one carbon atom separating the amino and carboxyl groups

alpha-carbon (or α-carbon) the first carbon atom bonded to a functional group; in an amino acid, the carbon that separates the amino and carboxyl groups

2-Amino acids

Most naturally occurring amino acids are known as **2-amino acids** (or **alpha-amino acids**) (Figure 15.3.3). In 2-amino acids, both the amino and carboxyl group are bonded to the **alpha-carbon** (or **α-carbon**), making them the 'standard' amino acids involved in protein synthesis. The structures of some amino acids are shown in Figure 15.3.4. Glycine is the simplest amino acid.

The structures of 20 common amino acids can be found in the *Formula and Data Book*.

FORMULA AND DATA BOOK

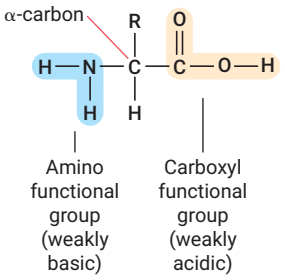


FIGURE 15.3.3 General structure of an α-amino acid

Amino acid side chains

The R group shown in Figure 15.3.3 is a carbon-containing side chain. Side chains can be categorised into three broad groups:

- non-polar R groups
- polar R groups capable of forming ions (generally with an additional $-NH_2$ or $-COOH$ group as part of the R chain)
- polar R groups that generally do not form ions (generally with an $-OH$ or $-SH$ group as part of the R chain) **(Figure 15.3.4)**.

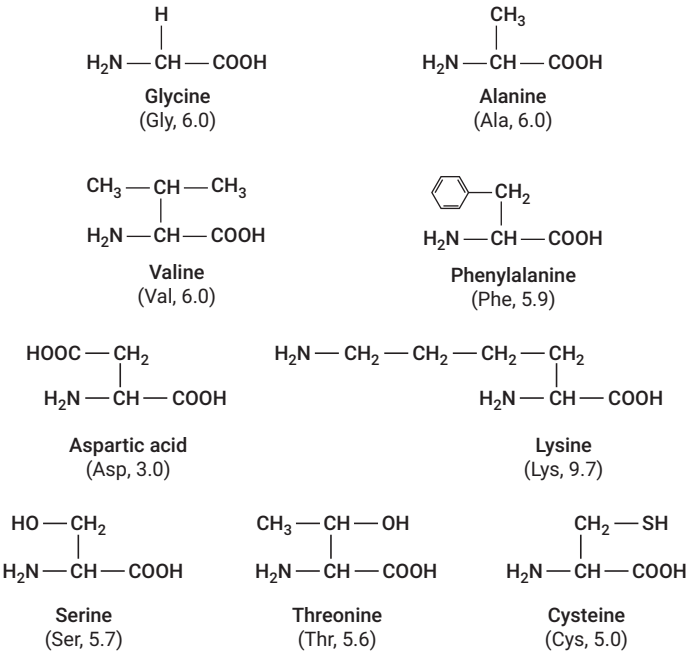


FIGURE 15.3.4 Common amino acids found in proteins. Their usual abbreviations are given in brackets along with their isoelectric points (the pH at which they exist as the neutral molecule).

As you have learned previously, the side chains can contribute to some of the properties of the amino acid polymer.

Acid–base properties and zwitterion formation

The amino acids shown in Figure 15.3.5 have been written as neutral molecules. However, the acidic –COOH group tends to lose a proton to form $–COO^-$, while the basic amine group $–NH_2$ tends to gain a proton to form $–NH_3^+$. This results in a dipolar ion called a **zwitterion**. 2-Amino acids easily form zwitterions because of the proximity of the amino and carboxyl groups. Therefore, in aqueous solution, amino acids exist as an equilibrium mixture of neutral molecules with the dipolar ion **(Figure 15.3.5)**.

zwitterion the form of an amino acid in which the amino group is protonated at the same time as the carboxyl group is deprotonated, so that there is no net charge

The dipolar ion structure of zwitterions means amino acids exhibit some of the properties of ionic substances – they form crystalline solids, have relatively high melting points and are soluble in water.

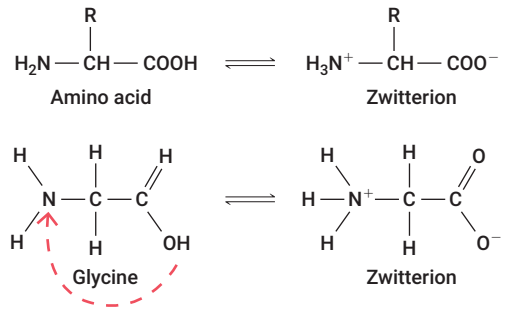


FIGURE 15.3.5 Zwitterion formation in glycine

Syllabus link
Chapters 4 and 5 describe the behaviours of acids and bases.

Recall that the –COOH group is a weak acid and $–NH_2$ is a weak base. This means the pH of a solution containing the amino acid affects the nature of the zwitterion. In strongly acidic solutions (low pH), the $–COO^-$ group gains a proton to become –COOH while the $–NH_3^+$ does not change. So the zwitterion changes to a positive cation **(Figure 15.3.6)**.

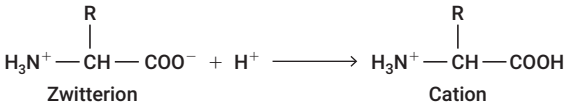


FIGURE 15.3.6 An amino acid in acid conditions

In alkaline solutions (high pH), the $–NH_3^+$ group loses a proton while the $–COO^-$ group does not change. So the zwitterion changes to a negative anion **(Figure 15.3.7)**.

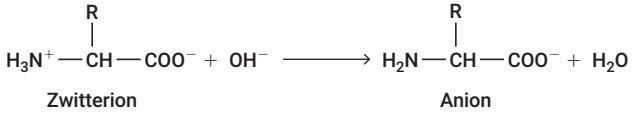


FIGURE 15.3.7 An amino acid in alkaline conditions

At low pH, amino acids exist as positively charged species, whereas at high pH, they exist as negatively charged ions. At the isoelectric point, both groups are ionised, forming a zwitterion, which has an overall neutral charge. These properties are crucial for their roles in buffering and biological systems.

isoelectric point the pH value at which there is no net charge on an amino acid

The pH at which an amino acid exists as an overall neutral zwitterion is called the **isoelectric point**. This is different for different amino acids because of the influence of the different R groups. At pH values less than the isoelectric point, the zwitterion will exist as the cation, and at pH values higher than the isoelectric point, the zwitterion will exist as the anion (Figure 15.3.8). This becomes a useful property to help separate a mixture of amino acids in solution. You will examine analytical techniques used to separate a mixture of amino acids in Chapter 16.

Weblink
Acid and base behaviour of amino acids

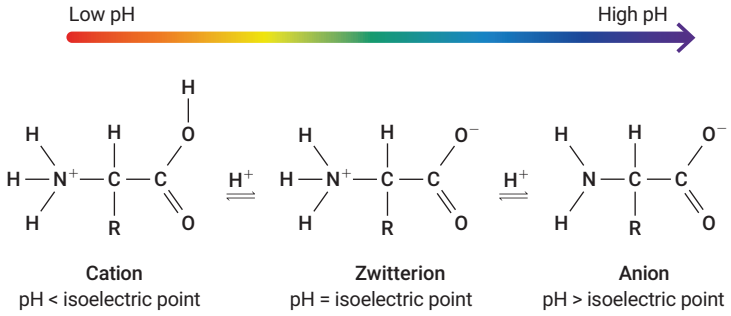


FIGURE 15.3.8 The behaviour of amino acids at different pH values

Tripeptides

Unlike nylons, which have a regular repeating unit, polypeptides can have various combinations of amino acids joined together with peptide bonds. A chain consisting of only two amino acid units is called a **dipeptide**; a chain consisting of three is a tripeptide. These smaller units can become the building blocks of much larger protein molecules. In Chapter 18, you will learn how to construct and name tripeptides.

dipeptide two amino acids joined together with a peptide bond

N-terminus the amino acid on the end of a peptide chain that has the free amine group

C-terminus the amino acid on the end of a peptide chain that has the free carboxyl group

By convention, peptide and protein structures are generally drawn with the amino acid with the amine group free (**N-terminus**) on the left and the amino acid with a free carboxyl group (**C-terminus**) to the right. Biochemists have developed a shorthand way of drawing them. Each of the 20 amino acids that make up the body's proteins has been given a three-letter abbreviation, as can be seen in the examples in Figure 15.3.9. Ser–Ala–Cys stands for a tripeptide with the amino acids serine, alanine and cysteine joined together. Serine has the N-terminus and cysteine has the C-terminus.

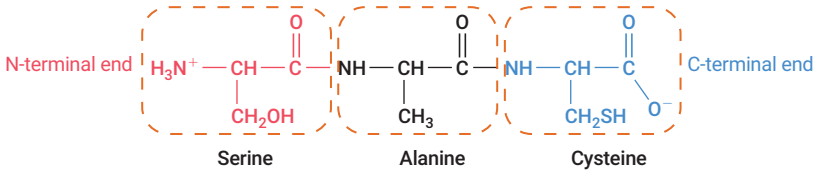


FIGURE 15.3.9 The tripeptide Ser–Ala–Cys

When hundreds to thousands of amino acid units join, the result is a protein. So, proteins are giant polypeptides. In any protein, there is still an amino group at one end and a carboxyl group at the other.

LEARNING CHECK 15.3

DESCRIBING

1 **a** Draw the general structure of an amino acid and label the two functional groups of this molecule.
   b **Describe** how the general structure of the amino acid forms a zwitterion by drawing a suitable annotated diagram.

2 **Describe** the relationship between the isoelectric point and the charge formed of a zwitterion.

3 **Describe** the three main categories of amino acids, based on their side chains.

APPLYING

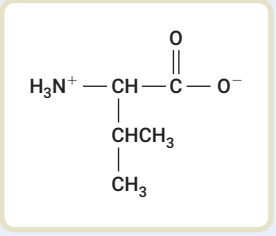
4 **Contrast** the formation and structure of an amide link and a peptide link.

5 Draw the structural formula of the tripeptides formed between the following amino acids and identify the peptide links between them.
   a Alanine, cysteine and glycine
   b Glycine, serine and phenylalanine

6 Draw the structural formula of the zwitterion form of:
   a valine
   b lysine
   c serine.

ANALYSING

7 **Predict** what would happen to the structure of this zwitterion under conditions of high pH. Draw your response.



15.4 Saccharide polymers

Carbohydrates, which include simple sugars, are natural condensation polymers. They are the most widely distributed and abundant compounds in the biosphere. The carbohydrate cellulose, the main component of plants, is probably the most abundant organic compound on Earth **(Figure 15.4.1)**. Cellulose is indigestible to humans but is part of the fibre needed in a balanced diet.

Carbohydrates are a diverse group of molecules, but they are all made up of the same three elements – carbon, hydrogen and oxygen – and there are always twice as many hydrogen atoms as there are oxygen atoms. The most common formula for carbohydrates is $C_6H_{12}O_6$. Carbohydrates are named because their formula can be written as $C_x(H_2O)_y$.

NataliTerr/Shutterstock.com

FIGURE 15.4.1 Cellulose forms the cell walls of plant cells.

The structures of carbohydrates feature a ring containing carbon atoms (usually four to six) and one oxygen atom. The carbons of the ring are bonded to –OH groups and H atoms. Two or more rings may be joined together to make bigger molecules. The –OH groups participate in hydrogen bonds, which makes starch and sugar soluble in water.

monosaccharide the simplest form of sugar that cannot be broken down into smaller units

Complex carbohydrates such as cellulose and starch are polymers made from simple units (sugars) called **monosaccharides (Figure 15.4.2)**, meaning single (one) sugar, that are joined through a condensation polymerisation reaction.

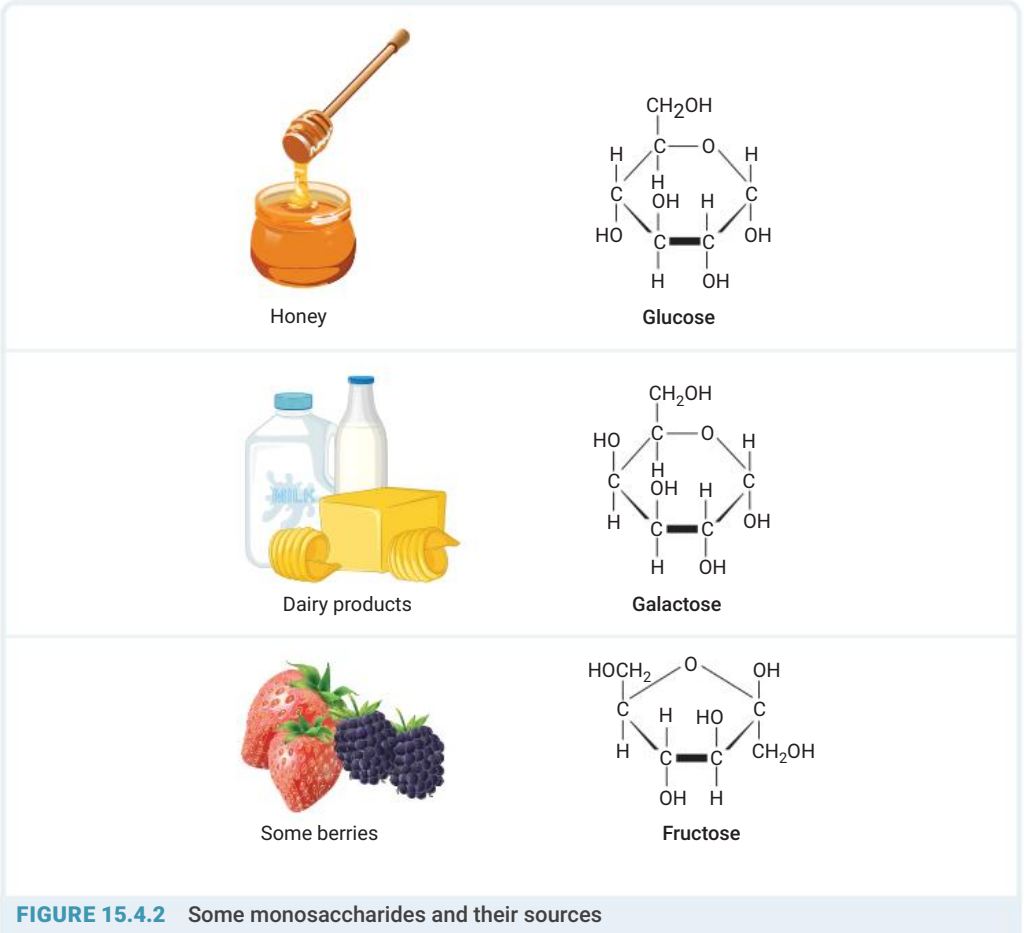


FIGURE 15.4.2 Some monosaccharides and their sources

Monosaccharides

Monosaccharides are commonly referred to as simple sugars. They are all isomers of $C_6H_{12}O_6$. The monosaccharides glucose, galactose and fructose have different structures and properties, as shown in **Figure 15.4.3**.

The thick wedge-shaped bonds in the ring indicate that the plane of the ring is perpendicular to the paper. The H atoms and –OH and $-CH_2OH$ groups attached to the ring are above and below that plane. The positioning of these groups is important because it determines which compound the structure represents. Glucose and galactose differ only in the location of one –OH group, yet they have noticeably different properties.

Monosaccharides can also exist in a different form, in which the molecules are in a chain rather than a ring. The structures of glucose, galactose and fructose in chain form are shown in **Figure 15.4.4**.

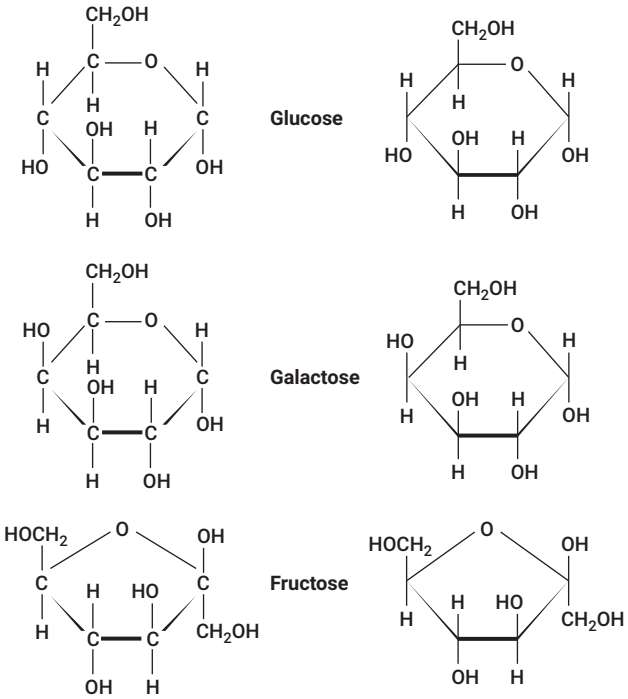


FIGURE 15.4.3 Structures of three common monosaccharides. The left-hand structures show all the atoms of the molecules; in the right-hand ones, the carbon atoms are not labelled.

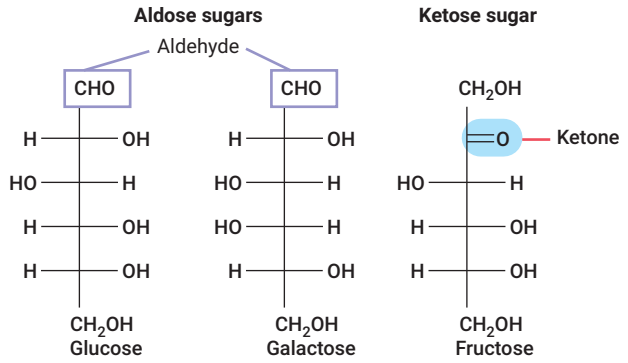


FIGURE 15.4.4 Glucose, galactose and fructose in chain form

FORMULA AND DATA BOOK

When drawn in this form, we can see that the glucose and galactose molecules have an aldehyde functional group, represented as –CHO, whereas fructose has a ketone functional group, represented as –C=O. Consequently, glucose and galactose are known as **aldose** sugars and fructose is a **ketose** sugar. Glucose and galactose are also sometimes known as **reducing sugars**, because of the reactions they participate in as a result their aldehyde group. Glucose, fructose and galactose are all white crystalline, sweet-tasting compounds. Of the three, glucose is the most important in human nutrition because our bodies use it as a source of energy.

There are two isomers of glucose, called α-glucose and β-glucose, shown in Figure 15.4.5. The α form of glucose has the OH group on C1 below the plane of the ring, whereas in β-glucose it is above the plane of the ring.

aldose a sugar containing an aldehyde group

ketose a sugar containing a ketone group

reducing sugar another name for an aldose sugar

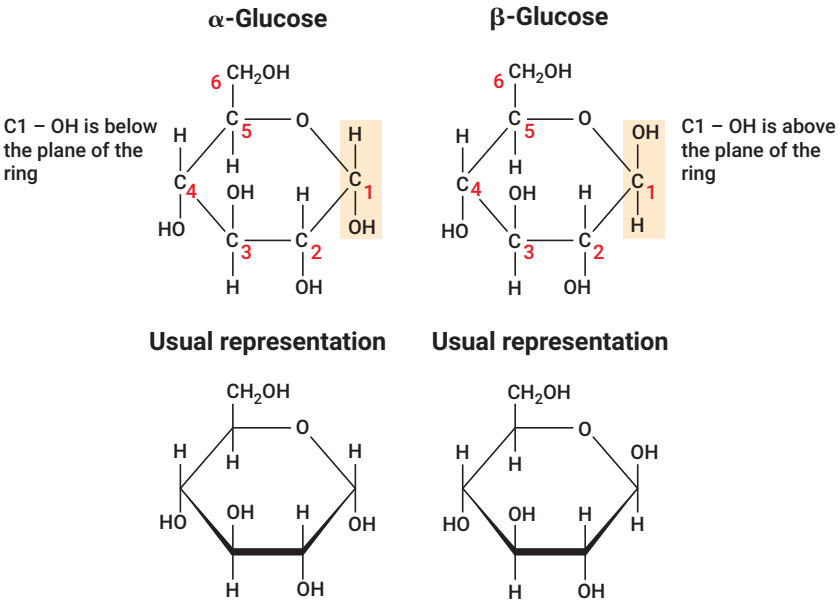


FIGURE 15.4.5 The α and β forms of glucose

Disaccharides

disaccharide a sugar made from two monosaccharide units

glycosidic link the ether bond (–C–O–C–) that connects two monosaccharide units in a carbohydrate

Two monosaccharides join to form a **disaccharide**. The link that joins the monosaccharides together is called the **glycosidic link**, –C–O–C–. Common disaccharides are shown in Table 15.4.1. In Chapter 18, you will learn about the process by which monosaccharides react to form disaccharides and the way in which these molecules are linked.

TABLE 15.4.1 The composition of some common disaccharides

Disaccharide	Monosaccharides units
Sucrose	Glucose + fructose
Maltose	Glucose + glucose
Lactose	Glucose + galactose

Syllabus link
Chapter 18 describes the process involved in the formation of disaccharides in more detail.

While the joining of monosaccharides sounds simple, when the structural formulas are considered, the situation becomes more complicated because there are different isomers and different forms of these isomers.

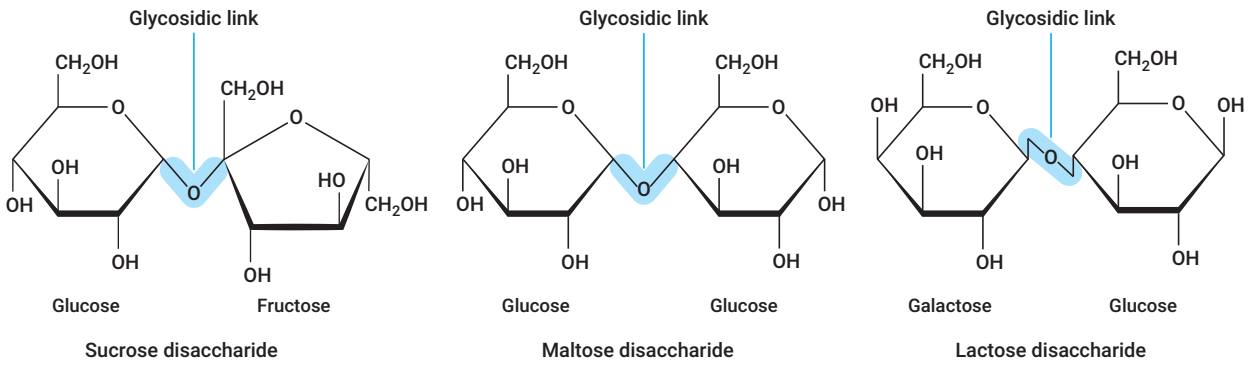


FIGURE 15.4.6 The structures of disaccharides sucrose, maltose and lactose

Maltose is produced when two glucose monomers join, and lactose is produced when a glucose monomer and a galactose monomer join. Sucrose, maltose and lactose have different properties because of their different structures. Maltose and lactose are not as sweet as sucrose, whereas fructose is sweeter than sucrose. Their melting points are lactose 253°C, sucrose 156°C and maltose 160°C. They have similar densities.

Disaccharides are too large to pass through cell membranes, so they need to be broken down to their constituent monomers in the digestive system (e.g. Figure 15.4.7). You will learn more about how this occurs in Chapter 18.

Weblink
Structure and function of carbohydrates

Worksheet
Proteins and saccharides

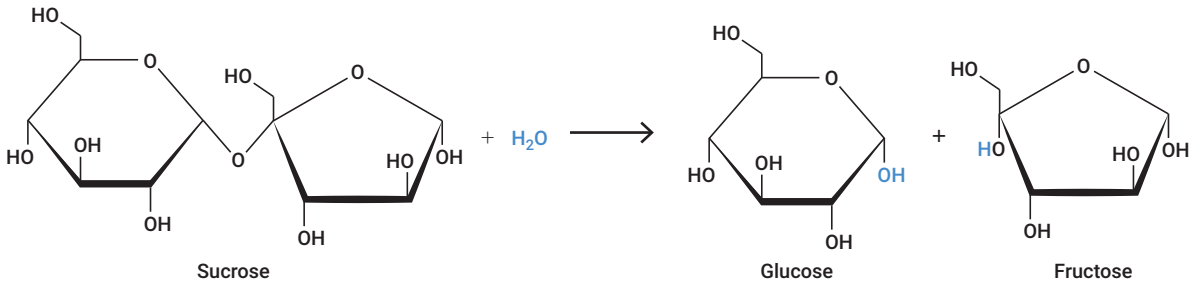


FIGURE 15.4.7 The hydrolysis of sucrose

LEARNING CHECK 15.4

DESCRIBING

1 **Describe** the differences between monosaccharides and disaccharides.
2 **Identify** the type of linkage that joins saccharide monomer units together.
3 **Identify** the type of molecule formed when two saccharide units are joined.

APPLYING

4 **Explain** why monosaccharides and disaccharides are soluble in water.

CHAPTER SUMMARY

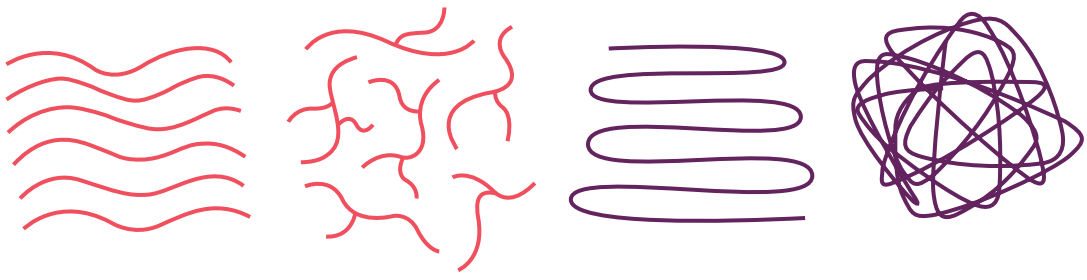
Polymers

- Polymers are long chains of monomers joined together. Structural features of polymers determine properties such as strength, density and biodegradability.
- Structural features include crystallinity, branching, chain length, side groups and cross-linking.

Strength	Strong → linear, crystalline structures (e.g. HDPE, isotactic PP) Weaker → branched, amorphous structures (e.g. LDPE, atactic PP)
Density	High density → tightly packed chains (HDPE). Low density → branching reduces alignment (LDPE)
Biodegradability	Biodegradable → hydrolysable ester bonds (e.g. PLA, polyesters) Non-biodegradable → non-hydrolysable bonds (e.g. Teflon)

Addition polymers

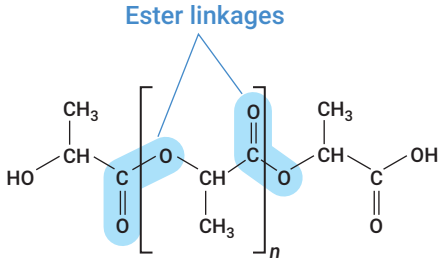
- Polyethene is formed by the addition of ethene monomers.
  - LDPE: Branched structure → low density, flexible, weak
  - HDPE: Linear chains → high density, strong, rigid

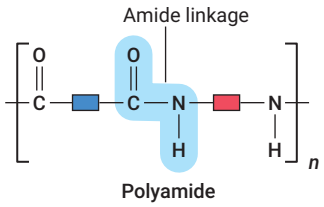


- Polypropene is formed by the addition of propene monomers.
  - Atactic: Random methyl groups → amorphous, weak, soft
  - Isotactic: Regular methyl groups on one side→ crystalline, dense, strong
  - Syntactic: Alternating methyl groups → balanced strength and flexibility
- Polytetrafluoroethene (Teflon) is formed by the addition of tetrafluoroethene monomers. It contains strong C–F bonds. It is chemically inert, non-stick and heat-resistant.

Condensation polymers

- Polyamide (nylon) is formed through amide links/peptide bonds.
- Polyesters are joined together by ester links.
- Polylactic acid is a biodegradable polyester formed through reversible ester links.

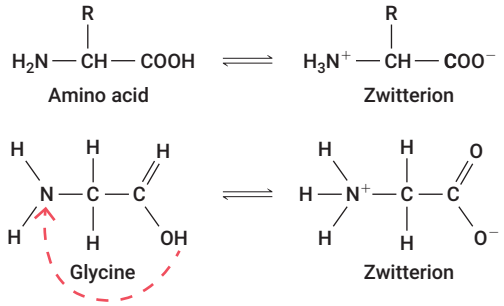




Amino acids

- Amino acids contain both amino group and carboxyl group, enabling amphoteric behaviour.
- Zwitterions form at the isoelectric point where the molecule is electrically neutral. They gain a H^+ in acidic conditions and lose a H^+ in basic conditions

The formation of a zwitterion from glycine

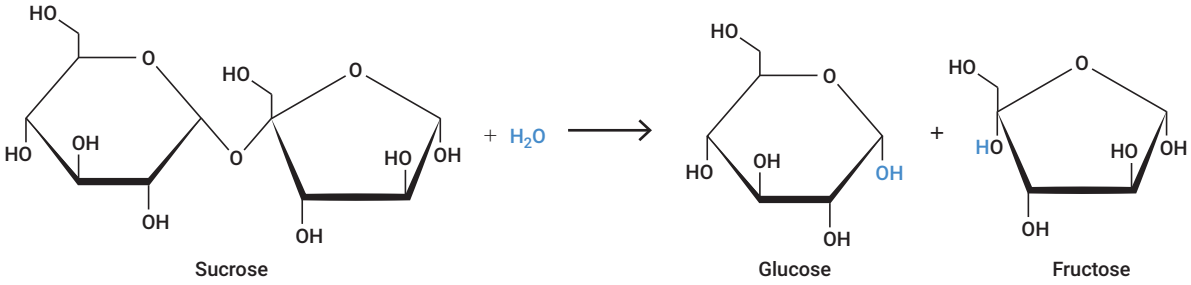


- Dipeptides and tripeptides contain two and three amino acids respectively that are held together by peptide bonds. They can be separated by hydrolysis.

Saccharides

- Monosaccharides are simple sugars like α and β glucose and serve as monomer units
- Disaccharides are formed when two monosaccharides join by glycosidic bonds in condensation reactions. They can be separated by hydrolysis.

Hydrolysis of sucrose



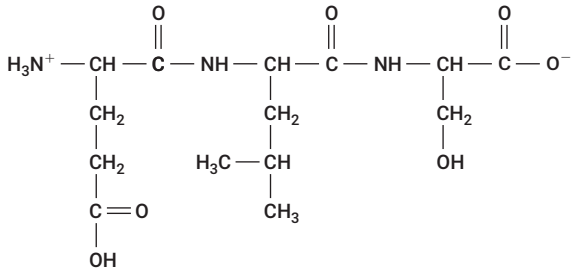
CHAPTER EXAM

MULTIPLE CHOICE

1. In general, polymers with more linear chains have:

A a lower melting point than those with branches.
B are less dense than those with more branches.
C are more flexible than those with more branching.
D are more crystalline than those with more branching.

2. Select the abbreviated name of the following tripeptide:



A Ser–Leu–Ala
B Glu–Ala–Glu
C Glu–Leu–Ser
D Ser–Ser–Leu

3. A sample of polypropene has the methyl side chains randomly arranged in relation to the chain. It is known as:

A syntactic.
B atactic.
C HDPE.
D isotactic.

4. Identify the structural feature that best explains why HDPE has greater strength and density than LDPE.

A HDPE has a highly branched structure, whereas LDPE has a linear structure.
B HDPE has a linear structure, whereas LDPE has a highly branched structure.
C HDPE is cross-linked, whereas LDPE is not.
D HDPE has higher biodegradability due to its structure.

5. Identify which of the following is not an important structural feature of a polymer.

A Crystallinity
B Cross-linking
C Solubility
D Side groups

6. What type of polymer is polyethene?

A Addition
B Elimination
C Substitution
D Condensation

7. A functional group in glucose, galactose and fructose is the:
   - **A** carboxyl group.
   - **B** amino group.
   - **C** hydroxyl group.
   - **D** halogen.

8. Identify the polymer that has the highest biodegradability due to its ester linkages.
   - **A** Polypropene (PP)
   - **B** Nylon (polyamide)
   - **C** Polylactic acid (PLA)
   - **D** Polytetrafluoroethene (Teflon)

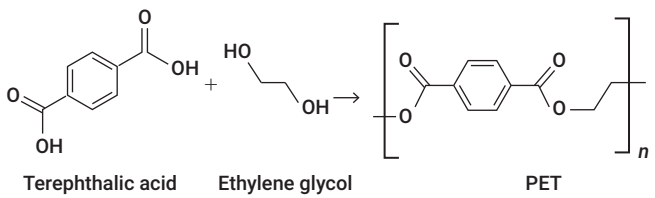
9. Identify the structural feature of polytetrafluoroethene (Teflon) that gives it its unique properties such as low friction and chemical resistance.
   - **A** Cross-linking between polymer chains
   - **B** The presence of branched carbon chains
   - **C** Biodegradable ester linkages within the polymer
   - **D** Strong C–F bonds and a highly symmetrical, linear structure

10. Identify the row of the table that correctly matches the polymer with its structural feature and property.

	Polymer	Structural feature	Property
A	Polypropene	Methyl side chains	Biodegradable
B	HDPE	Branched chains	Flexible
C	LDPE	Tightly packed chains	High melting point
D	Polytetrafluoroethene (Teflon)	Fluorine atoms along the polymer chain	Chemically unreactive

SHORT RESPONSE

11. Polyethene terephthalate (PET) is one of the most common polyesters. It has a range of uses but is mostly noted for its widespread use in plastics such as in bottles and containers for liquids and foods. Part of the reaction to produce PET is shown below:



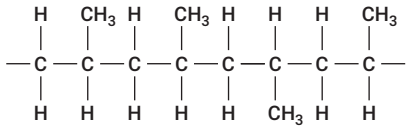
Terephthalic acid Ethylene glycol PET

   - **a** **Identify** which two functional groups are required on the monomers to manufacture a polyester.
   - **b** **Identify** the name of the other product of this reaction.
   - **c** **Identify** the link that joins these monomer units together.
   - **d** **Explain** how the ester bonds in PET are formed during the polymerisation process.
   - **e** **Describe** two properties of PET that make it suitable for use in food and beverage containers and relate these properties to its molecular structure.

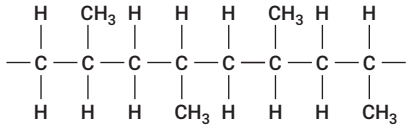
12. **Compare** aspartic acid and lysine in terms of:

- **a** side chains
- **b** isoelectric point
- **c** form of zwitterion at pH 7.

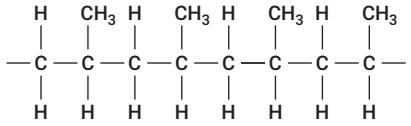
13. The polymer polypropylene is made by the addition polymerisation of propene. Depending on the reaction conditions, different types of polypropene can be formed, as shown in the following diagram:



Polymer 1



Polymer 2

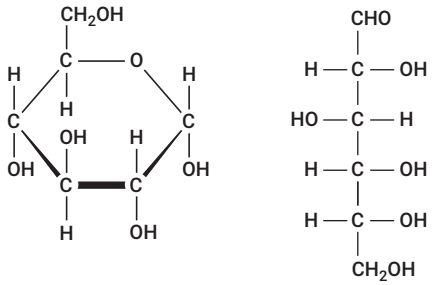


Polymer 3

- **a** **Identify** and describe the differences in the structures of the three polymers.
- **b** **Predict** which of the three polymers would be expected to have the lowest melting point. **Justify** your answer by referring to the structures of the three polymers.
- **c** **Explain** why polypropene products should be recycled when they are no longer useful.

CROSS-CHAPTER QUESTION

14. Glucose is the most abundant monosaccharide. Examine the structural formula for glucose.



a **Explain** why glucose is highly soluble in water.
b **Calculate** the molecular mass of the saccharide molecule.
c **Calculate** the percentage of oxygen and carbon in one glucose molecule.
d **Determine** a balanced equation for the formation of a disaccharide molecule from two glucose units.
e **Determine** the empirical formula of the glucose monosaccharide.

DATA ANALYSIS

15. Analyse data

The following table shows the tensile strength range of some common plastics.

Type of polymer	Tensile strength (MPa)	Structure type
HDPE	20–37	Linear
LDPE	8–12	Branched
Atactic PP	2–4	Branched
Syntactic PP	10–25 (approx.)	Branched/linear
Isotactic PP	30–35	Linear
Nylon	45–80	Linear
PLA	50–70	Linear

a **Identify** the tensile strength range of nylon
b **Identify** the tensile strength range of LDPE.
c **Contrast** the tensile strength range of the atactic polypropylene (PP) and the PLA plastics.
d **Identify** the relationship between tensile strength range and the type of polymer structure.

SCIENCE AS A HUMAN ENDEAVOUR

Syllabus dot point

- 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.

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Early and modern methods for visualising molecules

How organic compounds function and behave and their properties are heavily influenced by their structure. Advances in technology mean that we can use computer programs to visualise the three-dimensional structure of a compound. However, this was not always the case.

Early methods for visualising molecules

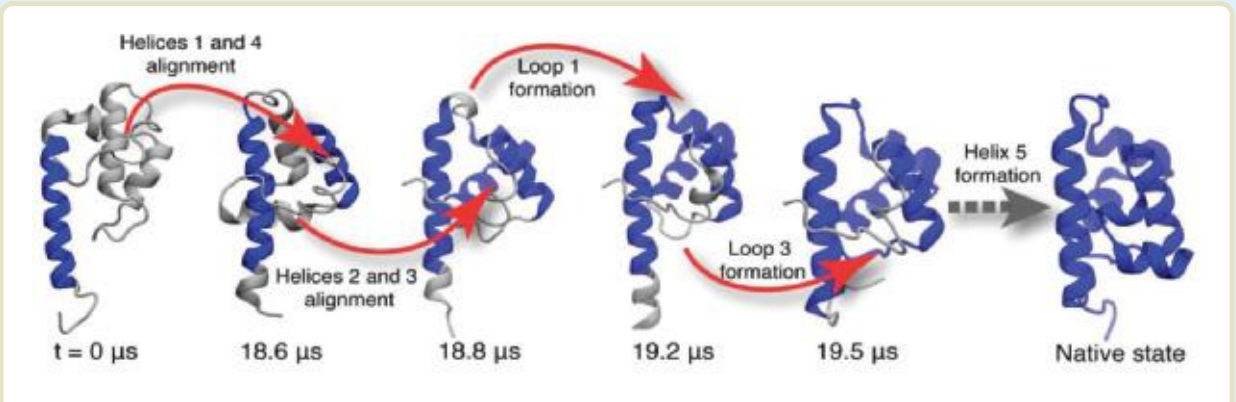
In the early 1900s, scientists used techniques such as X-ray diffraction to attempt to identify the structure of molecules. In 1937, Max Pertuz (1914–2022) embarked on a project to determine the structure and function of the complex molecule haemoglobin, the protein in red blood cells that is responsible for carrying oxygen around the body. In this technique, X-rays pass through crystals and deflect off atoms. They then interact with each other on the other side to produce a pattern of spots called an X-ray diffraction pattern. Perutz collaborated with John Kendrew (1917–97), and incorporated other methods into his research, and together Perutz and Kendrew were awarded the Nobel Prize for Chemistry in 1962 'for their studies of the structures of globular proteins'.

Adding modelling and technology

In the mid-1900s, mathematical models were introduced that took into account the interactions between particles of an atom, as well as between atoms in a molecule as described by classical physics. This led to the development of molecular mechanics. The introduction of computers to molecular modelling helped to speed up the typically manual calculations and allowed researchers to store more data, prompting the expansion of this method.

Building from visualising individual molecules, molecular dynamics was developed as a method to simulate the movement of atoms and molecules over time. Because of computational limitations, researchers could only simulate over short periods of time. However, as technology improved, researchers could simulate more complex processes, including the folding of proteins **(Figure 1)**.

Researchers Martin Karplus (1930–2024), Michael Levitt (1947–) and Arieh Warshel (1940–) were able to use molecular dynamics and computer modelling, in conjunction with other theories such as quantum mechanics, to develop a way to model complex chemical systems. The team was awarded the Nobel Prize for Chemistry in 2013 for 'the development of multiscale models for complex chemical systems'.



MD Simulation of Protein Folding, University of Illinois Board of Trustees and others. https://www.ks.uiuc.edu/Research/folding/

FIGURE 1 An example of the use of molecular dynamics in visualising the transition states of protein folding

What's happening today

AlphaFold, an AI system developed by Google DeepMind, can predict the structures of proteins with incredible speed and accuracy. In collaboration with European Molecular Biology Laboratory's European Bioinformatics Institute, more than 200 million protein structures have been predicted and are available online for free. Scientists have used Alphafold to identify the full structure of a crucial protein related to malaria, enabling research into a vaccine to help combat the disease **(Figure 2)**.

Folding@home is a free protein folding software available to anyone with a computer. This project encourages the collaboration of citizen scientists and scientific researchers in finding out more about biology and how proteins interact with different diseases. The hope is that this leads to further understanding of disease, resulting in innovation in developing therapeutics.

The models and techniques described here are only some examples of what has been achieved in the field of the visualisation of organic structures. Many more techniques and models are available that have led to our current understanding of what organic molecules look like and how they behave. This continuous evolution of computational modelling has allowed us to develop more targeted and effective therapeutics. Modern drug design relies on our ability to visualise and predict how drug molecules will interact with target molecules in the body. As computer technology and artificial intelligence continues to advance, we will be able to have a better, more accurate understanding of the world.

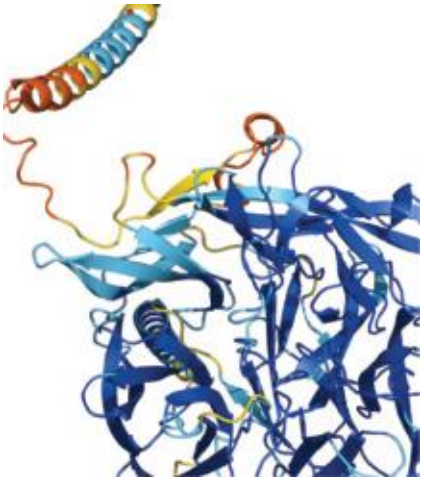


FIGURE 2 The 3D structure of a protein believed to have the potential to protect against the malaria parasite

Weblinks
AlphaFold
Folding@home

CHAPTER 16

Analytical techniques

Aiaikawa/Shutterstock.com

SYLLABUS DOT POINTS

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.*

*Note: Simulations may be used.

Introduction

In order to understand how bonds are formed and how molecules react, chemists must be able to determine the structures of organic compounds. This knowledge enables a better understanding of how biological molecules (e.g. amino acids, proteins, enzymes and DNA) function. Understanding the detail down to the individual atoms has revolutionised the development of new medicines and promises advances in the early diagnosis of cancers.

The use of techniques such as chromatography, electrophoresis, mass spectrometry and infrared spectroscopy has led to revolutionary breakthroughs in determining the structure and function of molecules.

ASSUMED KNOWLEDGE

- ✓ The strength of intermolecular forces is in the order: hydrogen bonding > dipole–dipole attractions > dispersion forces.
- ✓ Different types of organic compounds have different functional groups.
- ✓ Organic compounds can be represented as molecular formulas as well as structural formulas.
- ✓ Organic reactions can produce different types of organic compounds.
- ✓ Amines and carboxylic acids have acid and base properties due to their functional groups (–NH_2 and –COOH respectively).
- ✓ 2-Amino acids have a general structure – an amino group, a carboxyl group, an R group and a H bonded to the alpha-carbon.
- ✓ 2-Amino acids can form zwitterions, and depending on the nature of the solution, act as acids or bases.
- ✓ The isoelectric point (pI) can influence the acidic or basic behaviour of amino acids.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ identify the stationary and mobile phase in paper and thin-layer chromatography
- ✓ explain how polarity affects the movement of a sample
- ✓ calculate retention factor
- ✓ identify factors that affect the migration of amino acids in chromatography
- ✓ analyse data to determine the identity of amino acids in paper and thin-layer chromatography
- ✓ determine the polarity of amino acids based on R group
- ✓ identify how the pH of a buffer affects the formation and polarity of ions of amino acids including isoelectric point
- ✓ determine the migration of amino acids in different buffer solutions
- ✓ calculate retention factor for electrophoresis
- ✓ analyse electrophoresis data to identify amino acids
- ✓ identify parent molecular ion peak and base peak in a mass spectrum
- ✓ describe how an organic molecule may fragment
- ✓ identify molecular fragments in a mass spectrum
- ✓ analyse mass spectra to determine the identity and structure of an organic molecule
- ✓ identify the class of compound and bonds in an infrared spectrum
- ✓ analyse infrared spectra to determine the identity and structure of an organic molecule.

chromatography a group of techniques that separate substances based on differential distribution between a stationary phase and a mobile phase

adsorb to be attracted to the surface of the material; the opposite of desorb

stationary phase the immobile surface that different components of a mixture can adhere to when carried along by the mobile phase

desorb the action of a substance moving from the stationary phase to the mobile phase; the opposite of adsorb

mobile phase the fluid used to carry the components of a mixture up the stationary phase so they can separate

16.1 Chromatography

Chapter 12 of *Nelson QCE Chemistry Units 1 & 2* provides a detailed explanation of the principles of **chromatography**, and how data obtained from chromatography can be used to separate and determine the different components in a mixture. As previously discussed, the chemical basis of all chromatography techniques is that different substances are attracted to and **absorb** onto a surface (called the **stationary phase**) and detach (**desorb**) into the solvent (the **mobile phase**) at different rates. In fact, the component molecules may attach to the stationary phase, then dissolve in the mobile phase (solvent) and travel a little further, then attach to the stationary phase again, and so on, as shown in **Figure 16.1.1**.

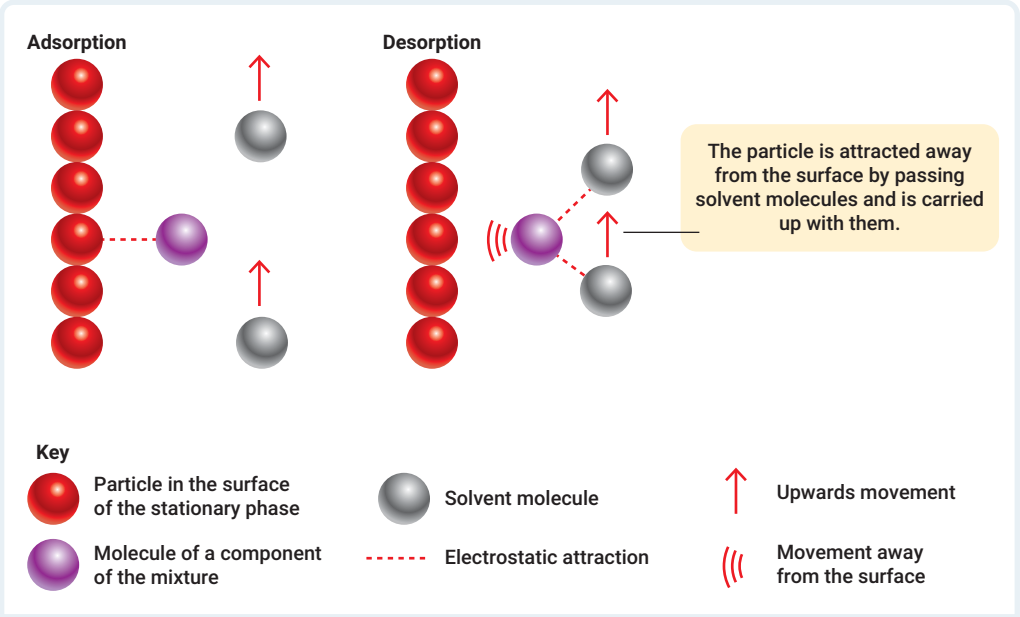


FIGURE 16.1.1 Absorption and desorption during chromatography. Note: The attracted particles will be much closer together than shown here.

retention factor (R_F) the distance travelled by the components of a sample from its origin divided by the distance moved by the solvent from the origin (also called retardation factor)

Provided the conditions (stationary phase, mobile phase and temperature) are kept the same, then the **retention factor (R_F)** (also called retardation factor), which is ratio of the distance moved by each component (or fraction) of the sample to the distance moved by the solvent, should be the same:

$$R_F = \frac{\text{distance moved by the amino acid}}{\text{distance moved by the solvent}}$$

The R_F value must be between 0 and 1. Consequently, R_F is unique for each compound and can be used to positively identify it.

KEY FORMULA

Retention factor

$$R_F = \frac{\text{distance moved by the amino acid}}{\text{distance moved by the solvent}}$$

Paper and thin-layer chromatography techniques for amino acid analysis

Separating the components of mixtures depends largely on differences in the strength of the intermolecular forces (dipole–dipole attractions, dispersion forces, hydrogen bonding) between the component molecules, the mobile phase and the stationary phase.

Different components in a mixture adsorb onto a surface and desorb into a solvent at different rates. This difference is due to many factors of the substance being tested, including:

- the different types of polar groups
- the amount of charged and polar chemical groups
- its molecular weight
- its geometry
- the positions and numbers of carbon–carbon double bonds.

How fast the components move up the plate depends on the strength of attraction between the molecules of the component and the:

- solvent molecules (mobile phase)
- stationary phase.

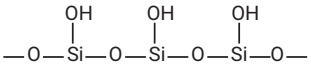
The more strongly a component attaches to the stationary phase, the more slowly it moves in the direction of flow of the mobile phase. Components that attach only weakly to the stationary phase, but dissolve readily in the mobile phase, move up the stationary phase faster.

Molecules of higher molecular weight with fewer polar sites tend to travel further up the stationary phase, despite the downward pull of gravity.

The degree to which components can be separated also depends on the length of time the stationary phase is in contact with the solvent. When components have very similar R_F values, the separation may require two or more processes with different solvents.

Table 16.1.1 compares paper and thin-layer chromatography.

TABLE 16.1.1 Comparison between paper and thin-layer chromatography

Feature	Paper chromatography	Thin-layer chromatography
Stationary phase	Liquid; water bonded to the cellulose fibres of the paper, highly polar	Solid; silica layer deposited on a glass or plastic plate, surface silicon atoms bonded to –OH groups, polar 
Intermolecular bonds	Hydrogen bonds, dipole–dipole attractions, ion–dipole bonds	Hydrogen bonds, dipole–dipole attractions, ion–dipole bonds
Mobile phase	Commonly an alcohol–water mixture	May be an alcohol–water mixture or organic mixture

Migration of amino acids in the mobile phase

As you learnt in Chapter 15, all 20 of the 2-amino acids (also called alpha-amino acids) have a common structure in which an amino ($-NH_2$) and a carboxyl ($-COOH$) functional group are attached to the same carbon atom (alpha-carbon). The general structure of an alpha-amino acid was shown in Figure 15.3.3.

Differences in the chemical structures of the alpha-amino acids are due to the R side-chain groups. These R groups are also attached to the alpha-carbon, and may be:

- non-polar (e.g. alanine)
- polar groups capable of forming ions (generally with an additional $-NH_2$ or $-COOH$ group) (e.g. lysine and aspartic acid)
- polar groups that generally do not form ions (generally with an $-OH$ or $-SH$ group) (e.g. serine and cysteine).

The broad groups and their intermolecular interactions are:

- non-polar side groups; for example, alanine and valine attract through dispersion forces
- polar side groups capable of forming ions (generally with an additional $-NH_2$ or $-COOH$ group); for example, lysine and aspartic acid can form ion–dipole bonds
- polar side groups that generally do not form ions (generally with an $-OH$, $-NH$ or $-C=O$ group); for example, serine and asparagine can form hydrogen bonds (these may also form dipole–dipole bonds)
- polar side groups (such as $-C=O$ and $-SH$); for example, serine and cysteine can form dipole–dipole bonds).

FORMULA AND DATA BOOK

In both paper and thin-layer chromatography, the stationary phase is polar. Paper is more polar than the silica layer in thin-layer chromatography. Amino acids move through the paper or thin layer at different rates because of their different polarities and ionic characteristics as well as different solubilities in the stationary and mobile phases.

The solvent mixture normally contains several components, one of which is usually water and another of which is a less polar solvent. As the solvent mixture moves along the stationary phase by capillary action, the amino acids with the more polar R groups (e.g. aspartic acid) absorb onto the polar stationary phase and move at slower speeds. Amino acids with a non-polar R group (e.g. leucine) are more soluble in the less polar mobile phase, so continue to move up the paper or thin-layer plate. Amino acids with intermediate polarity will be in equilibrium between the two phases and will move partway up the paper or thin-layer plate. Note that the more carbon and hydrogen in the structure, the less polar it will be. Polar groups increase polarity, but ionising groups increase polarity more than polar groups.

Weblink
Thin-layer chromatography simulation

Identifying the amino acids

All 20 alpha-amino acids are colourless, so the separated amino acids are detected by using a solution of the chemical ninhydrin. Ninhydrin reacts with the amino N to give a purple colour. (In this way, concentrations of 10^{-8} M can be detected.)

After the mobile phase has flowed through the stationary phase for a suitable time, the paper or thin-layer chromatogram is dried out (by exposing it to a flow of air in a fume cupboard). The dried chromatogram is then sprayed with a ninhydrin solution and warmed in an oven for a few minutes to allow the purple spots to develop. These spots correspond to the positions of the amino acids. They will fade over time, so it is advisable to outline the spots with a pencil.

There are three ways of identifying the amino acids in the sample. In the first method, the spots of unknown amino acids are compared to spots of known amino acids (standards), under the same conditions of stationary phase and mobile phase. If the sample travels the same distance up the plate as the standard, then it is the same amino acid. This is shown in **Figure 16.1.2**.

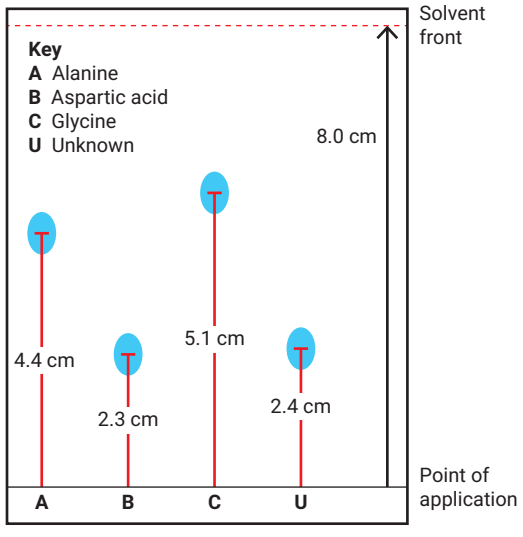


FIGURE 16.1.2 Thin-layer chromatography plate of an unknown amino acid and three known amino acid samples

In the second method, a standard mixture of several amino acids is used; the order in which these will separate under the conditions of the experiment is known, so just one standard is run beside the sample to be analysed. This produces several spots, but these can be identified because the order is known. Again, a comparison of the distances travelled between the known and unknown samples allows identification of the unknown, as seen in **Figure 16.1.3**, which shows amino acids on chromatography paper after development with ninhydrin.

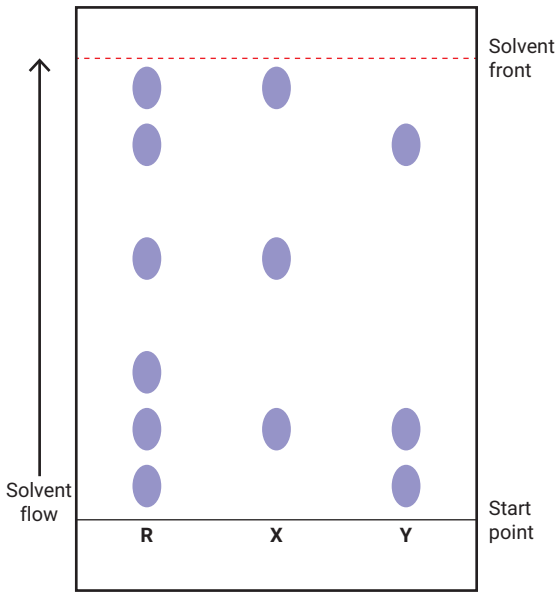


FIGURE 16.1.3 A developed chromatogram. R is the reference sample containing known amino acids and X and Y are the samples being analysed.

In the third method, the experimental R_F value of an unknown is compared with a table of known amino acids and their R_F values for the same solvent and stationary phase under the same conditions.

PRACTICAL ACTIVITY 16.1.1

PAPER CHROMATOGRAPHY OF AMINO ACIDS

Introduction

Paper chromatography is an analytical technique for distinguishing between different amino acids on the basis of their chemical properties. The stationary phase is the water molecules trapped in the cellulose structure of the chromatography paper. The mobile phase is a mixture of 1-butanol, water and glacial acetic acid. As the mobile phase moves up the paper by capillary action, the rate at which the amino acids move up the paper is determined by their relative affinity for stationary phase and mobile phase. Comparison of the R_F of an unknown amino acid mixture to the R_F of known amino acids on the same chromatogram can be used to identify the amino acids in the unknown mixture.

Research question

Can paper chromatography be used to identify the amino acids in an unknown mixture of amino acids?

Aim

To use paper chromatography to identify amino acids in an unknown mixture

Materials

- 1% solutions of leucine, alanine, phenylalanine, aspartic acid and serine
- mixture of unknown amino acids
- 10 mL solvent of a 4:1:1 mixture of 1-butanol, glacial acetic acid and distilled water
- ninhydrin spray (2% solution in ethanol)
- chromatography paper (21 cm × 10 cm)
- 6 capillary tubes
- 600 mL beaker
- aluminium foil to cover top of the beaker
- distilled water
- measuring cylinder
- ruler
- pencil
- stapler
- drying oven
- gloves

RISK ASSESSMENT

What are the risks in doing this investigation?	How can you manage these risks to stay safe?
Ninhydrin can stain the skin.	Wear gloves, avoid contact with ninhydrin spray, work in a fume hood.
The solvent is a toxic and flammable liquid.	Keep solvent away from flames and heat sources. Do not come into contact with the liquid or breathe the fumes. Perform experiment in a fume hood.

Copy and complete the risk assessment table. Add any more risks you can think of, as well as ways to manage them. Ask your teacher to check your risk assessment before you proceed.

Procedure

1. Wearing gloves, obtain a clean piece of chromatography paper. Do not handle the paper with bare hands because oil in the skin can contaminate the chromatogram.
2. Use a pencil (not ink) to draw a line across the long side of the paper approximately 2 cm from the bottom. Starting from one edge, every 3 cm on the line draw a circle 2 mm in diameter until there are six circles.
3. Label each circle in pencil with the amino acid and unknown (Figure 16.1.4).

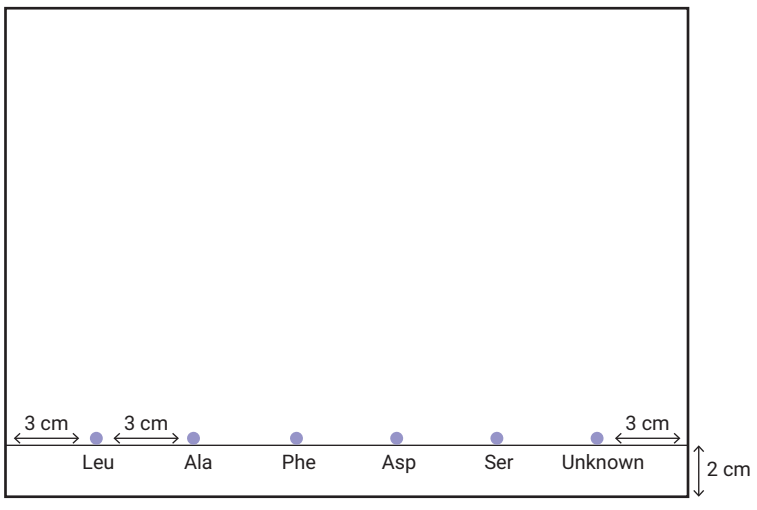


FIGURE 16.1.4 How to set up the chromatogram

4 Use a capillary tube to place a small drop of an amino acid in the corresponding circle on the pencil line. Use a clean capillary tube for each amino acid and the unknown. Ensure the drop does not extend beyond the circle.

5 Allow the drops to dry. Repeat the process, adding another drop of each acid to the corresponding drop.

6 After all samples are dry, roll the paper into a cylinder with the drops and line on the outside. Line up the top and bottom and staple towards the top and base leaving a small gap between the two edges of the paper. It is important the edges of the paper are not touching (Figure 16.1.5).

7 Pour 10 mL of the solvent mixture into the 600 mL beaker. Take the beaker to the fume hood and carefully stand the stapled chromatography cylinder in the beaker. Avoid splashing the solvent onto to the paper. Ensure the cylinder does not touch the sides of the beaker.

8 Cover the beaker with aluminium foil and allow the solvent front to migrate up the paper until it is 1 cm from the top edge. Do not allow it to reach the top of the paper.

9 Remove the paper from the beaker and use a pencil to immediately mark the position of the solvent front before it dries. (Make sure you are wearing gloves.) Allow it to air dry in a fume hood.

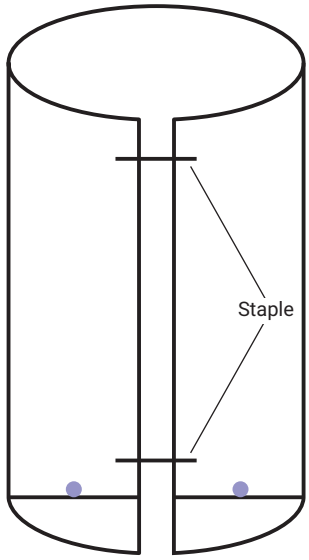


FIGURE 16.1.5 Stapling the chromatography paper

10 Once it is completely dry, remove the staples and hang it in the fume hood.

11 Your teacher will spray the paper with the ninhydrin solution. After the spray has dried, place the paper in an oven at 100°C for 3–4 min to allow the colour to develop.

12 Note the spots and circle each one because the ninhydrin will fade over time. Measure and record the distance moved by the solvent and each of the amino acids. (Measure to the centre of each amino acid spot.)

Results

1 Record distance (cm) the solvent front moved.

2 Copy and complete the following results table for distance moved by the amino acids (cm). Add more rows as needed.

Amino acid	Distance (cm)	R_F value
Unknown mixture		

Analysing results

3 Calculate the R_F value for each amino acid and each component of the unknown and add this to the table of results.

Interpretation

4 Identify the amino acids in the unknown mixture.

5 **a** Use the results to rank the amino acids tested from most polar to least polar.

b Compare the structures of the amino acids and explain if the results are consistent with their polarity.

Evaluation

6 Why is it important initially to keep the spots of amino acid above the solvent reservoir level?

7 Compare your results with those of other students. Did you get similar R_F values for the same amino acids? Suggest why or why not.

8 The R_F values of amino acids differ in different solvents. Suggest a reason for this.

9 What problems did you encounter? What errors can you identify?

LEARNING CHECK 16.1

DESCRIBING

1 **Define**:
   - **a** adsorb
   - **b** desorb
   - **c** component
   - **d** retention factor.

2 **Explain** how components of a sample can be effectively separated by paper chromatography.

3 **Explain** the relationship between R_F and polarity of an amino acid in thin-layer chromatography.

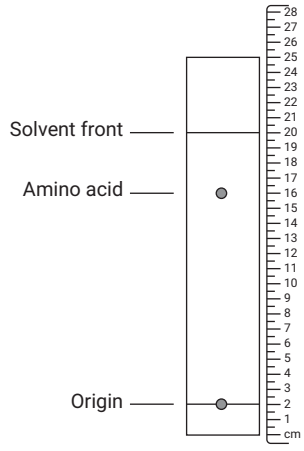
APPLYING

4 In Figure 16.1.3, the standard sample contained leucine, alanine, glycine, serine, lysine and aspartic acid. The order of their rates of travel up the paper under the conditions used is the order of listing: leucine is the fastest, aspartic acid is the slowest. By comparing the location of spots on the chromatogram, **identify** the amino acids present in samples X and Y.

5 If two amino acids have the same R_F value in a solvent, suggest how they might be separated.

 Modified from VCAA 2014 SA Q14

6 A thin-layer chromatography (TLC) plate was set up with a non-polar solvent, hexane, and a polar stationary phase, silica gel. The chromatogram below was obtained. A ruler was then placed next to the plate.



a **Calculate** the R_F value for the amino acid.
b The amino acid was thought to be either valine, glutamic acid or cysteine. **Determine** which of these is most likely. **Justify** your choice.

ANALYSING

7 **a** If you suspected one of the amino acids in the mixture you analysed in Practical activity 16.1.1 was not one of the known amino acids used for comparison on the same chromatogram, **infer** how you could use its R_F value to narrow down which of the other 15 amino acids it might be.
b **Develop** a process for identifying the unknown.

16.2 Electrophoresis

gel electrophoresis the process of separating large charged molecules by placing them in an electric field and observing their migration through a medium such as a gel

The technique of **gel electrophoresis** is commonly used to separate and analyse mixtures of compounds such as amino acid molecules. It is also used to identify proteins (after they have been hydrolysed to their component amino acids) and DNA.

The technique is straightforward and easily reproducible. It is a sensitive and accurate process that can clearly distinguish different amino acids with very similar compositions.

Migration of amino acids through the gel

Amino acid molecules may be charged, due to the ionisation of the amino and carboxyl groups, which can become protonated or deprotonated according to the pH of the surrounding solution. As you learnt in Chapter 15, the isoelectric point (pI) is the pH at which there is no net charge on the amino acid.

Weblinks
Electrophoresis
Isoelectric points and electrophoresis

The isoelectric point depends on the structure of the amino acid. The pI of amino acids with non-polar R groups is close to 6.0. The pI of amino acids with acidic R groups (e.g. aspartic acid) is much lower than 6 because a lower pH is needed to suppress the ionisation of the acidic R group. The pI of amino acids with basic R groups (e.g. lysine with $-NH_2$ at the end of the R group) is much greater than 6 because a higher pH is needed to suppress the ionisation of this basic group. **Figure 16.2.1** shows the forms of aspartic acid at different pHs.

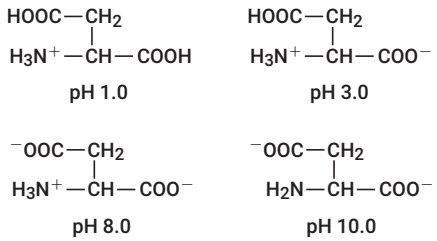


FIGURE 16.2.1 Forms of aspartic acid at different pH values (isoelectric point 3.0)

For example, glycine in near neutral solution exists as the neutral zwitterion (pI = 6.1), but in acid solution (e.g. pH 2), the carboxylate ion ($-COO^-$) accepts a proton:

$$\underset{\text{(overall neutral)}}{{}^+H_3N{-}CH_2{-}COO^-} + H^+ \rightarrow \underset{\text{(positive)}}{{}^+H_3N{-}CH_2{-}COOH}$$

This produces a positive ion that migrates towards the negative electrode in electrophoresis.

If the zwitterion is placed in alkaline solution (e.g. pH 11), then it gives up a proton from the $^{+}H_3N-$ and becomes negatively charged:

$$^{+}H_3N{-}CH_2{-}COO^{-} + OH^{-} \rightarrow H_2N{-}CH_2{-}COO^{-} + H_2O$$

(overall neutral) (negative)

Consequently at pH 11, the negative ion migrates towards the positive electrode, whereas at pH 2, it migrates towards the negative electrode and at pH 6–8 it does not migrate at all.

Effect of different buffer solutions on separation

Generally, if the **buffer** used has a low pH, all the –COOH groups will exist as –COOH groups and all the $-H_2N$ groups will pick up a hydrogen ion and form $^{+}H_3N-$. This means all the amino acids are positive and so will move towards the negative electrode. They move at different rates depending on whether they have a 1+ or 2+ charge.

buffer a solution that maintains a constant pH when small amounts of acid and base are added

If the buffer solution used has a high pH, then all the –COOH groups will exist as $-COO^{-}$ groups and all the $-H_2N$ groups will exist as $-H_2N$ groups. This means all the amino acids will carry a negative charge and move towards to positive electrode. Similarly to low pH, they move at different rates depending on whether they have a 1– or 2– charge.

For buffer solutions of intermediate pH, the isoelectric point of each amino acid needs to be considered. If an amino acid is placed in a buffer solution and the pH of the surrounding buffer solution is greater than the pI, the amino acid molecule will carry a net negative charge. If the pH of the surrounding solution is less than the pI, the molecule will carry a net positive charge.

The rate at which the amino acids travel is also affected by their size. Those with lower molecular masses travel faster. For example, the smaller aspartic acid travels faster than larger glutamic acid. Amino acids with bulky groups (such as benzene and other rings) travel more slowly than amino acids with unbranched chains.

Using electrophoresis

Electrophoresis works on a very similar principle to chromatography. It can be defined as the separation of charged particles on the basis of their different rates of migration through a medium such as a gel. The gel is the equivalent of the stationary phase in chromatography. There is no mobile phase in gel electrophoresis because the movement of the molecules is the result of the electric field that is applied across the gel, which causes a force to act on charged particles within it.

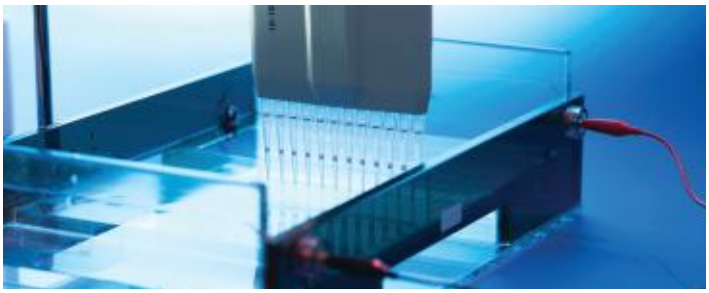
The equipment is set up as shown in the diagram in **Figure 16.2.2**.

In gel electrophoresis:

1. Samples of amino acid molecules are placed into wells at one end of the gel.
2. Buffer solutions at either end of the gel produce a pH gradient, a gradual change in pH across the gel.
3. As a result of the buffer solution at the start of the gel, various side chains in the amino acids become ionised. They then interact with the **electric field** across the gel and begin to move, or migrate, across the gel.
4. The rate of migration changes according to the size of the amino acid molecules and the extent to which they are charged:
   - The larger the molecule, the slower it will move.
   - The greater the charge on the molecule, the greater the force imposed through interaction with the electric field and so the greater the acceleration.

   Therefore, over time, different molecules in a sample will spread across the gel because they are moving at different speeds.

electric field a region of influence around a charged particle where a force is exerted on other charged objects



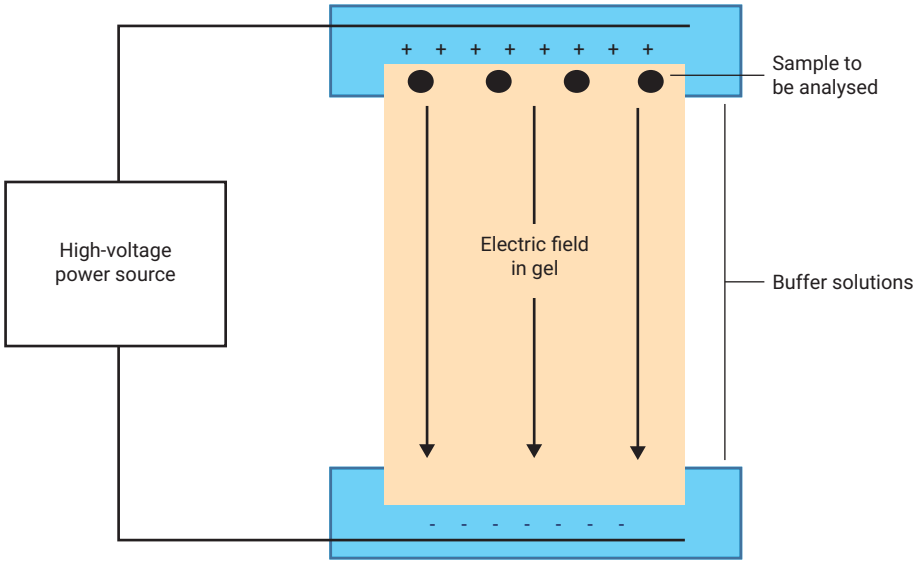


FIGURE 16.2.2 Electrophoresis equipment

Weblink
Gel electrophoresis simulation

Worksheet
Chromatography and electrophoresis

FORMULA AND DATA BOOK

5. Because of the pH gradient across the gel, eventually each amino acid reaches a pH that is equal to its isoelectric point. At this pH, the amino acid becomes neutral and so is no longer soluble. Therefore, it becomes focused into a band on the gel, which can be detected, often with UV light or ninhydrin solution.
6. The sequence of bands from different amino acid samples can be clearly identified and then compared.

LEARNING CHECK 16.2

DESCRIBING

1 **Define**:
   - **a** electrophoresis
   - **b** migration
   - **c** electric field
   - **d** isoelectric point
   - **e** buffer solution.

2 **Explain** why an electric field is necessary in electrophoresis.

3 **Explain** why, in electrophoresis, different amino acid molecules move at different speeds across the gel.

4 **Explain** why, in electrophoresis, it is necessary to have buffer solutions at different levels, providing a pH gradient across the gel.

APPLYING

5 In an electrophoresis experiment, the solution is buffered at pH 4.0.

- **a** **Identify** which electrode each of the amino acids, glycine, valine and phenylalanine travel to. **Explain** why.
- **b** **Determine** which of these three amino acids will travel the greatest distance in a given time and which will travel the least. **Justify** your choice.

6 **a** Using Figure 16.2.1 if necessary, **identify** which electrode in an electrophoresis experiment aspartic acid will move towards in a solution buffered at pH of:

- **i** 1.0
- **ii** 3.0
- **iii** 8.0
- **iv** 11.0.

b **Explain** how the distance moved (in a given time) by aspartic acid in a buffer solution at pH 11.0 would compare with the distance moved in a buffer solution at pH 8.0.

7 **Construct** a table to compare chromatography and electrophoresis analytical techniques.

ANALYSING

8 **a** In order to identify an amino acid, Q, a chemist ran electrophoresis experiments on it using buffers at pH 7.0, 5.0 and 3.0. The developed electrophoresis strips are shown in Figure 16.2.3a. **Deduce** which of the amino acids in Figure 16.2.4 that Q is most likely to be. **Explain** your reasoning.

b Electrophoresis experiments were run on another amino acid, T, using buffers at pH 11.0, 6.0 and 3.0. Results are shown in Figure 16.2.3b. **Identify** T from the amino acids in Figure 16.2.4. **Explain** your reasoning.

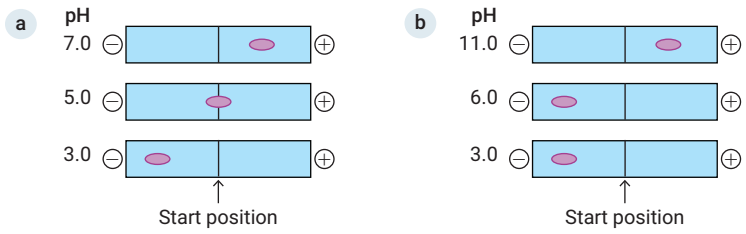


FIGURE 16.2.3 Results from an electrophoresis experiment

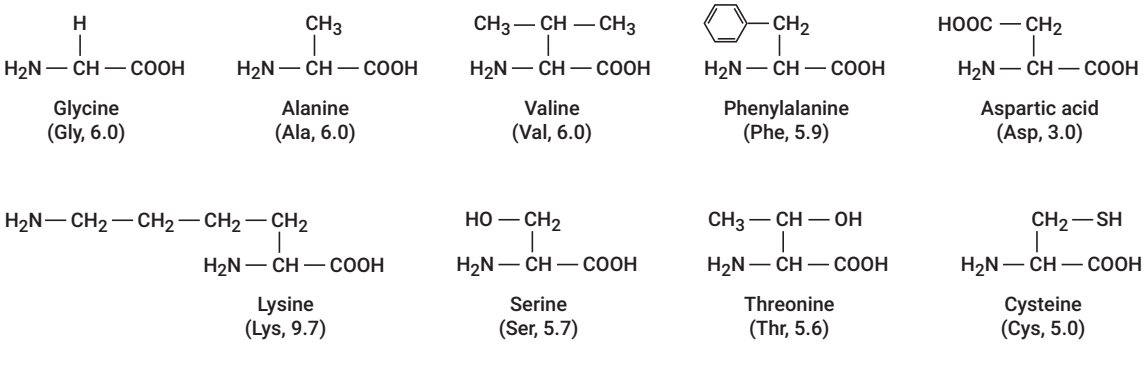


FIGURE 16.2.4 Common amino acids in proteins and their isoelectric points

9 **a** To identify the amino acids in a mixture, a chemist ran an electrophoresis experiment using a buffer of pH 6.0. The result is shown in Figure 16.2.5a. If the only possibilities are the amino acids in Figure 16.2.4, **identify** as many spots (labelled P, Q, R, S) as you can. (You will not be able to identify them all from this one experiment.)

b The chemist repeated the experiment at pH 5.0 and obtained the result in Figure 16.2.5b. If possible, **identify** additional spots and suggest possibilities for any spot(s) you are unable to identify. **Explain** the basis of your identifications.

Data from Debra Smith et al. Chemistry in Use Book 2, McGraw-Hill Pty Ltd, Figure Q c i & ii p191.

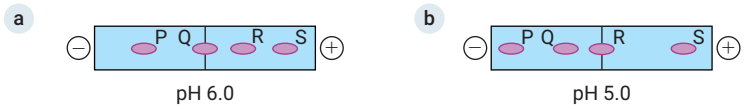


FIGURE 16.2.5 Results from an electrophoresis experiment

16.3 Mass spectrometry

Mass spectrometry can tell chemists a lot about the structure of a substance, such as the molar mass (M) and elements present, and it can detect the isotopes of an element. The use of mass spectrometers to determine the isotopic composition of an element, and therefore the relative atomic mass, is covered in more detail in Chapter 4 of *Nelson QCE Chemistry Units 1 & 2*. Mass spectrometry has many uses, from radioactively dating fossils to detecting drugs in sport supplements. Mass spectrometers are found in many locations, including on satellites, where they can identify particles intercepted in the solar wind. Mass spectrometry only requires a small amount of material but offers a wealth of information.

Principles of mass spectrometry

The principles of mass spectrometry were explained in detail in Chapter 4 of *Nelson QCE Chemistry Units 1 & 2* on pages 68–70.

Essentially, a vaporised sample is injected into the ionisation chamber of a mass spectrometer. There, it is bombarded with high-energy electrons that can knock an electron off the molecule or atom. The resultant particle that is positively charged is the **molecular ion (M^+)**.

molecular ion (M^+) the ion formed when a molecule is ionised without being fragmented in a mass spectrometer

Usually only one electron is knocked off, so the charge is typically 1+. If more than one electron is knocked off, then the charge corresponds to the number of electrons removed. In the original molecule, every electron was paired, so when an electron is knocked off, the resulting molecular ion has an unpaired electron. This molecule is called a **radical** and is represented by the dot, "•", as shown in Figure 16.3.1.

radical a molecule with an unpaired electron; generally highly reactive

Smith et al. 2010 Chemistry in use. Book 2

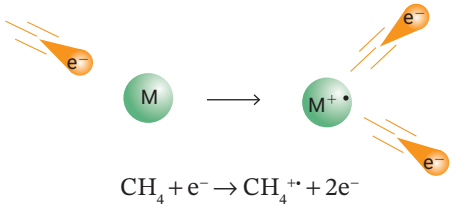


FIGURE 16.3.1 The formation of a positive ion by electron bombardment. M represents an atom or a molecule.

These positive particles are accelerated along the path by an electrical field. They then pass through a magnetic field, which deflects the ions based upon mass (m) and charge (z). Smaller, higher charged particles are easier to deflect. By varying the strength of the magnetic field, the ions can be separated by their mass and collected by a detector. The intensity of the ion beam hitting the detector provides a measure of abundance. Only the positive ions formed are detected, as a result of their charge. Uncharged radicals are not detected. The results are presented as a mass spectrum: a plot of m/z versus abundance.

The firing of high-energy electrons onto an organic molecule can cause the molecule to fragment. The initial molecular cation can break to form a smaller cation and a free radical. A free radical still has an unpaired valence electron and is very reactive. The free radical is neutral and uncharged, so it is not detected by mass spectrometry.

The initial molecular free radical of methane can fragment in a mass spectrometer as shown:

$$CH_4^{+\bullet} \rightarrow CH_3^+ + H^\bullet$$

$$\text{or } CH_4^{+\bullet} \rightarrow CH_3^\bullet + H^+$$

In these cases, the mass spectrometer would only detect the CH_3^+ and the H^+, as they are both positively charged.

Interpreting mass spectra

The plot produced by a mass spectrometer is called a mass spectrum and has a series of lines at different m/z (mass/charge) values along the x-axis. A cation will be detected at the point that corresponds to the mass of the particle, which is the atomic mass unit. The height of the peak corresponds to the abundance of the species. The largest peak is called the **base peak,** and it is assigned a relative abundance of 100 per cent. The other peaks are plotted as a relative percentage to the base peak. Mass spectra have a percentage scale on the y-axis.

base peak the largest peak in a mass spectrum; assigned a value of 100% with other peaks relative to it

The most important peak on the mass spectrum is the molecular ion ($M^{+\bullet}$) or **parent molecular ion**. The molecular ion gives the molecular mass of the original compound.

parent molecular ion the molecular ion that gives the molecular mass of the original compound in mass spectrometry

Fragmentation pattern

The way organic molecules fragment provides clues to the structure of the molecule. When ethanoic acid (CH_3COOH) is injected into a mass spectrometer, a range of peaks is observed (see Figure 16.3.3). Notice that the parent molecular ion at the m/z 60 peak is not the most abundant peak. The most abundant peak is the base peak at m/z 43. The other common peaks present are at m/z 45 and 15.

The parent ion (CH_3COOH^+) has many different possibilities for fragmentation. This fragmentation is shown in **Figure 16.3.2**.

If the bond between the two carbons breaks, then there are two possible peaks: a peak corresponding to the cation CH_3^+ at an m/z 15 and a peak corresponding to $COOH^+$ at m/z 45. Notice, in **Figure 16.3.3**, that the peak at 45 is much bigger than the peak at 15. This indicates that the fragmentation:

$$CH_3COOH^+ \rightarrow CH_3^\bullet + COOH^+$$

is more common than:

$$CH_3COOH^+ \rightarrow CH_3^+ + COOH^\bullet$$

Remember that radicals are not detected by mass spectrometry. If the single covalent bond between the C and O is broken, resulting in the loss of OH, then there are two possible fragments: CH_3CO^+ (m/z 43) and OH^+ (m/z 17).

In mass spectrometry, you can look at the peaks on the mass spectra. A peak of 15 indicates a CH_3^+ and that the methyl group is present.

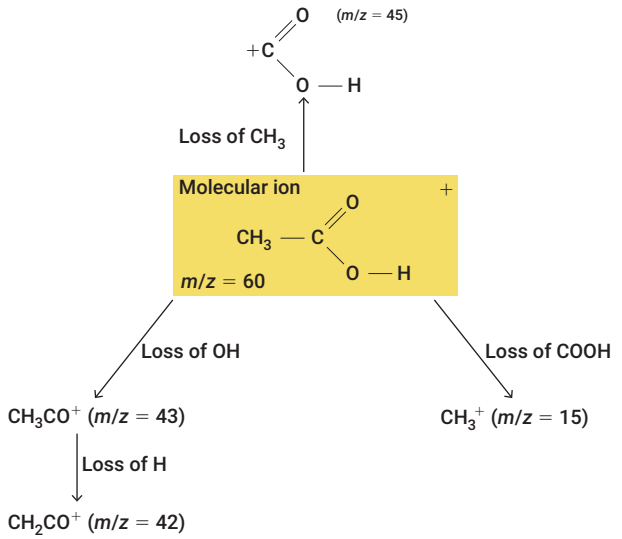


FIGURE 16.3.2 A simplified fragmentation pattern of molecular ion CH_3COOH^+

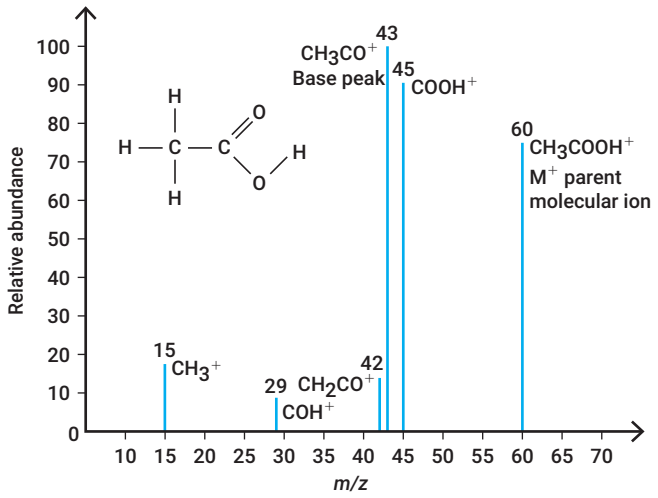


FIGURE 16.3.3 A simplified mass spectrum of ethanoic acid (CH_3COOH). The parent ion and base peak are identified.

Weblinks

Fragmentation patterns in the mass spectra of organic compounds

Interpreting mass spectra

TABLE 16.3.1 Commonly formed fragments of organic molecules

Relative mass	Fragment
15	CH_3^+
17	OH^+
29	$CH_2CH_3^+$, CHO^+
31	OCH_3^+
45	$COOH^+$, $OCH_2CH_3^+$

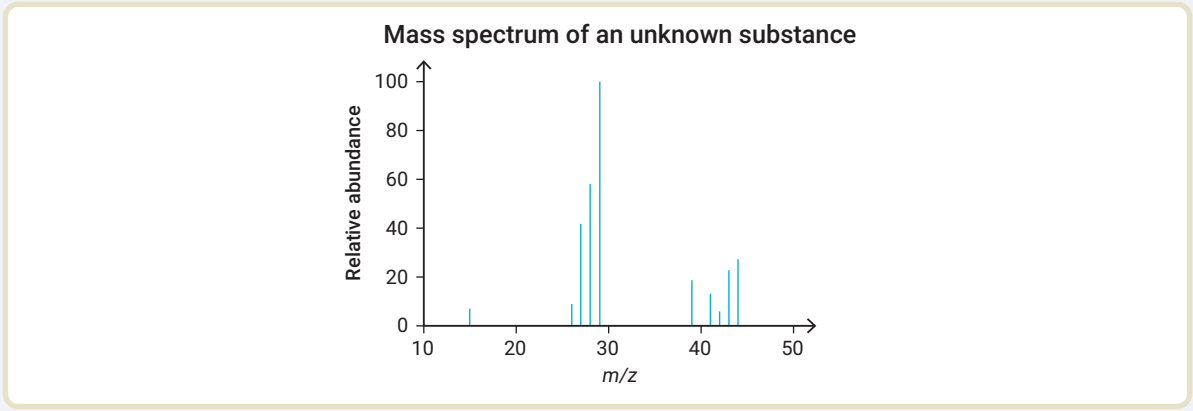
Alternatively, you can look at the differences in peak values. The parent molecular ion has a value of 60 and there is a peak at *m*/*z* 45. This difference, 15, could indicate loss of a methyl group. The peak at *m*/*z* 43 is 17 less than the parent peak. This could indicate loss of an OH group. A loss of an H atom could explain a peak at *m*/*z* 59.

Therefore, mass spectrometry is one technique that can be used, usually in conjunction with other techniques, to provide information about the structure of an organic molecule.

Table 16.3.1 shows common fragmentations that occur in organic molecules.

WORKED EXAMPLE 16.3.1

The following mass spectrum is of an unknown substance. Chemical testing has identified the compound as an alkane.



a Identify the alkane.
b Account for the peaks at 15, 28, 29 and 43.

ANSWERS

a 1 Identify the largest mass because this will be the parent molecular ion.

Largest mass is 44.

2 Use the general formula of alkanes (C_nH_{2n+2}) to determine an alkane that has a mass of 44.

C = 12, H = 1

Try C_3H_8; $12 \times 3 + 1 \times 8 = 44$

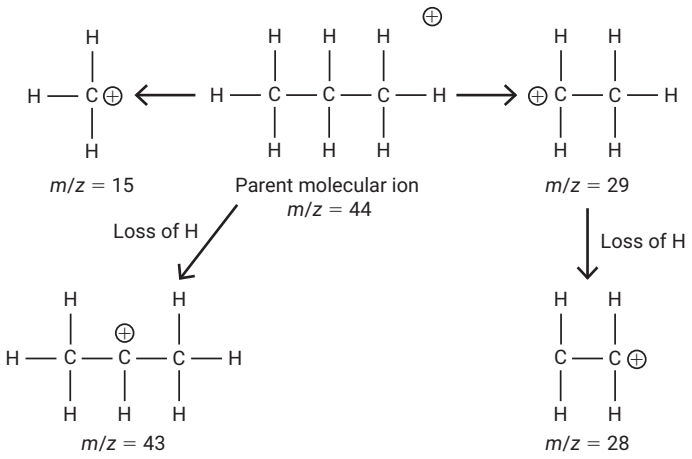
Parent molecular ion is propane.

b 1 Use Table 16.3.1 to identify possible fragments.

$15 = CH_3^+$

$29 = CH_2CH_3^+$

2 Draw a structural diagram of the parent molecular ion and possible fragments.



3 Calculate the mass of fragments, remembering a difference of 1 means a loss of a H.

$15 = CH_3^+$, $28 = CH_2CH_2^+$, $29 = CH_2CH_3^+$, $43 = CH_3CHCH_3^+$

LEARNING CHECK 16.3

DESCRIBING

1 **Define**:

a radical
b ionisation
c parent molecular ion
d mass-to-charge ratio
e base peak.

2 State which peak in a mass spectrum indicates the molecular mass of the compound.

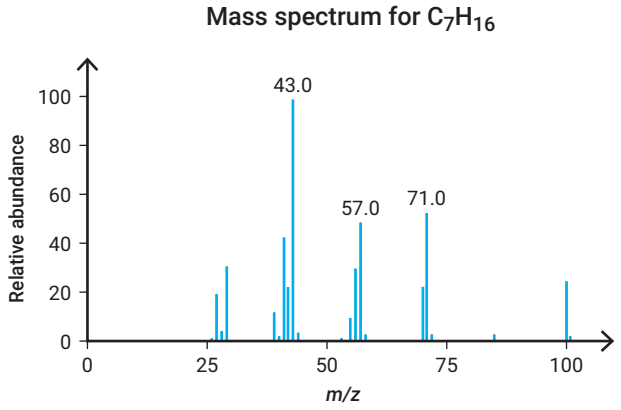
3 **Identify** when you could get a peak larger than the parent molecular ion.

4 **Explain** how a mass spectrum can be used to help determine the structure of a compound.

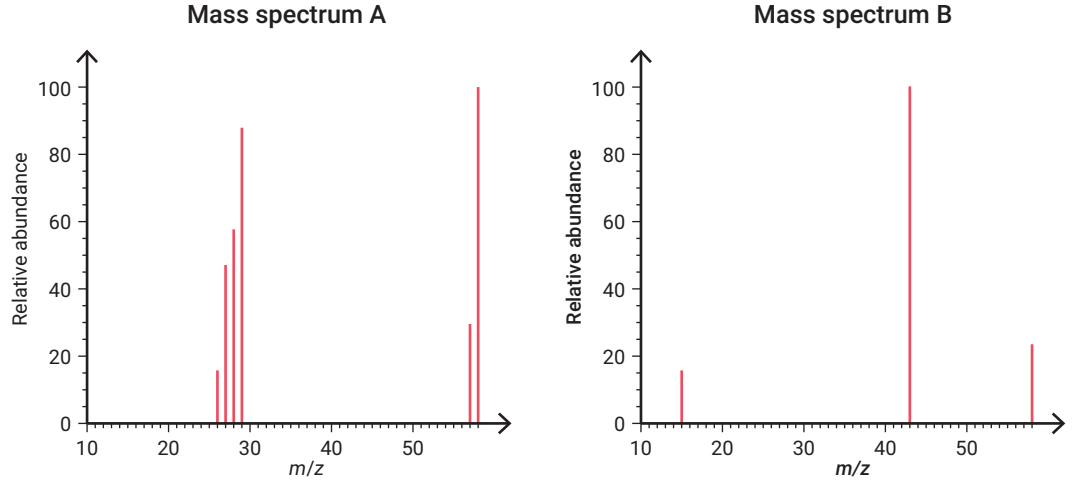
APPLYING

5 The mass spectrum of hexane shows strong peaks at *m/z* values of 15, 29, 41 and 57. **Identify** the possible fragments at these values.

6 The following mass spectrum is for C_7H_{16}. **Determine** the fragments that give the indicated main peaks in the spectrum.



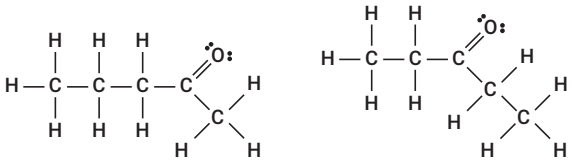
7 **Identify** which of the following mass spectra is for propanone and which for propanal. Justify your choice by accounting for the main peaks.



ANALYSING

8 The chemical composition of a compound was found to be $C_5H_{10}O$. The two possible structural isomers are shown.

a **Identify** the mass-to-charge ratio (*m*/*z*) you would expect for the parent ion for each isomer.



Structure A

Structure B

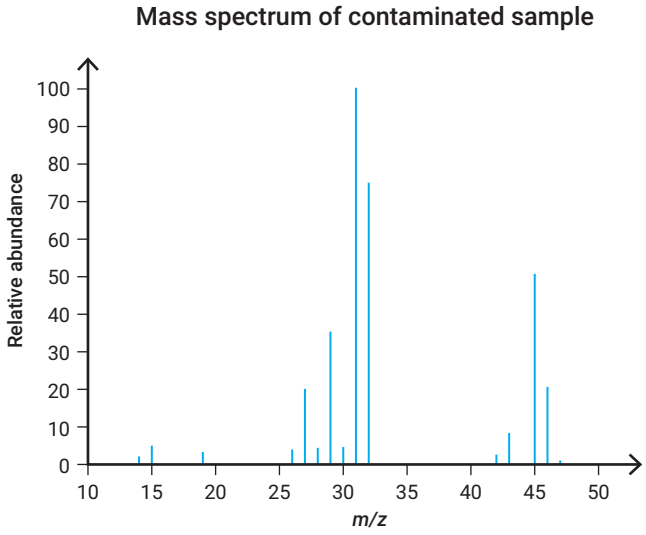
b The base peak for Structure A occurs at *m*/*z* 43, whereas the base peak for Structure B occurs at a *m*/*z* 57. **Analyse** these two peaks.

c The mass spectrum of the compound did not have a peak at 29. **Explain** how this enables the structure of the compound to be determined.

9 There was concern at a bioethanol plant that the ethanol had become contaminated with methanol. To check this, a chemist tested a sample and obtained the following mass spectrum for the sample. **Compare** the spectrum of the contaminated sample with that of ethanol in Figure 16.3.3.

a **Explain** how the chemist determined that the sample was contaminated.

b **Justify** that the contaminant was methanol.



16.4 Infrared spectroscopy

Infrared spectroscopy is a useful technique for determining the bonds or functional groups that are present or absent in a compound. It is a relatively cheap and easy technique and is used in industrial applications for monitoring chemical pathways, in forensic examinations and in drug development.

Principles of infrared spectroscopy

Molecules are constantly moving. The two basic modes of vibration are stretching and bending. A simple diatomic molecule is like two heavy spheres connected by a spring; the spheres can vibrate backwards and forwards around their equilibrium position, as shown in Figure 16.4.1. In polyatomic molecules, such as water, the general vibration modes are shown in Figure 16.4.2.

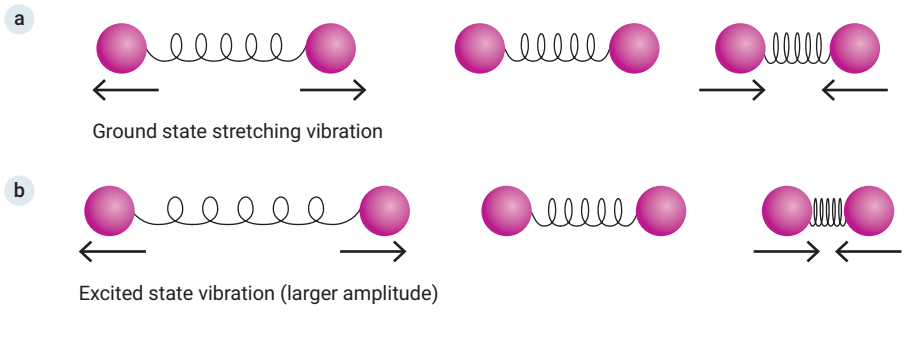


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FIGURE 16.4.1 Vibrations of the (a) ground state and (b) excited state of a diatomic molecule

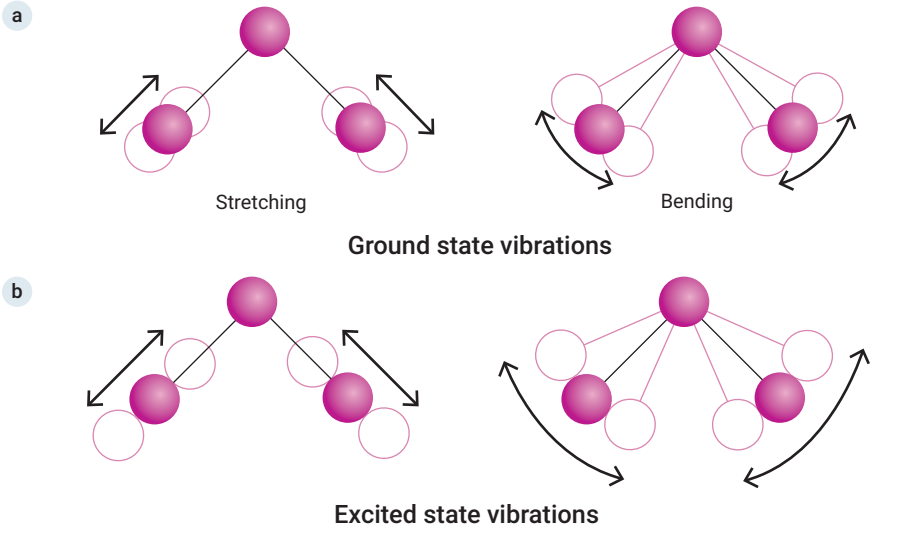

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FIGURE 16.4.2 Vibrations of the (a) ground state and (b) excited state of a triatomic molecule

The vibrations may be symmetrical or asymmetrical. A molecule can absorb infrared energy and change to a higher energy vibration mode. The molecules will now vibrate with more energy and amplitude. The spring will be stretched to greater lengths and compressed more, as shown in Figure 16.4.1. When bending vibrations are excited, the change in angle is greater, as shown in Figure 16.4.2b. This is not true for diatomic molecules such as O_2 and N_2; these molecules cannot be detected by infrared spectroscopy.

The energy absorbed depends upon the bond length, the bond strength and atom size. Heavier atoms require more energy to increase vibration. Double bonds require more energy than single bonds to increase vibration. Measurement of the absorbance will determine which bonds are present. Typical absorption values are shown in Table 16.4.1.

TABLE 16.4.1 Characteristic infrared absorption frequencies of some common functional groups

Class of compound	Bond	Band positions (cm^{-1})
Alkanes, alkyl groups	C–H	2850–2960
Alkenes	C–H	3020–3100
	C=C	1620–1680
Alkyl halides	C–Cl	600–800
	C–Br	500–600
	C–I	490–620
Alcohols	O–H	3200–3600 (strong, broad)
	C–O	1050–1410
Amines	N–H	3300–3500
	C–N	1030–1230
Carbonyl compounds (e.g. carboxylic acids, esters)	C=O	1700–1750
Carboxylic acids	O–H	2500–3000 (strong, broad)

During infrared spectroscopy, a sample is placed in a cell that is in a beam of infrared radiation. A number of different frequencies are absorbed by the compound. The percentage transmitted is recorded against the energy of the frequency. The *x*-axis is the wavenumber (cm^{-1}), which is the inverse of wavelength (cm). The *x*-axis of the infrared spectrum always shows a dramatic change.

Unlike mass spectra, infrared spectra consist of a series of troughs from a base line, so the spectra look 'upside down'. The *y*-axis is the percentage of light transmitted. The base line shows 100 per cent of the light still being transmitted.

Interpreting infrared spectra

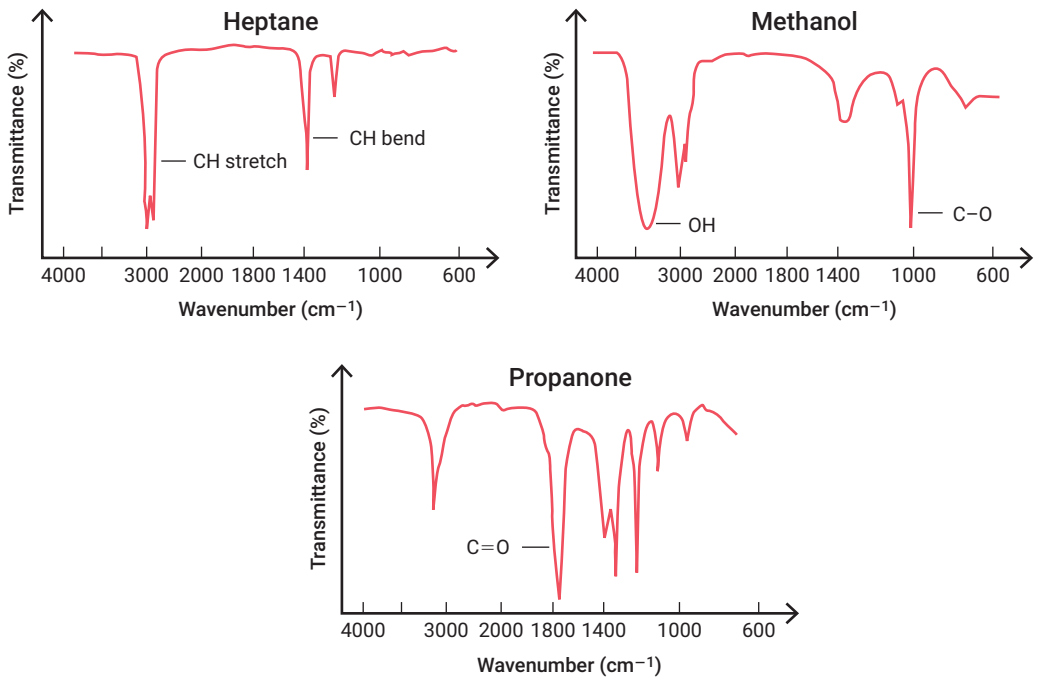
To interpret infrared spectra, look for key troughs or absorption bands. Many bands can be ignored because they are caused by the many different vibrational modes of the molecules and do not provide useful information. The key area to examine is in the higher wavenumber region. Notice in the spectra in **Figure 16.4.3** that the scale on the *x*-axis changes. The troughs to the right of around 1400 cm^{-1} are called the fingerprint region.

Almost every organic molecule has a C–H bond (where a hydrogen is attached to a carbon), which absorbs somewhere in the range 2800–3000 cm^{-1}. This trough does not provide much information and neither does the band due to a C–C bond.

The O–H bond in alcohols typically absorbs at 3200–3600 cm^{-1}, whereas the O–H bond in carboxylic acids typically absorbs at 2500–3000 cm^{-1}. However, because it is usually broad, there may be some overlap of values between these two compounds. The C=O bond at 1700 cm^{-1} is also very useful in distinguishing between them. The presence of a broad trough at 3000–3200 cm^{-1} could indicate that the compound is an alcohol. But when it is also present with a band at 1700 cm^{-1}, the compound could be a carboxylic acid.

Weblink
Infrared spectroscopy

FORMULA AND DATA BOOK



Weblink
IR spectroscopy

Worksheet
Infrared spectroscopy and mass spectroscopy

FIGURE 16.4.3 Infrared spectra of heptane, methanol and propanone (CH_3COCH_3). The broad trough at around 3200 cm^{-1} is characteristic of an alcohol O–H stretch. Other vibrations that cause the major absorption bands are also identified.

fingerprint region a region in an infrared spectrum of absorption of 1400 cm^{-1} or less, where it is difficult to assign peaks to specific bonds; the region is used to identify a molecule by comparing it to a library standard

Spectra fingerprint region

Each compound has a unique **fingerprint region** – the region at less than about 1400 cm^{-1}. It can be difficult to assign absorption peaks in this region to specific bonds but by comparing it to the spectrum of a known sample, an unknown compound can be identified. The fingerprint region can also indicate whether the sample is pure, if it matches that of a pure standard. The trough may be of different intensities due to the concentration differences between the two samples.

LEARNING CHECK 16.4

DESCRIBING

1 **Explain** why infrared light is absorbed by some molecules.

2 **Explain** why infrared spectroscopy is sometimes referred to as vibrational spectroscopy.

3 **Explain** what is meant by the 'fingerprint region' and why it is so named.

4 a **Identify** which of the following compounds would show a broad peak at 3300 cm^{-1}: 1-propanol, 2-propanol, ethane, ethanol, ethanoic acid, methanoic (formic) acid, ethyl ethanoate, butanoic acid, 1-chloroethane, 1-methylamine.

b **Identify** a characteristic peak(s) that could be used to identify the compounds not included in your answer to part a.

APPLYING

5 Two compounds, X and Y, react with sulfuric acid to produce a compound that smells like nail polish remover (methyl ethanoate). Two students tried to make this compound.

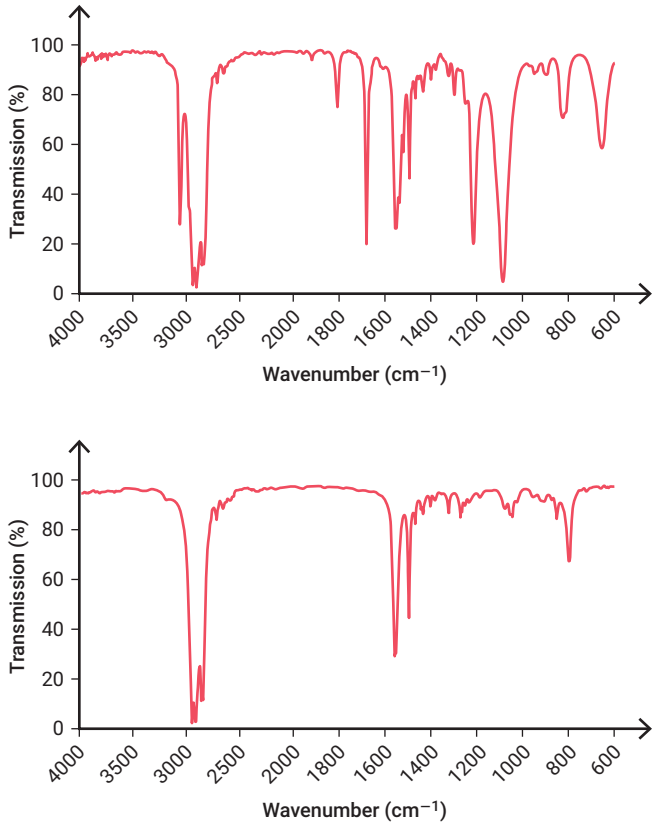
- **a** **Describe** what they would see in the infrared spectrum to distinguish between X and Y.
- **b** **Deduce** what they would see in the infrared spectrum for methyl ethanoate.
- **c** **Explain** how they would be able to say that the sample is pure.

6 **Determine** how infrared spectroscopy could be used to distinguish between the following pairs of compounds.

- **a** Ethane and ethene
- **b** Ethanol and propanol
- **c** 2-Chloropropane and iodomethane
- **d** 1-Propanol and propanoic acid

ANALYSING

7 **Compare** the following two spectra. **Determine** which spectrum is of 1-hexene and which is of hexane and **justify** your decision. **Determine** the fragments responsible for the main absorption bands.



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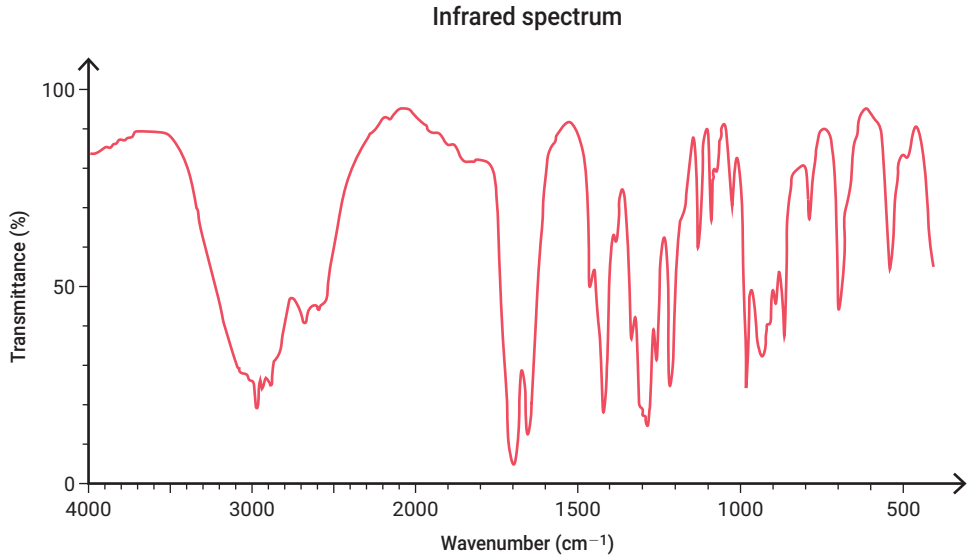
8 A student investigated an organic substance, Compound Y, with the molecular formula $C_5H_8O_2$. The infrared spectrum of Compound Y is shown here.



a State the wavenumbers of three peaks and **identify** the bond(s) responsible for each peak.

b **Deduce** a possible structure for the compound.

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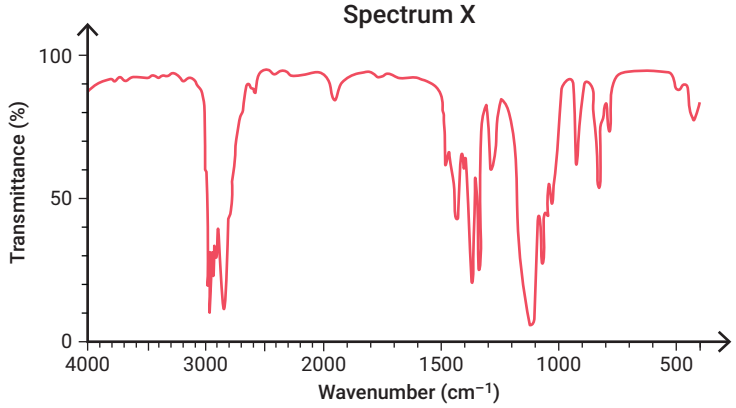
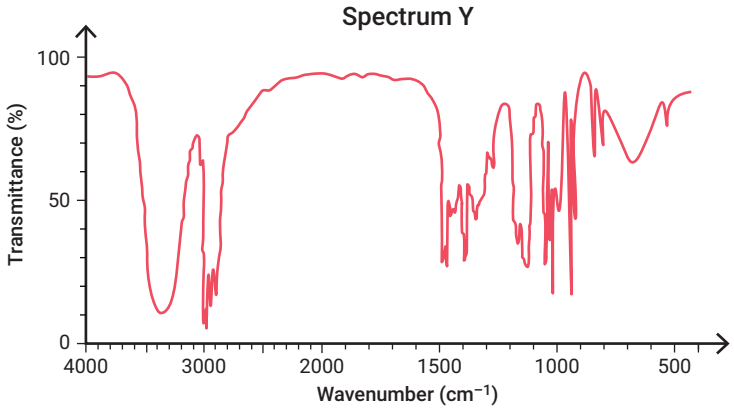
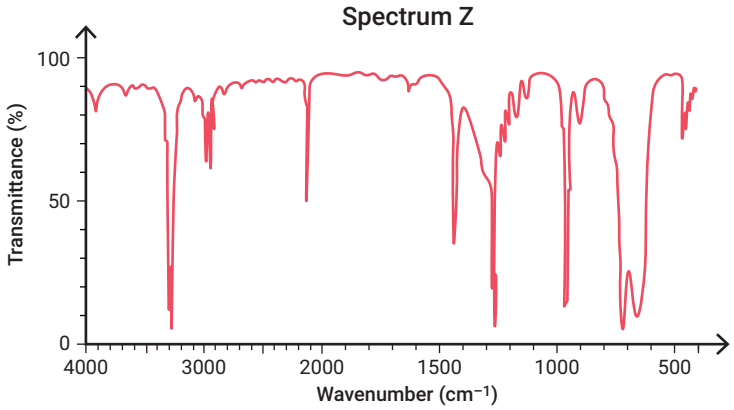
9 **Determine** which of spectra X, Y or Z is consistent with the product of hydration of 2-butene. **Justify** your choice.







16.5 Combining analytical techniques

Although a lot of information can be obtained by a single technique, much more information can be gained by combining techniques. Each technique provides one piece of the puzzle that is used to determine the whole structure **(Table 16.5.1)**. In 2002, the Nobel Prize in Chemistry was awarded for the development of a mass spectrometric analysis to John B. Fenn (1917–2010) and Koichi Tanaka (1959–).

When you only have a small amount of sample, it is important to maximise the amount of information you can obtain from the techniques. The improved sensitivity of instruments over time has meant that more information can now be obtained. Precious artworks can be tested for authenticity by chromatography, mass spectrometry and infrared spectroscopy; the pigments, glues and even the wooden frames can be analysed to determine if they originate from the same era. Electrophoresis is widely used in analysis of forensic evidence from crime scenes.

TABLE 16.5.1 Techniques used to identify compounds

Technique	Main feature	What it does
Mass spectrometry	High-energy electrons produce cations, which are separated due to the mass-to-charge ratio.	Determines molecular mass, isotopic abundances
Infrared spectroscopy	Infrared radiation increases the energy of the vibrational modes of the organic molecule.	Determines functional groups present
Chromatography	Organic compounds are separated according to their different adsorption and desorption rates between the mobile and the stationary phases.	Separates components
Electrophoresis	Organic compounds are separated by charge and size.	Separates components

ACTIVITY 16.5.1

MATCHING STRUCTURES

Research question

How can infrared and mass spectra be used to determine structures of organic compounds?

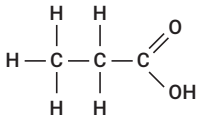
Aim

To identify structures from infrared and mass spectra data provided

Procedure

1 Examine the six molecules a–f and the six pairs of spectra 1–6.

a



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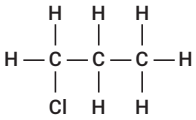

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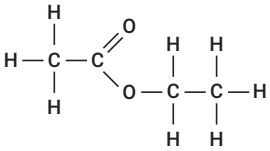

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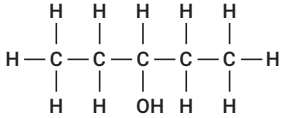
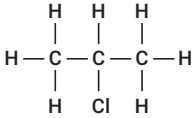
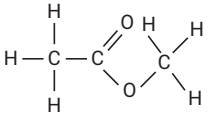


e



f

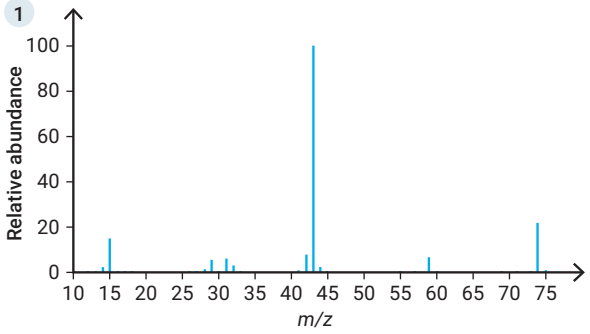


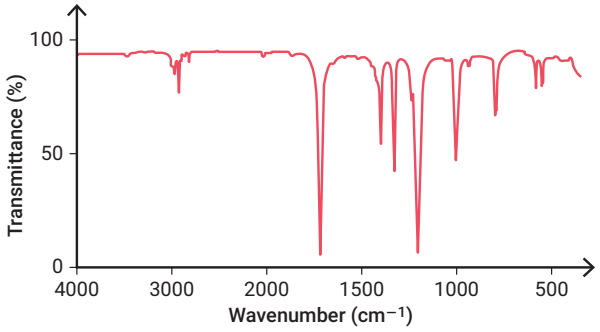
2 Match the mass spectra to the organic molecules. (Hint: Calculate the molecular mass.)

3 Look for possible common fragments.

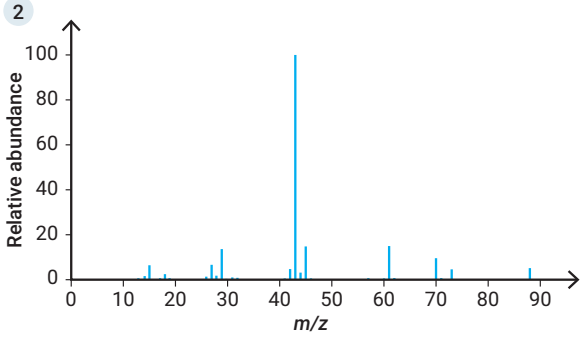
4 Look for key functional groups in the infrared spectra.

1


Relative abundance
100
80
60
40
20
0
10 15 20 25 30 35 40 45 50 55 60 65 70 75
m/z


Transmittance (%)
100
50
0
4000 3000 2000 1500 1000 500
Wavenumber (cm⁻¹)

2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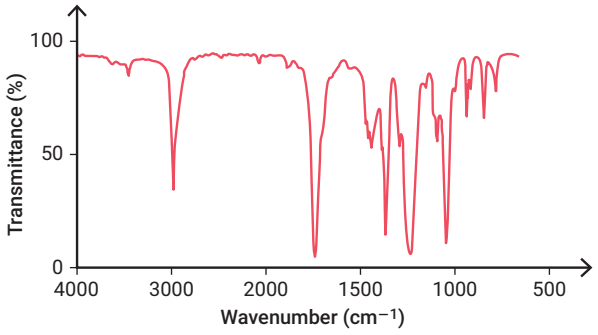
40
20
0
0 10 20 30 40 50 60 70 80 90
m/z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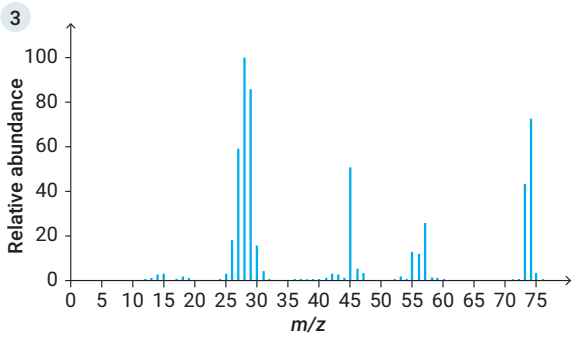
Wavenumber (cm⁻¹)

3


Relative abundance
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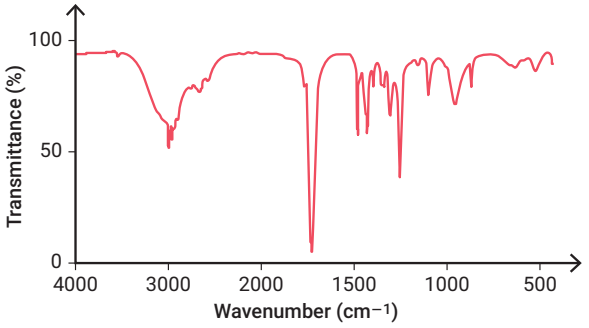
60
40
20
0
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75
m/z


Transmittance (%)
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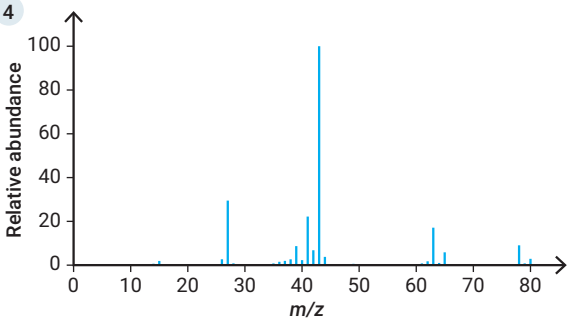
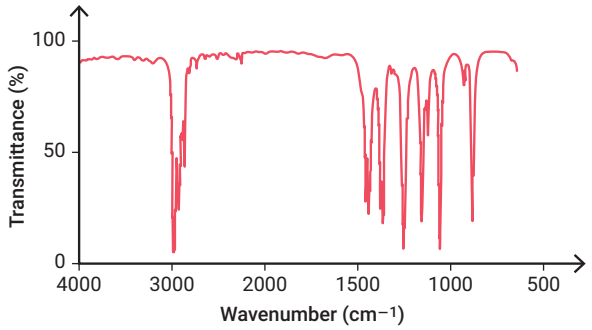
0
4000 3000 2000 1500 1000 500
Wavenumber (cm⁻¹)

4


Relative abundance
100
80
60
40
20
0
0 10 20 30 40 50 60 70 80
m/z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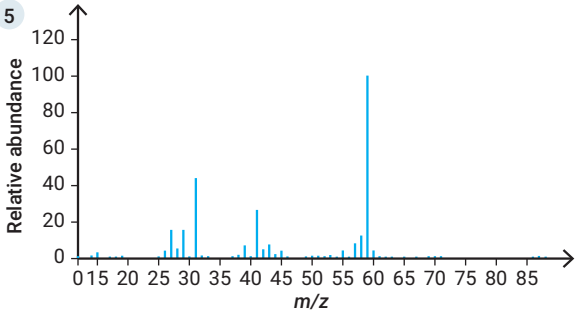
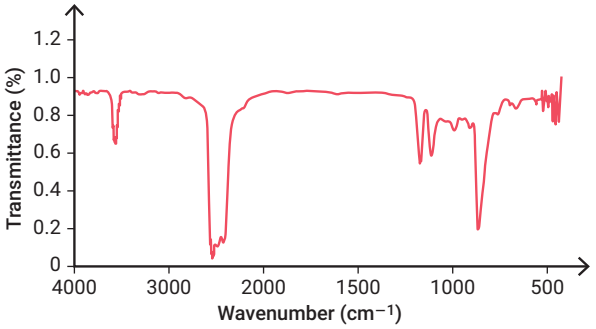
Wavenumber (cm⁻¹)

5





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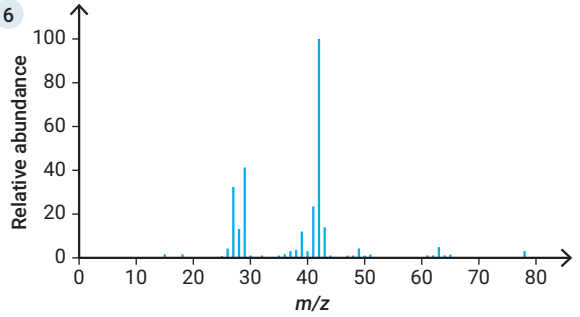
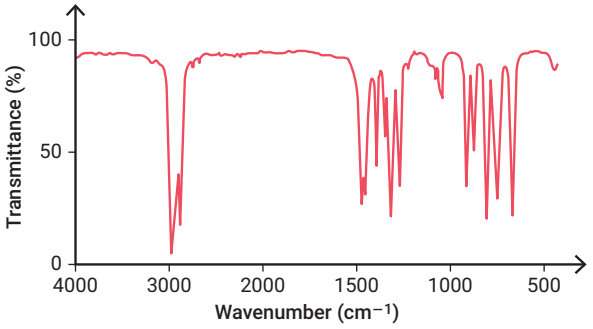




Interpretation

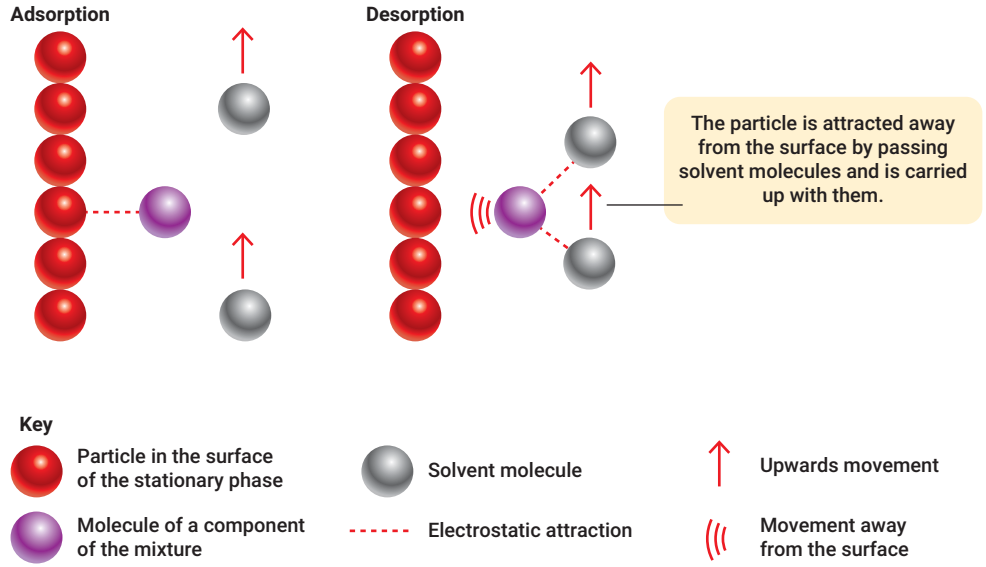
1 Which pair of spectra belongs to each compound?

2 Give the correct IUPAC name for each compound.

CHAPTER SUMMARY

Chromatography

- Paper and thin-layer chromatography have a polar stationary phase.
- Amino acids can be separated on the basis of their intermolecular attractions to the stationary phase and mobile phase (solvent).
- Amino acids with more polar R groups are absorbed onto the polar stationary phase and move slower.
- Amino acids with a non-polar R group are more soluble in a less polar mobile phase, so will continue to move upwards.
- Amino acids with intermediate polarity will be in equilibrium between the two phases and will move partway up the paper or thin-layer plate.



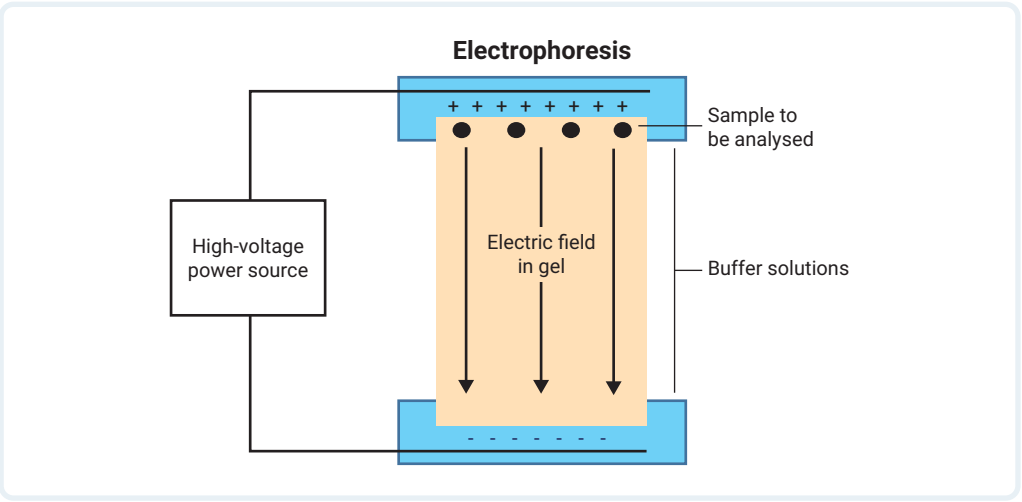
Note: The attracted particles will be much closer together than shown here.

- The retention factor (R_F) is unique for each compound and can be used to positively identify it:

$$R_F = \frac{\text{distance moved by the amino acid}}{\text{distance moved by the solvent}}$$

Electrophoresis

- Gel electrophoresis is the process of separating large charged molecules by placing them in an electric field and observing their subsequent migration through a medium such as a gel.



- Whether amino acids are charged depends on the pH of the buffer solution in the gel and the isoelectric point (pI) of the amino acid.
  - If pH > pI, the amino acid molecule will carry a net negative charge and move towards the positive terminal.
  - If pH < pI, the molecule will carry a net positive charge and move towards the negative terminal.
- The greater the charge on the molecule, the faster it moves through the gel.
- Amino acids with lower molecular masses move faster.
- Amino acids with bulky groups (such as benzene and other rings) move more slowly than amino acids with unbranched chains.
- As with chromatography, the retention factor (R_F) can be used to identify amino acids.

Mass spectrometry

- In mass spectrometry, an organic molecule loses an electron and becomes the parent molecular ion (typically M^+), which is detected.
- Uncharged particles are not detected.

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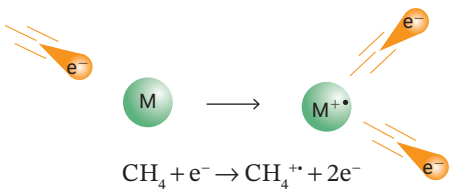
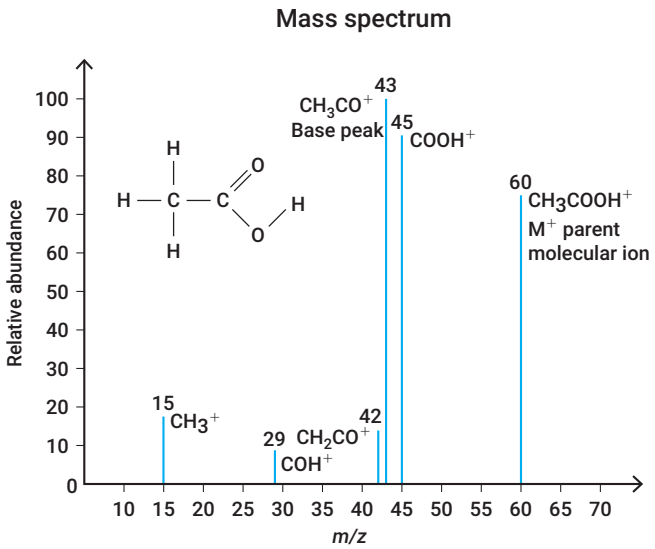


- The original molecule fragments when passing through a mass spectrometer.
- The resulting mass spectrum will contain a series of lines of differing relative intensity at different mass (m)/charge (z) ratios.

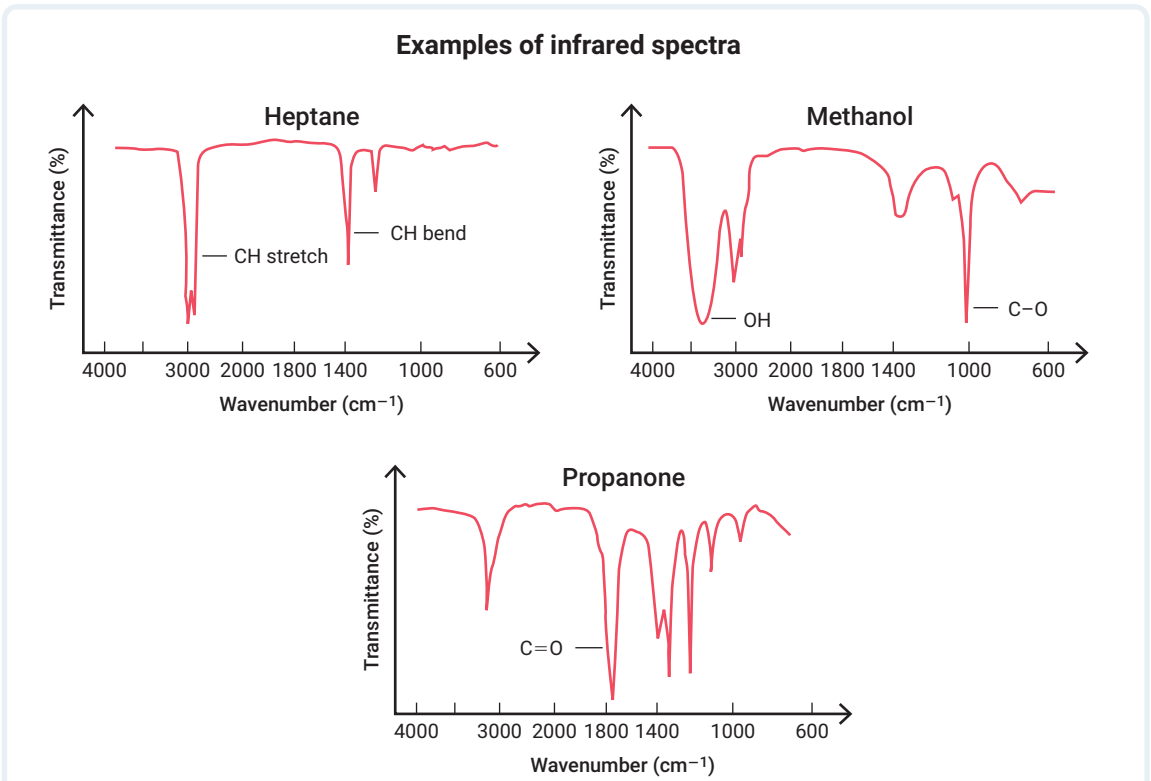
- Each line on a mass spectrum represents a different molecular ion.
- The base line is the most common fragment and has a relative intensity of 100%.
- The parent molecular ion has the largest m/z ratio and can be used to identify the original molecule.



Infrared spectroscopy

- Infrared spectroscopy measures the frequency (cm^{-1}) of energy absorbed by bonds in molecules as they stretch and bend.
- Bands in the infrared spectra are used to identify the bonds present in a molecule.

Smith et al. 2010 Chemistry in use. Book 2



- The region less than about 1400 cm^{-1} is called the fingerprint region and is unique to a compound.
- The fingerprint region is used to confirm the identity of the unknown compound by comparing it to a known sample.

MULTIPLE CHOICE

1. Consider the following statements about paper chromatography that uses a non-polar solvent to analyse a solution:

I Non-polar molecules in the solution will be attracted to the solvent particles by dispersion forces.

II Polar molecules in the solution will be attracted to the stationary phase by hydrogen bonding.

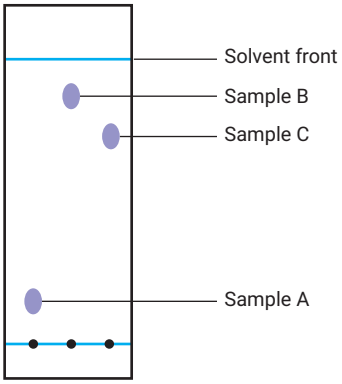
III Polar molecules in the solution will travel through the paper more rapidly than non-polar molecules.

Which of these statements are true?

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

 Modified from VCAA 2013 MCQ Q7

2. The thin-layer chromatography plate shown below has a polar stationary phase. It was developed using hexane as the solvent.



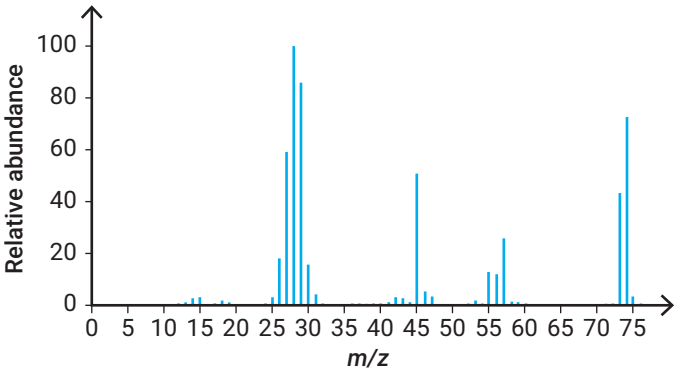
Which sample has the least polar molecules?

A Sample A
B Sample B
C Sample C
D There is not enough information to determine which sample has the least polar molecules.

3. Which one of the following analytical techniques involves the motion of ions of different mass in a magnetic field?

A Paper chromatography
B Thin-layer chromatography
C Mass spectrometry
D IR spectroscopy

4. The mass spectrum of propanoic acid is shown below.



What fragment must have been lost from the molecular ion to account for the high peak at *m*/*z* 73?

A H

B H^+

C H_2

D H_2^+

5. A drop of solution containing amino acid X was placed on the base line of a thin-layer chromatography plate. The rate at which X moves up the plate is most directly related to the:

A concentration of X.

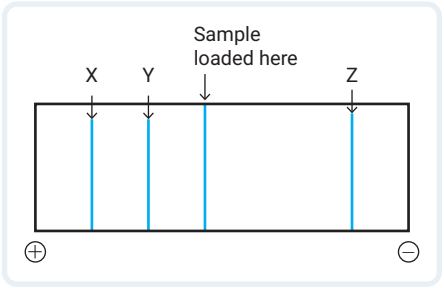
B rate of flow of the solvent.

C relative attraction of X and the stationary phase.

D relative solubility of X in the solvent used for the mobile phase.

Questions 6 and 7 refer to the following information.

Gel electrophoresis can be used to separate and identify a mixture of amino acids. The gel resulting from an experiment to separate a mixture of three amino acids X, Y and Z was carried out at pH 7 and is shown below.



6. Which one of the following statements about the experiment is *not* correct?

A X has a lower molecular mass than Y.

B Y moves through the gel faster than Z.

C Z must have an isoelectric point greater than 7.

D X and Y must be negatively charged.

7. If the mixture was known to contain the amino acids glycine, lysine and glutamine, which of the following correctly identifies each of X, Y and Z?

A X is glutamine; Y is lysine; Z is glycine.

B X is glutamine; Y is glycine; Z is lysine.

C X is lysine; Y is glutamine; Z is glycine.

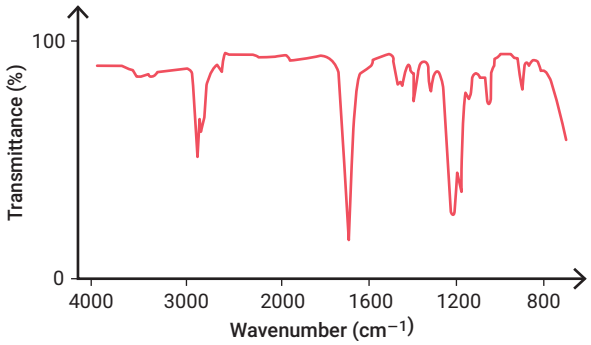
D X is glycine, Y is glutamine; Z is lysine.

©VCAA VCAA 2010 MCQ Q8

8. When a sample absorbs infrared radiation:

A covalent bonds are broken.
B covalent bonds stretch and vibrate.
C the spin alignment of certain nuclei changes.
D electrons in atoms move to higher energy levels.

9. The infrared spectrum of a compound X is shown below.

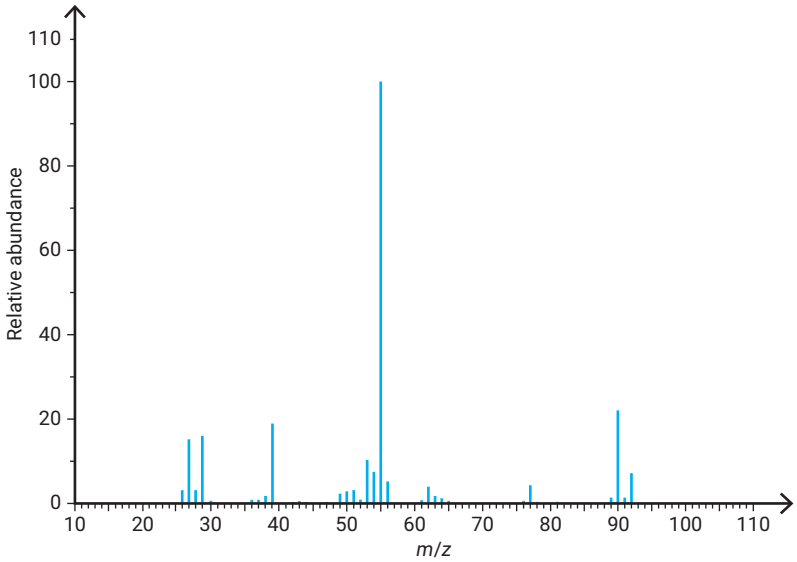


Identify which of the following is present in the compound.

A C=O **B** OH **C** NH_2 **D** C–N

©VCAA VCAA NHT 2018 MCQ Q23

10. The mass spectrum shown is for a molecule with the molecular formula C_4H_7Cl.



Data: SDBSWeb, <http://sdbs.db.aist.go.jp>, National Institute of Advanced Industrial Science and Technology

Which species is responsible for the base peak?

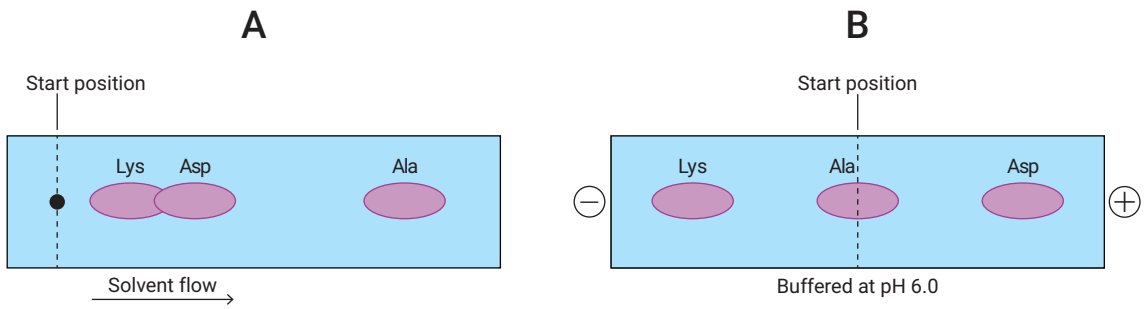
A $C_4H_7Cl^+$
B $C_3H_4Cl^+$
C $C_3H_5^+$
D $C_4H_7^+$

SHORT RESPONSE

11. **Identify** the best technique to:

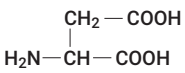
- **a** distinguish between carboxylic acids and amino acids
- **b** separate a mixture of amino acids
- **c** determine the molecular mass of a compound
- **d** identify the components of a protein.

12. Diagram A shows a paper chromatogram of a mixture of the three substances alanine, aspartic acid and lysine. Diagram B is the result of an electrophoresis experiment on the same mixture in a buffer at pH 6.0. Structures of the three substances, with their common abbreviations and their isoelectric points given in brackets, are shown below the diagrams.



Alanine (Ala, pI 6.0)

Lysine (Lys, pI 9.7)



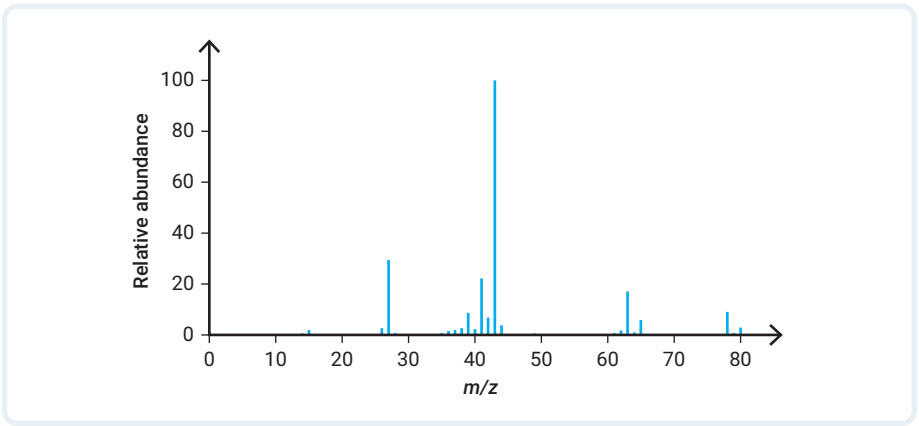
Aspartic acid (Asp, pI 3.0)

- **a** In diagram A, **explain** why there is a good separation between alanine and the other two, but only a poor separation between aspartic acid and lysine.
- **b** **Explain** why there is good separation between aspartic acid and lysine in the electrophoresis experiment in diagram B.
- **c** **Deduce** why alanine has hardly moved in the electrophoresis experiment.

CROSS-CHAPTER QUESTION

13. A compound was formed from the reaction of an alkene and HCl. The compound was 46% carbon and 9% hydrogen.

- **a** **Determine** the empirical formula for the compound.
- **b** Examine the mass spectrum of the compound. **Determine** the molecular formula for the compound.



c **Deduce** why the parent peak is not the peak with the largest m/z value in this case.

d Draw the possible isomers for the compound.

e **Identify** the fragments responsible for peaks at 43, 63 and 65.

f Use the mass spectrum to **determine** which one is the most likely isomer.

DATA ANALYSIS

14. Analyse data

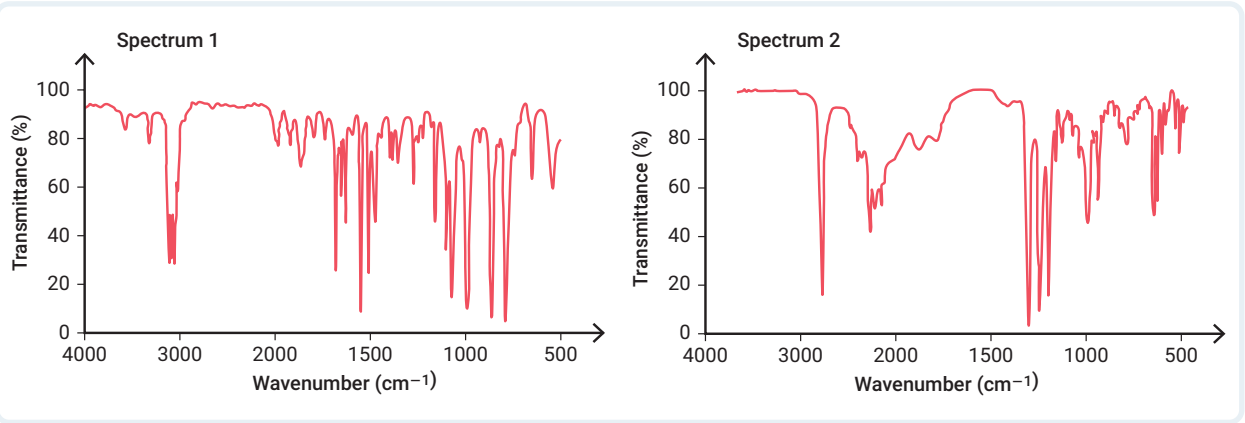
Two chemicals, A and B, have the same chemical composition: 54.55% C, 9.9% H, 10.7% N and the remainder oxygen.

a **Calculate** the empirical formula for the chemicals A and B.

Because they have the same composition and therefore, empirical formula, a chemist carried out chemical tests to try to distinguish them. Both chemicals A and B reacted with acids and bases.

b **Identify** the likely class of compounds that chemicals A and B belong to.

The chemist thought that A and B could be the same chemical, so they ran infrared spectra on both and obtained the following spectra.

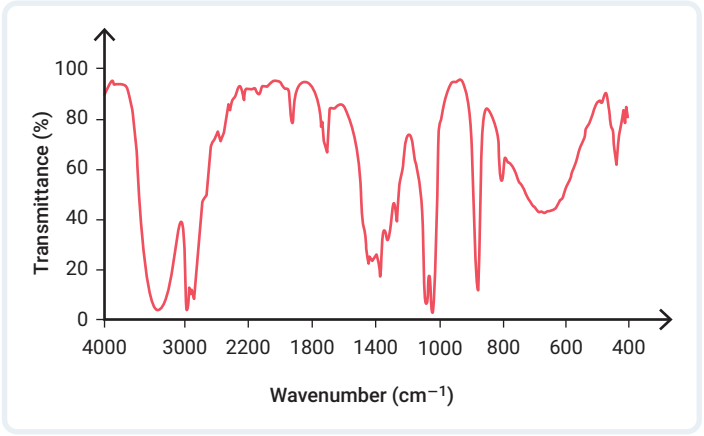


c **Explain** why the infrared spectra confirm that they are not the same sample.

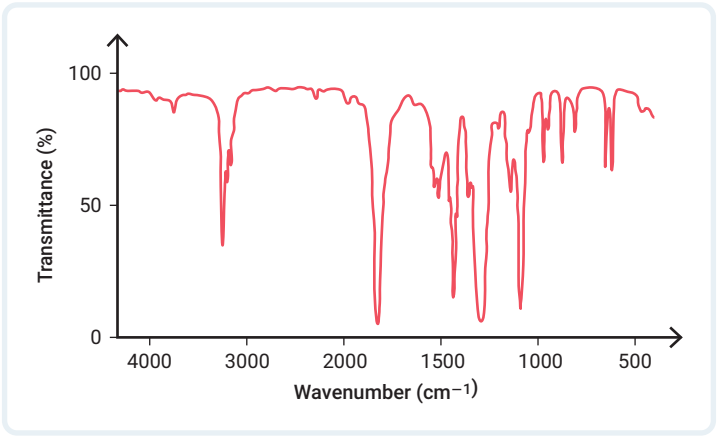
15. Analyse data

Compare the following infrared and mass spectra. Assign ethanol, ethanoic acid and ethyl ethanoate to the correct spectra.

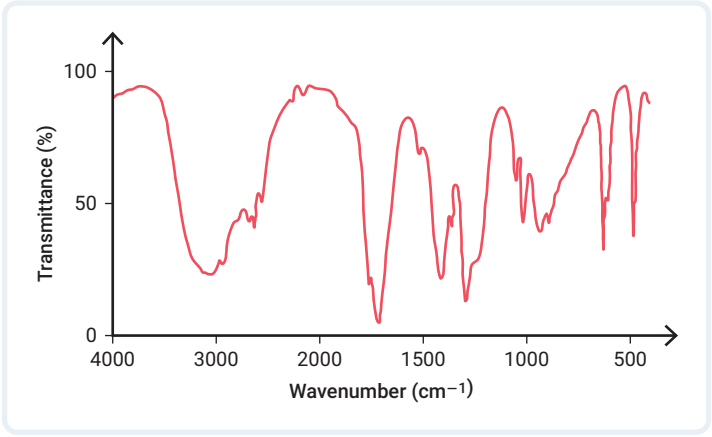
a



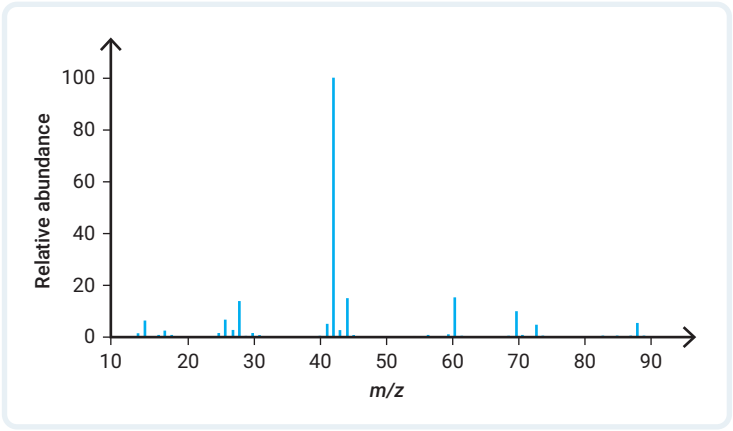
b



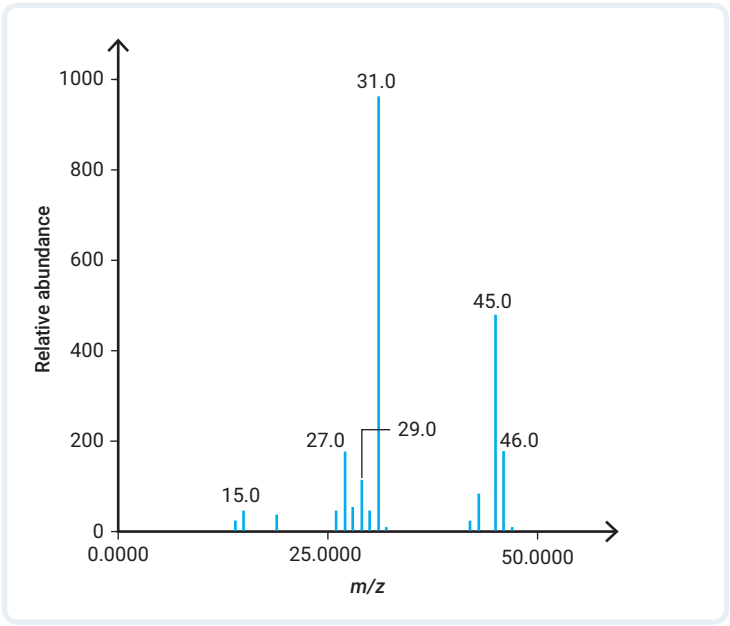
c



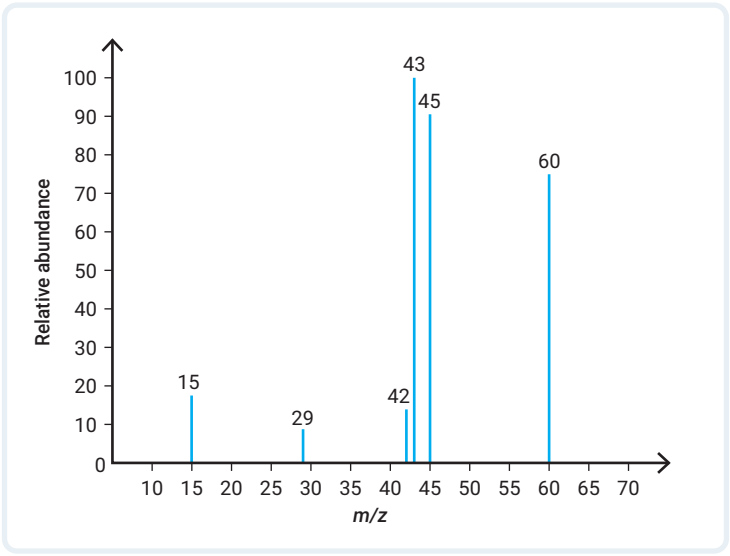
d


Relative abundance
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
m/z

e


Relative abundance
1000
800
600
400
200
0
31.0
45.0
27.0
29.0
46.0
15.0
0.0000
25.0000
50.0000
m/z

f


Relative abundance
100
90
80
70
60
50
40
30
20
10
0
43
45
60
15
29
42
10 15 20 25 30 35 40 45 50 55 60 65 70
m/z

CHAPTER 17

Chemical synthesis

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SYLLABUS DOT POINTS

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 and/or reaction conditions.
- Analyse and interpret data to determine the impact of reagents and reaction conditions on yield and rate of chemical synthesis processes.

Introduction

Knowing how compounds are produced allows us to manufacture chemicals for a variety of industries. For example, ammonia is widely used in agriculture, particularly in fertilisers, as well as in wastewater treatment and cleaning products. Sulfuric acid is often used in the production of fertilisers as well as in drug synthesis. Understanding these processes as well as the yield is very useful in industry.

Practical

- Percentage yield of carbon dioxide (online-only resource)

Worksheets

- Chemical synthesis for fuels
- Chemical synthesis processes

Nelson MindTap

To access resources above, visit **cengage.com.au/nelsonmindtap**

ASSUMED KNOWLEDGE

- ✓ Some chemical reactions are reversible.
- ✓ Le Châtelier's principle can be applied to determine the effect of changes of temperature, concentration, pressure and catalyst have on the position of equilibrium.
- ✓ The equilibrium constant (K_c) represents the relationship between product and reactant concentrations at equilibrium.
- ✓ The mole concept relates mass, number of moles and molar mass: $n = \frac{m}{M}$
- ✓ Limiting reactants can be determined by using the stoichiometric ratio of the balanced chemical reaction.
- ✓ Percentage yield can be determined by using the experimental and theoretical yield:

$$\text{Percentage yield } (\%) = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100$$

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ identify factors to consider in designing chemicals to optimise yield and rate of chemical synthesis processes
- ✓ calculate the theoretical yield of chemical reactions using limiting reactants
- ✓ calculate the percentage yield of chemical reactions
- ✓ describe the production of ammonia by the Haber process, using equations
- ✓ describe the production of sulfuric acid by the contact process, using equations
- ✓ describe the production of ethanol from fermentation and the hydration of ethene, using equations
- ✓ describe the operation of a hydrogen fuel cell under acidic and alkaline conditions, using equations
- ✓ analyse and interpret data to determine the impact of reactants and reaction conditions on yield and rate of chemical synthesis processes.

17.1 Factors to consider in designing a chemical synthesis

chemical synthesis the process of making a product through a series of reactions

reaction pathway a series of reactions leading to a specific outcome or product

reaction mechanism the steps involved in a reaction

Chemical synthesis involves selecting reactants to form a product with specific properties. A huge variety of substances are produced by chemical synthesis, including pharmaceuticals, fuels, cosmetics and cleaning products. First, a desired product is identified, and then the reactants and **reaction pathway** are developed.

The design of a chemical synthesis is affected by a number of factors. Often, the process is commercially driven; therefore, the aim is to produce the chemical as efficiently and cheaply as possible, without compromising on safety or environmental factors. In most cases, synthesis involves more than one step, and there may be more than one possible pathway or **reaction mechanism**. There are many factors to consider when deciding on the appropriate procedure; for example, other possible products, the availability and cost of reactants, and the conditions required for the reaction.

In a multistep reaction, each step has its own reactants, products and activation energy. These affect the speed of the reaction and the chemicals available for the next step. Along

the pathway, the products of one step may be used as reactants for another step. Therefore, these products are used up during the process. These chemicals are known as **intermediates**. An energy profile diagram can be used to represent the stages of the reaction (Figure 17.1.1).

intermediate a short-lived chemical species formed during a reaction

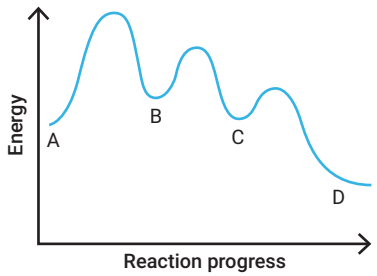


FIGURE 17.1.1 An energy profile diagram for a multistep reaction

In Figure 17.1.1:

- A is a reactant
- B and C are intermediates
- D is a product.

When choosing the most appropriate procedure, scientists also consider any side reactions that may occur and take steps to prevent these happening. This will maximise the purity of the product.

Maximising the yield of a reaction

When we perform calculations in chemistry, it is often assumed that all the reactants will react to form the products. In reality, this does not always happen. The yield of a reaction refers to the amount of product actually produced from the reactants. A reaction with a high yield produces a large amount of product from the reactants.

In industry, it is desirable to make as much of the product as possible. So the conditions are managed so that the position of equilibrium lies as far to the right as possible. Hence, at equilibrium, there is a much higher proportion of products than reactants, and a high proportion of the reactants have become products. The conditions required depend on the reaction; however, there are some common features:

- **Removing product:** Decreasing the concentration of a product favours the forward reaction, shifting the equilibrium to the right.
- **Recycling unused reactants:** This means there is less wastage, and the concentration of a reactant is increased. This favours the forward reaction, shifting the equilibrium to the right.
- **Conducting the reaction at an appropriate temperature:** The temperature used should favour the forward reaction so that equilibrium lies as far to the right as possible. However, the effect on the rate of the reaction and the cost of heating should also be considered.
- **Conducting the reaction at an appropriate pressure:** If the system involves gases, the pressure affects the position of equilibrium. Therefore, the pressure used should favour the forward reaction so that the equilibrium lies as far to the right as possible. However, the effect on the rate of reaction, cost and safety should also be considered.
- **Using a catalyst:** A catalyst can increase the reaction rate. This does not increase the yield directly, but it means that the product is produced in less time. It might also mean that the reaction can be carried out at a lower temperature without decreasing the reaction rate. If the reaction is exothermic, a lower temperature will also result in a higher yield.

Syllabus link
Chapter 19 in *Nelson QCE Chemistry Units 1 & 2* introduces reaction rates and catalysts.

Calculating theoretical yield: limiting reactants

theoretical yield the amount (mass) of a product that is produced from a complete reaction of the limiting reactant

limiting reactant the reactant that is completely consumed when a chemical reaction is complete

excess reactant the reactant that is not completely consumed when a reaction is complete

standard temperature and pressure (STP) a set of conditions commonly used when performing calculations on gases, such as gas density; standard temperature is 273 K (0°C), standard pressure is 1 atm (100 kPa)

standard laboratory conditions (SLC) a set of conditions commonly used when performing calculations on gases, such as gas density; standard laboratory temperature is 298 K (25°C), standard laboratory pressure is 1 atm (100 kPa)

Syllabus link
Chapter 9 in *Nelson QCE Chemistry Units 1 & 2* introduces limiting reactants and theoretical yield.

The **theoretical yield** is the amount of product that can theoretically be produced from the complete reaction of the limiting reactant. In reality, many factors affect how much product is produced. One of these factors is the amount of each reactant. As soon as one reactant runs out, the reaction can no longer proceed and no more product can be made. This reactant is known as the **limiting reactant**. The other reactants are the **excess reactants**.

Recall from Unit 2 that experiments can be carried out at **standard temperature and pressure (STP)**. They can also be carried under **standard laboratory conditions (SLC)**.

There are many methods for determining which chemical is the limiting reactant. In each case, the number of moles of each reactant is compared to the stoichiometric ratios needed in the reaction. One method is demonstrated in Worked example 17.1.1.

Once the limiting reactant has been determined, it is used to calculate the number of moles, and then the mass, volume or concentration of the product.

WORKED EXAMPLE 17.1.1

The synthesis of paracetamol ($C_8H_9NO_2$) is a three-step process. The final step is the reaction between 4-aminophenol (C_6H_7NO) and ethanoic anhydride ($C_4H_6O_3$):

$$C_6H_7NO(s) + C_4H_6O_3(aq) \rightarrow C_8H_9NO_2(s) + C_2H_4O_2(aq)$$

If 0.5 g of 4-aminophenol reacts with 0.4 g of ethanoic anhydride, what is the mass of paracetamol that can be produced?

ANSWER

1 Calculate the number of moles of each reactant.

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

$$n(C_6H_7NO) = \frac{0.5}{109.14} = 0.004\,58 \text{ mol}$$

$$n(C_4H_6O_3) = \frac{0.4}{102.1} = 0.003\,92 \text{ mol}$$

2 Determine the stoichiometric ratio (SR), using the coefficients from the equation, and the actual ratio (AR), using the number of moles calculated. Make sure that the same reactant is on top for both ratios.

$$SR = \frac{1}{1} = 1$$

$$AR = \frac{0.004\,58}{0.003\,92} = 1.168$$

3 Determine which reactant is limiting. If AR > SR, the reactant on the denominator is limiting. If SR > AR, the reactant on the top is limiting.

AR > SR, so the reactant in the denominator is limiting. Therefore, $C_4H_6O_3$ is limiting.

4 Use the number of moles of the limiting reactant to calculate the number of moles of the product that can be produced.

$$n(C_8H_9NO_2) = n(C_4H_6O_3)$$

$$n(C_8H_9NO_2) = 0.003\,92 \text{ mol}$$

5 Use the number of moles of the product to calculate the mass of the product that can be produced.

$$m = nM$$

$$m(C_8H_9NO_2) = 0.003\,92 \times 151.18 = 0.593 \text{ g}$$

The mass of paracetamol is 0.593 g.

The yield is usually given as a percentage of the possible yield. A yield of 90 per cent means that only 90 per cent of the theoretical amount of products that could be produced from the reactants is produced. To calculate this percentage, we need to:

- use stoichiometry to calculate the amount of product that can theoretically be produced from the reactants
- know the amount of product actually produced (through experimentation).

Then calculate the **percentage yield**:

$$\text{Percentage yield (\%)} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times \frac{100}{1}$$
$$= \frac{\text{actual mass}}{\text{theoretical mass}} \times 100$$

Weblink
Percentage yield

percentage yield the percentage of the maximum possible amount of product from a reaction that has experimentally been produced

WORKED EXAMPLE 17.1.2

If 5.0 g of sulfur reacts with excess oxygen to produce 7.50 g of sulfur dioxide, what is the percentage yield for the reaction?

ANSWER

1 Write a balanced equation.

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

2 Calculate the amount of product that could theoretically be produced.

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

$$n(S) = \frac{5.0}{32.06} = 0.156 \text{ mol}$$

The relationship between S and SO_2 is 1:1, so:

$n(SO_2) = n(S) = 0.156$ mol

3 Calculate the mass formed.

$m = n \times M$

$m(SO_2) = 0.156 \times (32.06 + 2 \times 16)$

$= 9.99$ g

This is the theoretical yield or theoretical mass.

4 Calculate the percentage yield.

Using the theoretical yield or mass that you calculated, and the experimental yield or actual mass (the mass obtained in the experiment) given in the question:

$$\text{Percentage yield (\%)} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times \frac{100}{1}$$
$$= \frac{\text{actual mass}}{\text{theoretical mass}} \times 100$$
$$= \frac{7.50}{9.99} \times 100$$
$$= 75.1\%$$

The percentage yield is 75.1%.

Practical
Percentage yield of carbon dioxide

17.1 LEARNING CHECK

DESCRIBING

1 **Explain** the difference between the rate of the reaction and the yield of the reaction.

2 **Identify** where equilibrium should lie to maximise the yield of the reaction.

3 **Identify** the maximum yield that is possible for a reaction.

4 **Identify** why it is important to remove the product to maximise the yield of a reaction.

APPLYING

5 **a** **Calculate** the mass of ammonia that can be produced from 5.0 L of hydrogen gas and 3.0 L of nitrogen gas at STP.

b **Calculate** the mass of sulfur trioxide that can be produced from 1 kg of sulfur dioxide and 1 kg of oxygen gas:
$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

6 The synthesis of aspirin (acetylsalicylic acid) involves the reaction:

$C_7H_6O_3(s)$	+	$C_4H_6O_3(aq)$	→	$C_9H_8O_4(s)$	+	$C_2H_4O_2(g)$
salicylic acid		ethanoic anhydride		acetylsalicylic acid		ethanoic acid

If 25.0 g of acetylsalicylic acid is produced when 30.0 g of salicylic acid reacts, **calculate** the percentage yield for the reaction.

7 The following reaction is exothermic:

$CaO(s) + H_2O(l) \rightleftharpoons Ca(OH)_2(s)$

Describe the effect on the yield of the reaction if the temperature is lowered.

8 During the production of oxygen gas by the electrolysis of water, 100 mL reacts to produce 65.0 g of oxygen gas:

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

Calculate the percentage yield of the reaction.

9 In the synthesis of aluminium chloride, 25.0 g of aluminium hydroxide reacts with hydrochloric acid:

$Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 3H_2O(l)$

If 20.0 g of aluminium chloride is produced, **calculate** the percentage yield for the reaction.

10 Chlorobenzene is used in the production of a range of chemicals, including dyes. It can be produced by the substitution reaction of benzene with chlorine:

$C_6H_6(l) + Cl_2(g) \rightarrow C_6H_5Cl(s) + HCl(g)$

Calculate the percentage yield for the reaction if 90.0 g of benzene produces 125 g of chlorobenzene.

11 In the synthesis of hydrochloric acid, 3.0 kg of chlorine gas is placed in a chamber with 150 g of hydrogen gas.

a Write a balanced equation for the reaction.
b **Identify** the conditions that would favour a high rate of production.
c Given that this is an exothermic reaction, state the conditions that would increase the yield of HCl.
d **Determine** the limiting reactant in this reaction.

17.2 Designing optimal processes

When designing reaction conditions, the rate at which the yield is produced must also be considered. In an ideal situation, the reaction would have a high yield, and this would be produced at a fast rate. As a result, a large amount of product is produced in a short time, thus maximising profit and minimising wastage. However, often a compromise must be reached between the yield and rate of the reaction when one condition has opposite effects on the yield and rate. Two examples of this are the Haber process and the contact process.

Haber process

Haber process the industrial production of ammonia

The **Haber process** is the main method for producing nitrogen-based fertilisers. It was developed in 1915 by German chemist Fritz Haber (1868–1934) and involves the reaction of nitrogen and hydrogen to form ammonia. The ammonia is then used as a feedstock for the production of fertilisers. An industrial plant can produce about 1000 tonnes of ammonia a day. To produce chemicals at this level, the reactions must be as efficient and profitable as possible.

Nitrogen and hydrogen gases are reacted together in the presence of a catalyst, at a temperature of 400°C and a pressure of 200 atm. The exothermic equilibrium reaction equation is:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

As with most industrial syntheses, conditions are chosen that maximise the yield and rate while being cost efficient and keeping safety issues in mind. Both yield and rate are affected by temperature and pressure. Figure 17.2.1 illustrates the effect of temperature and pressure on the equilibrium yield of ammonia. A high yield is promoted by high pressure and low temperature; however, when deciding on the optimum value for each of these variables, the cost and the reaction rate also need to be considered.

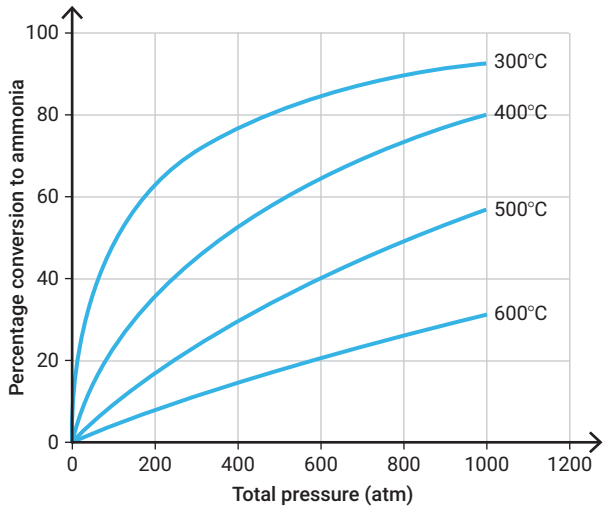


FIGURE 17.2.1 The effect of pressure and temperature on the equilibrium yield of ammonia

Weblink
Haber process

Temperature

Increasing the temperature increases the rate of the reaction because more particles will have sufficient energy for a successful collision.

Decreasing the temperature increases the yield because decreasing the temperature favours the exothermic reaction, according to Le Châtelier's principle. In the Haber process, the

Syllabus link
Chapter 2 discusses factors that affect equilibrium.

exothermic reaction is the forward reaction; therefore, decreasing the temperature will increase the yield of ammonia.

Cost must also be considered. It is very expensive to heat chemicals to extreme temperatures and so any benefits may be offset by the cost.

Therefore, a compromise is made between rate, yield and cost. A temperature of 400–450°C ensures that enough ammonia is produced in an adequate time.

Pressure

The rate of the reaction is increased by increasing the pressure of the system because this increases the concentration of the reactants and therefore the number of collisions.

Yield is also increased by increasing the pressure. Higher pressures favour the reaction that produces the least number of gaseous molecules. In the Haber process, this is the forward reaction and the yield of ammonia is increased.

Although a higher pressure increases both the yield and rate, extreme pressures have associated risks and costs. It is very expensive to produce and maintain a very high pressure. There is also the risk of explosions if the container cannot withstand the pressure.

A pressure of approximately 200 atm provides a balance between the high rate and yield, and the cost and risks associated with even higher pressures.

Catalysts

Catalysts do not affect the yield of the reaction, but they can affect the rate. In the Haber process, the catalyst is iron/iron oxide with a small amount of potassium oxide and aluminium oxide. This provides an alternative pathway for the reaction with a lower activation energy. Therefore, more particles have sufficient energy for a successful collision, and the rate of reaction is increased. Consequently, with a catalyst, the reaction can be carried out at a lower temperature, thus enabling a higher yield.

A diagram showing the equipment and method used in the Haber process can be seen in **Figure 17.2.2**.

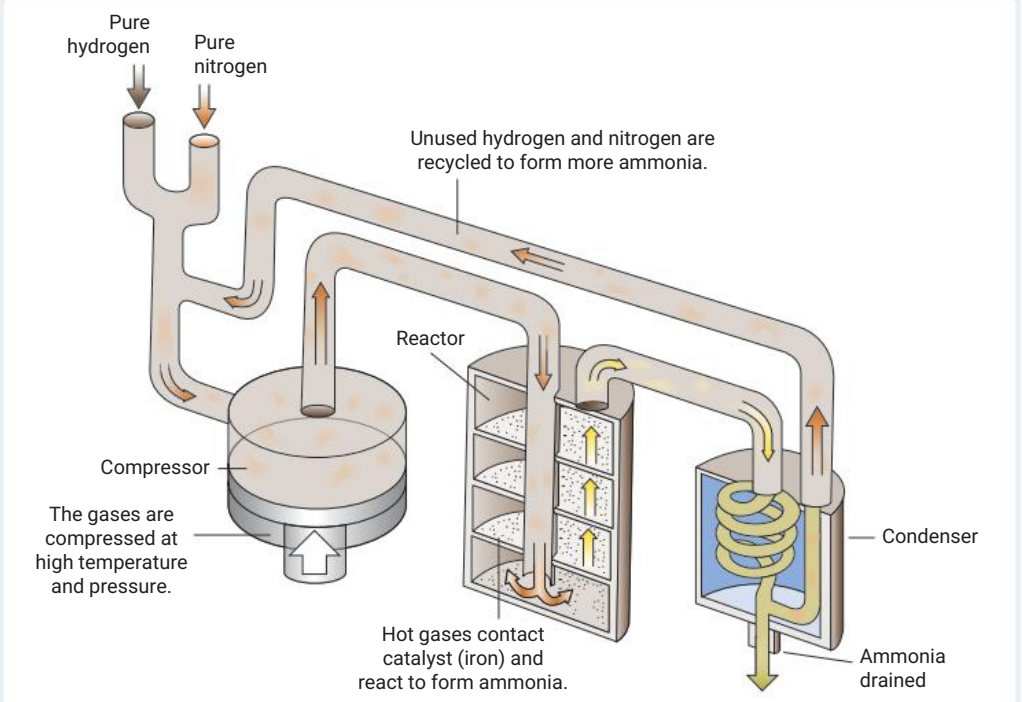


FIGURE 17.2.2 The industrial production of ammonia

- Nitrogen is sourced from the atmosphere; hydrogen is usually produced from methane, in a process called steam reforming.
- The nitrogen and hydrogen gases are heated to 400°C and fed into a compressor, which raises the pressure to 200 atm. These optimal 'compromise' values provide a sufficient yield of ammonia, at an acceptable reaction rate and economically viable cost.
- The gases are passed over beds of iron catalysts. The catalyst lowers the activation energy for this reaction and thus increases the rate of ammonia formation. As the gases pass over the catalyst, only about 15 per cent are converted to ammonia. The remaining gases are cooled and fed back over the catalyst beds. This recycling means that about 97 per cent of the nitrogen and hydrogen is eventually converted to ammonia.
- The gas mixture of ammonia and any unreacted nitrogen and hydrogen passes into a condenser, where it is cooled. Ammonia has the highest boiling point, so it condenses first, leaving nitrogen and hydrogen to be fed back into the reactor for further conversion.

Figure 17.2.3 summarises this process in a flow chart.

Weblinks
Control a Haber–Bosh animation plant interactive
Chemical equilibrium in the Haber process simulation

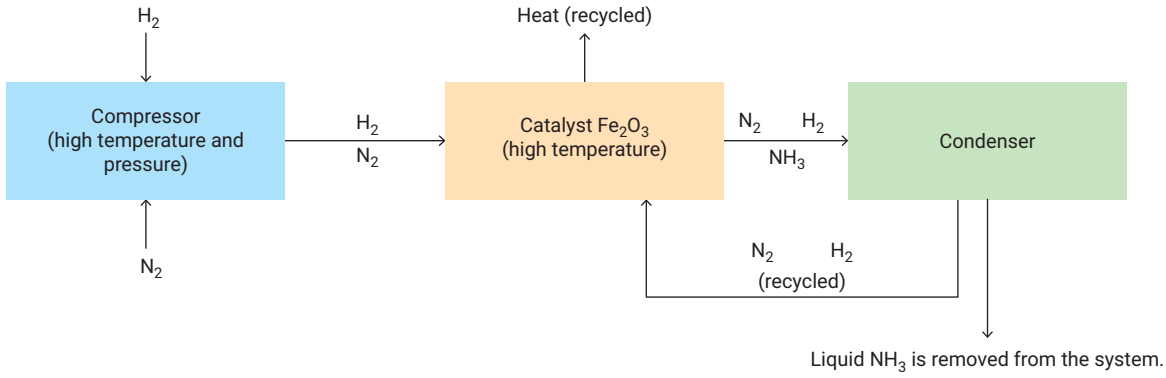


FIGURE 17.2.3 A flow chart illustrating the Haber process

Contact process

Sulfuric acid is one of the most important chemicals produced and used worldwide; it is used in the production of metals, paints, fertilisers, car batteries, detergents, dyes and fibres, and in agriculture.

It is produced by the **contact process**. This starts with sulfur or a sulfide, which undergoes a number of reactions to produce the acid. **Figure 17.2.4** outlines the contact process and the steps are described below.

contact process the industrial production of sulfuric acid

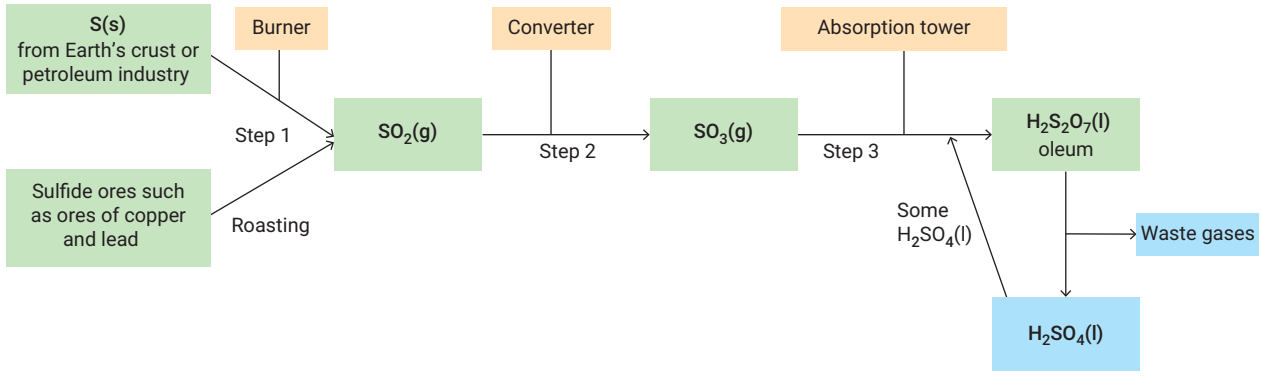


FIGURE 17.2.4 The steps of sulfuric acid production

Step 1: Production of SO_2

Sulfur is sourced from natural sulfur or sulfide ores. Oxygen is sourced from the air, which is cheap and readily available. An excess of air is used, which also provides the oxygen for step 2. This makes the process more efficient because the two reactants for the second step are already mixed together. However, the amount of air is controlled so that the ratio of sulfur dioxide to oxygen is 1:1.

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

or

$$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

Step 2: Production of SO_3

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1}$$

Step 2 is the most significant in the process and is where most consideration needs to be given to the reaction conditions in order to optimise the production of SO_3, and therefore of sulfuric acid. Stoichiometry, temperature, pressure and catalysts need to be considered.

Stoichiometric ratio of reactants

From the equation for step 2, you can see that the stoichiometric ratio of the two reactants is $2SO_2 : 1O_2$. However, a 1:1 ratio is used, which means there is an excess of oxygen. This has the combined effect of increasing the reaction rate and increasing the yield of sulfur trioxide.

Increasing the concentration of a reactant increases the reaction rate by increasing the frequency of collisions between reactant particles. As a result, the rate of the forward reaction increases, shifting the equilibrium to the right and producing more sulfur trioxide.

Temperature

The combustion of sulfur dioxide in step 2 is an exothermic reaction. Increasing the temperature increases the rate of reaction because more particles have enough energy for a successful collision. However, increasing temperature favours the endothermic reaction, which in this case is the reverse reaction. This decreases the yield of sulfur trioxide. **Figure 17.2.5** shows how the yield of sulfur trioxide depends on temperature.

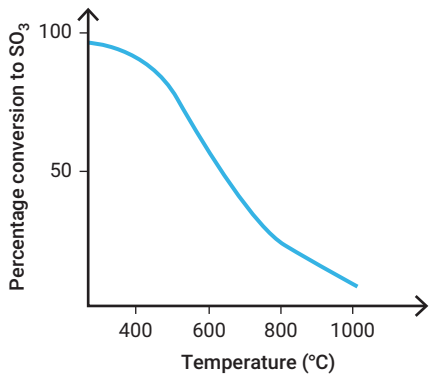


FIGURE 17.2.5 A graph of yield of sulfur trioxide against temperature

A compromise temperature of 400–450°C allows a relatively high yield of sulfur trioxide to be produced in a relatively short time.

Pressure

The pressure in the reaction chamber is 1–2 atm. A higher pressure than this would increase both the rate of the reaction and yield of sulfur trioxide. The rate of the reaction increases because the increased concentration of the reactants means more collisions between the particles. Since there are more gaseous molecules in the reactants than the products, an increased pressure increases the rate of the forward reaction more than the reverse. Therefore, equilibrium shifts to the right, increasing the yield of sulfur trioxide. However, it is very expensive to produce and maintain a high pressure safely; the cost outweighs any benefits. Therefore, a lower pressure of 1–2 atm is used.

Catalysts

The aim of the process is to produce as much sulfuric acid as quickly as possible. For this reason, a catalyst of vanadium(V) oxide (V_2O_5) is used. Although this does not affect the yield of sulfur trioxide, it increases the rate at which it is produced, thereby increasing the rate of the next step.

Weblinks
Manufacturing sulfuric acid
Contact process

Worksheet
Chemical synthesis processes

Step 3: Conversion of sulfur trioxide into sulfuric acid

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$
$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

It may seem counterproductive to add sulfuric acid when this is the desired product. If water was added directly to the sulfur trioxide, then sulfuric acid would be produced. However, this reaction is uncontrollable and produces a fog of sulfuric acid. By dissolving sulfur trioxide in sulfuric acid first, the reaction can be controlled and the sulfuric acid produced can be collected efficiently. All of the added sulfuric acid is recovered in the products.

17.2 LEARNING CHECK

DESCRIBING

1. Write a balanced equation to represent the Haber process and **identify** the reaction conditions that are used for optimal production of ammonia.
2. Write a balanced equation to represent the contact process and **identify** the reaction conditions that are used for optimal production of sulfuric acid.
3. Use Le Châtelier's principle to **explain** why temperature affects yield in the production of ammonia.
4. Use Le Châtelier's principle to **explain** why pressure affects yield in the production of sulfuric acid.
5. **Explain** why it is important to consider the molar ratio of reactant molecules in both the Haber and contact processes.
6. **Explain** why the use of a catalyst is critical to both the Haber and contact processes.
7. From what you have learnt about the Haber and contact processes, **identify** the factors that need to be considered in designing the industrial production of a chemical.

17.3 Synthesis of fuels

Most fuels are organic compounds. Coal and crude oil, carbohydrates, proteins and fats are all fuel sources used for particular purposes.

Carbohydrates are fuels that provide an energy source for living things. The oxidation of glucose in cells provides most of the energy needed for life.

As well as needing fuel for life, we also rely on fuels to produce electricity and power vehicles. Most transport fuels are derived from crude oil. Crude oil is a mixture of many hydrocarbons and is classed as a non-renewable fossil fuel because it is formed by the decomposition of prehistoric living things. Therefore, we need new sources of fuels to supplement and eventually replace the current fossil fuels.

biofuel a fuel produced from plants, algae or animal waste

Two categories of alternative fuels are biofuels and hydrogen. **Biofuels** are produced from renewable sources such as crops rather than from fossil fuels. Biofuels are classified as renewable sources of fuels because they can be continually produced from crops, algae or animal wastes. The two main biofuels currently used in Australia are ethanol and biodiesel. Ethanol is only used in Australia as a fuel additive; E10 fuel is a mixture of unleaded fuel and 10 per cent ethanol.

Weblink
Algae as a biofuel

Synthesis of ethanol

Two main processes used for synthesising ethanol are fermentation with yeasts and the hydration of ethene.

Fermentation is the most common method for the production of ethanol in beverages. This process is also increasingly being used to produce fuel alcohol and, since 2007, Australia has tripled its production of fuel ethanol by fermentation.

Fermentation

For fermentation:

- a suitable grain or fruit is mashed up with water
- an appropriate yeast strain is added
- air is excluded
- the mixture is kept at 37°C.

Enzymes in the mixture convert any starch or sucrose to glucose and fructose, and then the yeast consumes the monosaccharides and produces ethanol.

The equation for the fermentation of glucose ($C_6H_{12}O_6$) is:

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

disproportionation reaction typically a redox reaction, where a molecule is transformed into two or more dissimilar products

The overall reaction involving fermentation is a **disproportionation reaction** in which carbon atoms from glucose are simultaneously reduced in the formation of ethanol and oxidised in the formation of carbon dioxide.

Syllabus link
Chapter 8 discusses redox reactions.

FIGURE 17.3.1 Part of Wilmar's bioethanol Sarina distillery in North Queensland, which produces 60 million litres of bioethanol every year by fermenting molasses, a by-product of sugar production

Ethanol can be produced from both starch (e.g. from food crops such as sugar cane, corn or wheat) and cellulose (e.g. from non-food plant material such as wood or agricultural waste). Starch is made up of glucose units linked in an easily hydrolysed form (amylose and amylopectin). Cellulose is also made up of glucose units, but in a more complex and rigid structure, with strong hydrogen bonding that makes it harder to break down. Enzymes in yeast such as amylases easily convert starch to glucose, making the production process cheap and easy. Cellulose requires pretreatment with other substances such as acid, heat or enzymes to break down the tough, fibrous structure to glucose, which makes the production costs higher, and the process requires more energy. Using starch for the production of ethanol may compete with food supply, leading to concerns about food prices and land use. Using cellulose is more sustainable, because it uses waste materials and non-food crops, so does not affect food supply.

Syllabus link
Chapter 15 discusses carbohydrates.

Hydration of ethene

The most common method of producing ethanol in the developed world is the hydration of ethene, which is produced by the **catalytic cracking** of products from crude oil. Because ethene as a raw material is relatively cheap, approximately 95 per cent of the industrial ethanol made in the developed world is produced in this way. However, ethanol produced by this method is not considered a biofuel because it does not come from a crop.

catalytic cracking the process of heating large organic molecules and converting them into smaller, more useful molecules

This is an addition reaction and can be represented in the following equation:

$$\underset{\text{Ethene}}{CH_2{=}CH_2(g)} + H_2O(g) \rightarrow \underset{\text{Ethanol}}{CH_3CH_2OH(l)} \qquad \Delta H = -45\ \text{kJ mol}^{-1}$$

This reaction is exothermic, so a high yield is favoured by a low temperature. However, at low temperatures, the rate is too slow. At approximately 300°C, the yield is only about 5 per cent.

The number of product molecules is less than the number of reactant molecules, so the yield is also favoured by using a high pressure of 60–70 atm. Consequently, increasing the pressure and using a catalyst of phosphoric acid increases both the yield and rate of production of ethanol.

Syllabus link
Chapter 14 discusses addition reactions.

Hydrogen in fuel cells

A fuel cell is an electrochemical device. It converts chemical energy directly into electrical energy, through a process that is oxidation, although not combustion.

A **fuel cell** is a type of galvanic cell, so it has the same structure: an anode, a cathode, an electrolyte and the flow of electrons through an external circuit. However, a fuel cell is different from other cells because the fuel and oxygen are continuously fed into the cell; the electrodes do not need to be replaced.

Syllabus link
Chapter 9 discusses galvanic cells.

fuel cell a galvanic cell that generates electricity from a chemical reaction, but where there is a continuous supply of fuel and also removal of products

The most important design feature in a fuel cell is the membrane that separates the electrodes. It allows molecules and ions to migrate across it, so that the separate electrode reactions can occur, as chemicals and ions produced at the cathode are often used at the anode and vice versa. However, the membrane does not conduct the electrons; they must travel through an external circuit so that they can be harnessed as electricity. A key development in fuel cell technology is the improvement in membrane design, so that they work even more efficiently.

Hydrogen can be obtained from a number of sources, including an electrolytic cell, where it is obtained from the electrolysis of water powered by solar energy. Hydrogen is highly flammable and so needs to be stored carefully. However, if contained successfully, hydrogen is effectively a store of energy. It can be produced by using solar energy during the day, and then can produce electricity in the fuel cell when required.

Remember that in most fuel cells, hydrogen is oxidised at the anode and oxygen is reduced at the cathode with an overall reaction:

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

However, different types of fuel cells can use different types of electrolyte, which can alter the specific reactions occurring at each electrode. The two most commonly used electrolytes are acid, such as phosphoric acid, and alkaline, such as potassium hydroxide.

Acid electrolyte

With an acid electrolyte, the reactions at the electrodes are:

Anode: $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$ $E° = +0.00\ V$

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $E° = +1.23\ V$

A diagram for a hydrogen fuel cell with an acid electrolyte is shown in **Figure 17.3.3**.

Alkaline electrolyte

With an alkaline electrolyte, the reactions in the fuel cell are:

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ $E° = +0.40\ V$

Anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$ $E° = -0.83\ V$

Note that the overall cell potential is still 1.23 V, identical to that with the acid electrolyte, because the overall reaction is also the same. A diagram of the alkaline hydrogen fuel cell is shown in **Figure 17.3.4**.

Worksheet
Chemical synthesis for fuels

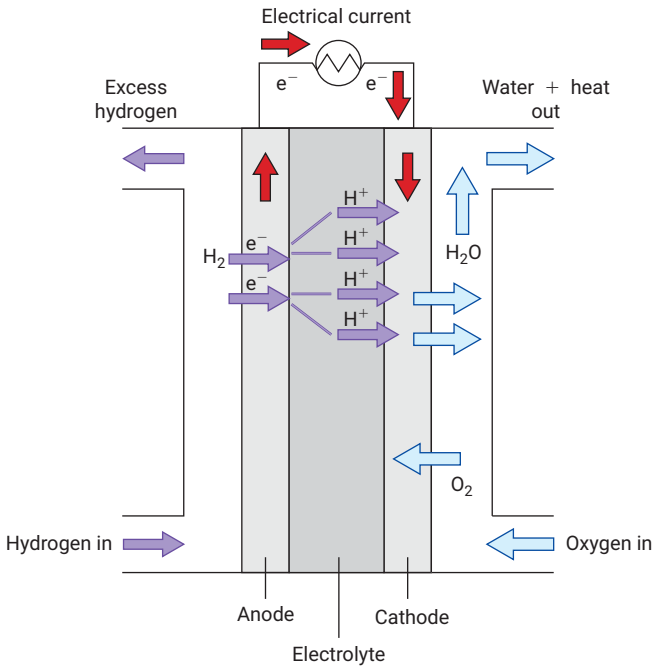


FIGURE 17.3.3 An acid hydrogen fuel cell

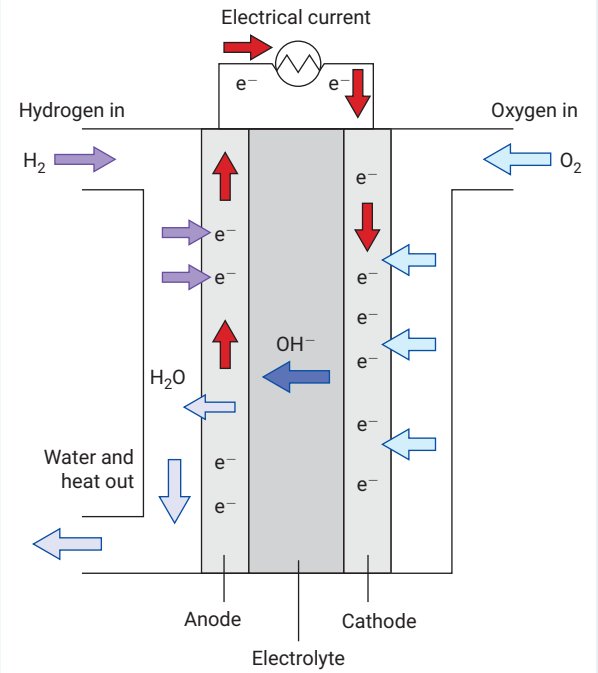


FIGURE 17.3.4 An alkaline hydrogen fuel cell

The fuel cell is compartmentalised so that hydrogen and oxygen are on opposite sides and the electrolyte is in the middle compartment. The electrodes are porous to allow the gas molecules to pass through. They are lined with a catalyst that helps break the bonds in the gaseous molecules. The most commonly used catalyst is platinum, although rhodium and nickel are also used. The use of a platinum catalyst is one of the main costs of a fuel cell.

Fuel cells can be stacked together to increase the total cell voltage, just as batteries are added in series to increase the total voltage output. The water produced must be removed from the cell; otherwise, the electrolyte will become diluted, which will affect the efficiency of the cell.

Some advantages of the hydrogen fuel cell are that it only produces water, whereas fossil fuels produce CO_2 gas. It is more efficient than directly combusting hydrogen to make water and electricity is released in a more controlled manner that minimises heat loss.

Disadvantages include:

- transporting the hydrogen fuel cell is difficult
- hydrogen is highly flammable
- the fuel cell needs a constant supply of hydrogen, which is currently more expensive than other fuels.

17.3 LEARNING CHECK

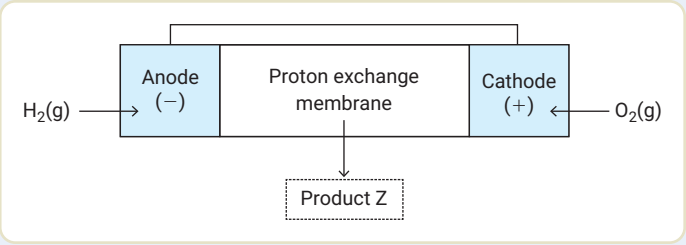
DESCRIBING

1 **Describe** a biofuel.
2 **Explain** why biofuels are produced.
3 **Describe** a fuel cell.
4 **Identify** the energy transformation that occurs in a fuel cell.
5 **Describe** the purpose of a catalyst.
6 **Identify** the most common catalyst used in fuel cells.
7 State the two types of chemical reactions that produce ethanol.
8 **Evaluate** whether the ethanol produced through both the reactions in Question 7 is considered a biofuel. Provide a reason for your choice.
9 Write the half-reactions for the fermentation of glucose to ethanol and water. Label each half-reaction as oxidation or reduction.
10 A fuel cell releases only a small voltage. How can this be used to provide the energy for a car?

APPLYING

 QCAA paper 1 2023 SA Q23

11 The diagram represents a hydrogen fuel cell with an acid electrolyte.



a **Determine** the redox half-equation occurring at the anode and cathode.
b **Identify** product Z.
c **Compare** the movement of electrons and hydrogen ions in the fuel cell.

CHAPTER SUMMARY

Factors in designing a chemical synthesis

- Factors include:
  - the reaction mechanism of the chemical reaction
  - the product is constantly removed from the reaction chamber
  - excess reactants are recycled
  - correct temperature and pressure for optimal yield of product
  - catalysts
  - safety and environmental concerns
  - economic issues.

Limiting reactants and percentage yield

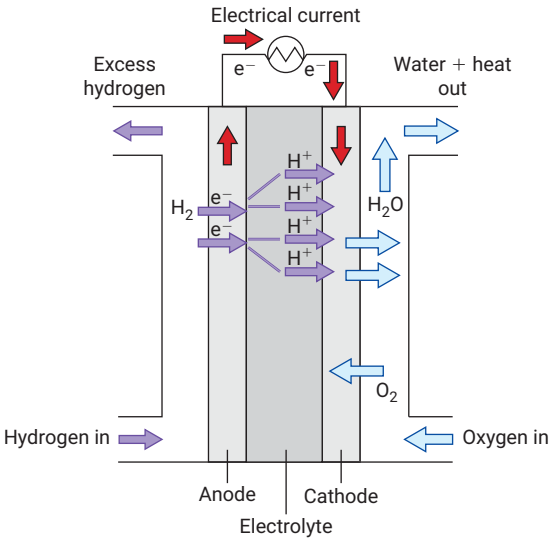
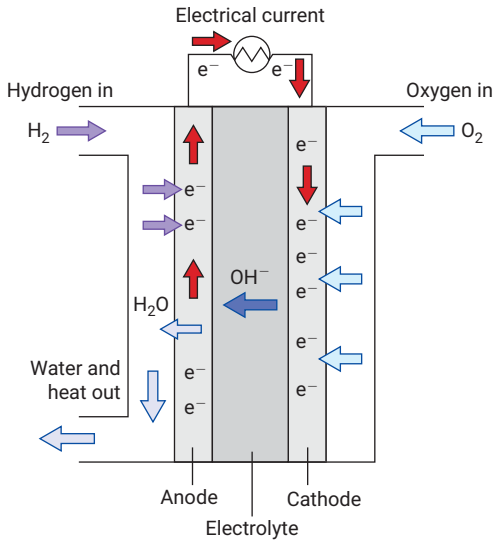
- The limiting reactant is the reactant that is completely consumed in a reaction, determining the maximum amount of product that can be formed.
- Steps to identify limiting reactant:
  1. Write the balanced chemical equation.
  2. Calculate the number of moles of each reactant: $n = \frac{m}{M}$
  3. Determine the mole ratio.
  4. Identify the limiting reactant.
  5. Use the limiting reactant to calculate the maximum yield of product.
- The percentage yield is the percentage of the maximum possible amount of product from a reaction that has been actually produced:

$$\text{Percentage yield (\%)} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

Designing optimal conditions for processes

	Haber process	Contact process
Reactions	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92.4$ kJ mol^{-1}	**Step 1:** $S(s) + O_2(g) \rightarrow SO_2(g)$ or $4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$ **Step 2:** $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -196$ kJ mol^{-1} **Step 3:** $SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$ $H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$
Optimal conditions	Temperature: 400–450°C Pressure: 200 atm Catalyst: iron/iron oxide	In step 2: A ratio of 1:1 sulfur dioxide to oxygen is used so oxygen is in excess. Temperature: 400–450°C Pressure: 2 atm Catalyst: vanadium(V) oxide (V_2O_5)

Synthesis of fuels

Fuel type	Fermentation	Hydration of ethene
Ethanol	$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$	$CH_2{=}CH_2(g) + H_2O(g) \rightarrow C_2H_5OH(l)$ $\Delta H = -45$ kJ mol^{-1}
	Uses renewable resources from biomass Temperature: 30–40°C (yeast) Pressure: 1 atm Catalyst: enzymes in yeast Reaction rate: slow (days)	Uses ethene from non-renewable fossil fuels Temperature: 300°C Pressure: 60–70 atm Catalyst: phosphoric acid (H_3PO_4) Reaction rate: fast (seconds to minutes)
	Acid electrolyte	**Alkaline electrolyte**
Hydrogen		
	Anode: $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$ $E° = +0.00$ V Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $E° = +1.23$ V $E°_{cell} = +1.23$ V Charge carrier: H^+	Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ $E° = +0.40$ V Anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$ $E° = -0.83$ V $E°_{cell} = +1.23$ V Charge carrier: OH^-

CHAPTER EXAM

MULTIPLE CHOICE

1. An alkaline hydrogen–oxygen fuel cell has the overall equation:

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

In this fuel cell, the species reacting at the cathode is:

A $O_2(g)$ and $H^+(aq)$.
B $H_2(g)$ only.
C $O_2(g)$ and $H_2O(l)$.
D $H_2(g)$ and $OH^-(aq)$.

Questions 2 and 3 relate to the Haber process, the equation for which is:

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92\ kJ\ mol^{-1}$

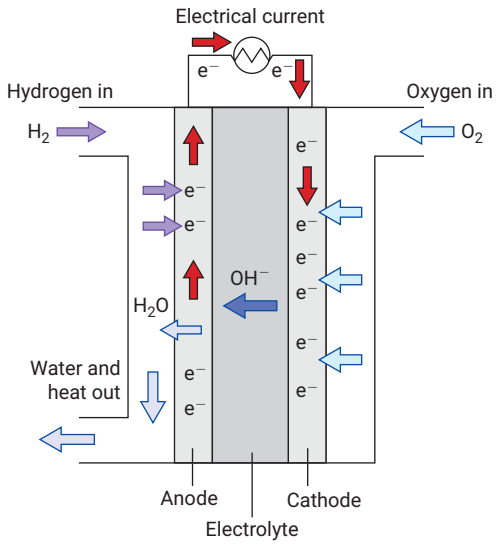
2. Identify which of the following will increase the rate of reaction.

A Increasing the temperature of the system
B Decreasing the concentration of $NH_3(g)$
C Increasing the volume of the system
D Decreasing the temperature of the system

3. Identify which set of conditions would achieve the maximum yield of ammonia.

A High temperature and high pressure
B Low temperature and high pressure
C High temperature and low pressure
D Low temperature and low pressure

4. Identify the operating conditions for this hydrogen fuel cell.



A Acidic conditions with hydrogen given off as an unused gas
B Alkaline conditions with hydrogen given off as an unused gas
C Acidic conditions with hydroxide ions present in the electrolyte
D Alkaline conditions with hydroxide ions present in the electrolyte

5. In the contact process, if 500.0 g of sulfur dioxide is converted to 596.3 g of sulfur trioxide, calculate the percentage yield.

A 75.4%
B 85.6%
C 90.0%
D 95.4%

6. To form ethanol biofuel in the fermentation of glucose, a catalyst is used because:

A more energy is required, and the rate of reaction is decreased.
B more energy is required, and the rate of reaction is increased.
C less energy is required, and the rate of reaction is decreased.
D less energy is required, and the rate of reaction is increased.

7. Ethanol can be produced by reacting ethene with steam in the presence of a catalyst. Which of the following conditions are required for this reaction to proceed efficiently?

A High temperature, low pressure, phosphoric acid catalyst
B Low temperature, low pressure, phosphoric acid catalyst
C High temperature, high pressure, phosphoric acid catalyst
D Low temperature, high pressure, sulfuric acid catalyst

8. Which statement about a hydrogen fuel cell operating under acidic conditions is correct?

A The anode reaction is $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$.
B Protons (H^+) migrate through the electrolyte to the cathode.
C The overall reaction is $H_2(g) + O_2(g) \rightarrow 2H_2O(l)$.
D Electrons flow from the cathode to the anode in the external circuit.

9. In a chemical plant producing sulfuric acid, engineers notice that after increasing the temperature slightly, the production of sulfur trioxide increased significantly. After some time, they are instructed to return the temperature to its original conditions. Deduce a reason for why the initial temperature increase was effective and why it was later reversed.

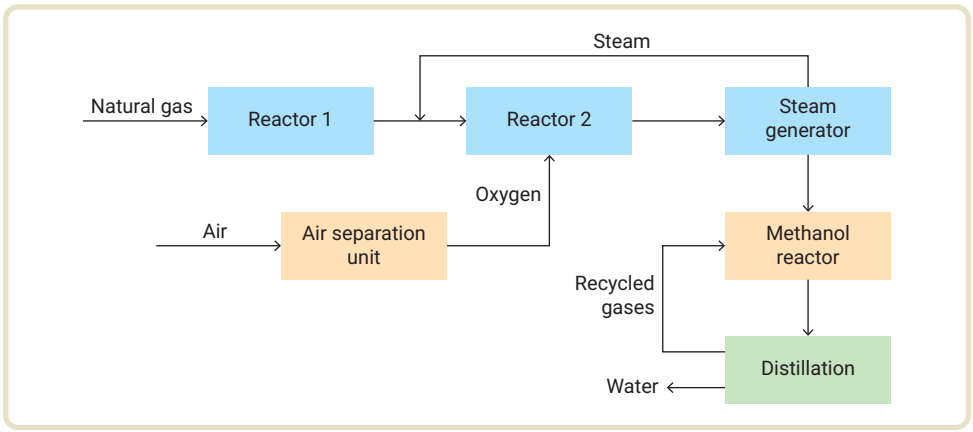
A The increase in temperature decreased the reaction rate, but the yield of sulfur trioxide increased because the reaction became more favourable at higher temperatures.
B The increase in temperature increased the equilibrium concentration of oxygen, leading to a higher sulfur trioxide yield, but the temperature was reversed to prevent catalyst degradation.
C The increase in temperature increased the concentration of sulfur dioxide, speeding up the reaction and increasing the yield, but the temperature was reversed to avoid an unwanted side reaction.
D The increase in temperature initially increased the reaction rate, but it decreased the sulfur trioxide yield because the reaction is exothermic. The temperature was reversed to restore optimal yield.

10. Identify which statement best explains why the use of a catalyst is important in chemical synthesis processes.

A The catalyst increases the equilibrium yield of the product by shifting the reaction to favour products.
B The catalyst increases the temperature of the reaction, speeding up the rate of the product formation.
C The catalyst reduces the pressure needed for the reaction, making it more cost-effective to produce the product at lower pressures.
D The catalyst lowers the activation energy of the reaction, allowing the reaction to reach equilibrium more quickly without affecting the equilibrium position.

SHORT RESPONSE

11. The diagram shows a flow chart of the industrial production of methanol.



– In Reactor 1, the following reactions occur at 800°C and 30 atm and with a nickel catalyst:

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = +208\ kJ\ mol^{-1}$

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad \Delta H = -41\ kJ\ mol^{-1}$

– In Reactor 2, the following reaction occurs at 1000°C and 30 atm and with a nickel catalyst:

$2CH_4(g) + O_2(g) \rightleftharpoons 2CO(g) + 4H_2(g) \quad \Delta H = -36\ kJ\ mol^{-1}$

– In the methanol reactor, the following reaction occurs at 350°C and 300 atm:

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(l) \qquad \Delta H = -103\ kJ\ mol^{-1}$

a **Identify** the raw materials, waste products and by-products if they exist. Explain why you identified the chemicals as you did.

b **Explain** why the step in the air separation unit is necessary.

c **Identify** places where chemicals can be recycled and what gases would be recycled in the different stages.

d **Identify** and **explain** the areas of the production process that would require high energy.

e **Identify** areas where energy could be recycled.

f **Explain** why catalysts are used in the production of methanol.

g **Explain** why the reaction in the methanol reactor occurs at high pressure.

12. The equation for the Haber reaction is:

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

The forward reaction is exothermic.

a **Calculate** the volume of ammonia produced from the complete reaction of 825 dm^3 of hydrogen gas.

b **Calculate** the maximum mass of NH_3 that can be produced from 2 g of N_2.

In an experiment, the theoretical maximum mass of ammonia was calculated to be 80 kg. The actual mass of ammonia obtained was 12 kg.

c **Calculate** the percentage yield of ammonia in this experiment.

CROSS-CHAPTER QUESTION

13. The following questions relate to the Haber process.

a A mixture of 5.00×10^{-2} mol of H_2 and 1.00×10^{-2} mol of N_2 is placed in a 5.00 L container at 448°C and allowed to come to equilibrium. At equilibrium, the concentration of NH_3 is 1.87×10^{-3} mol L^{-1}. **Calculate** K_c at 448°C for this reaction.

b **Predict** how the reaction will proceed to reach equilibrium if we start with a mixture of 1.00×10^{-2} mol L^{-1} NH_3, 5.0×10^{-3} mol L^{-1} H_2 and 1.5×10^{-2} mol L^{-1} N_2.

c If 0.500 mol of N_2 and 1.500 mol of H_2 are reacted in a sealed container, **calculate** the theoretical yield of ammonia at equilibrium if the reaction proceeds to completion.

d Using Le Châtelier's principle, **explain** how increasing the concentration of nitrogen or hydrogen gas affects the equilibrium position in the Haber process.

DATA ANALYSIS

14. Interpret evidence

Ethanol can be made by reacting ethene with steam. The following table provides information about the percentage yield of ethanol at different temperatures and pressures.

Pressure (atm)	Percentage yield (%)		
	300°C	400°C	500°C
40	16	12	6
80	30	22	12
120	42	30	17
160	50	36	21

a **Identify** the trend in percentage yield as pressure increases.

b **Identify** the trend in percentage yield as temperature increases.

c **Determine** the temperature and pressure conditions that give the highest percentage yield of ethanol.

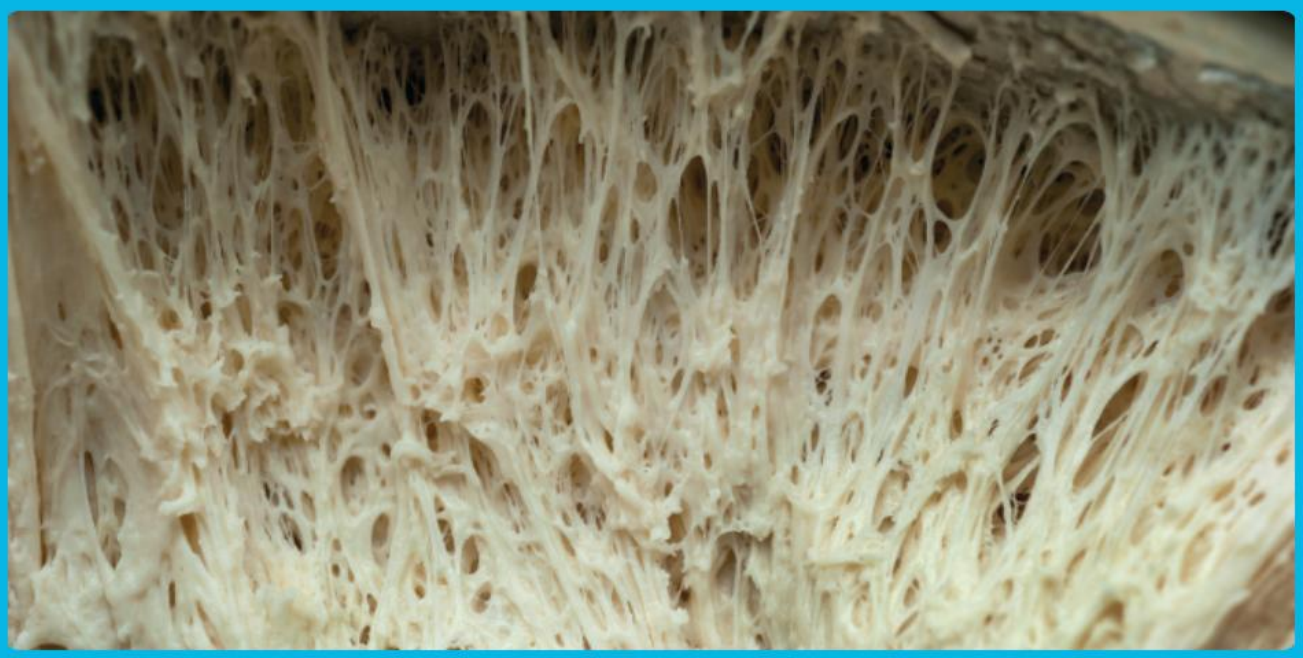
d Suggest why 70 atm is used in the industrial production of ethanol rather than the pressure in part c.

e If the industrial reaction occurs at 400°C, **predict** the percentage yield at 100 atm.

f If K_c for this reaction is 100 at 300°C and 1.3×10^{-4} at 500°C, **deduce** whether the forward reaction is exothermic or endothermic. Provide reasoning for your answer.

CHAPTER 18

Macromolecules: Polymers, proteins and carbohydrates



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SYLLABUS DOT POINTS

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 monosaccharide monomers are joined by glycosidic bonds.

SCIENCE INQUIRY

- Investigate the properties of polymers.

Introduction

The structure and function of organic materials was covered in detail in Chapter 15. Polymers are giant molecules, often called macromolecules, which form when many smaller molecules, called monomers, are joined by covalent bonds. The process of linking monomers together is called polymerisation.

The two most common polymerisation reactions are:

- addition polymerisation, which involves an addition reaction
- condensation polymerisation, which involves a condensation reaction.

Practicals

- Making polylactic acid
- Making nylon (online-only resource)

Worksheets

- Polymer formation
- Sugars and proteins

Nelson MindTap

To access resources above, visit **cengage.com.au/nelsonmindtap**

ASSUMED KNOWLEDGE

- ✓ The structural features of amino acids, tripeptides, monosaccharides and disaccharides can be described.
- ✓ The structural features of polyethene, polypropene and polytetrafluoroethene can be described.
- ✓ The structural features of polylactic acid, nylon and polyester can be described.

LEARNING OUTCOMES

By the end of this chapter, you should be able to:

- ✓ describe the production of addition and condensation polymers
- ✓ explain the key differences in the formation of addition and condensation polymers
- ✓ identify the functional groups involved in addition and condensation reactions
- ✓ identify the monomers used to synthesise common addition polymers, including polyethene, polypropylene and polytetrafluoroethene
- ✓ write and describe chemical equations representing the polymerisation of addition polymers
- ✓ describe the process of condensation polymerisation, including the formation of by-products
- ✓ describe the synthesis of condensation polymers such as carbohydrates, polylactic acid, nylon and polyester
- ✓ name tripeptides
- ✓ identify that tripeptides are formed when amino acid monomers are joined by peptide bonds
- ✓ identify that disaccharides are formed when monosaccharide monomers are joined by glycosidic bonds.

18.1 Describing the production of addition polymers

Addition polymers form by adding together molecules without the loss of any atoms. This is done by addition polymerisation, which is a type of addition reaction.

For addition polymerisation to occur, the monomer must have a double bond between two carbon atoms. Breaking the double bond allows each carbon to form single bonds between the monomers. The number of monomer units that make up these polymers may range from 100 to more than 100 000. The structure of the monomer determines the structure and properties of the polymer formed.

The general process for the formation of addition polymers is shown in **Figure 18.1.1**.

Polymers from ethene

One of the most common examples of addition polymerisation reactions is the production of polyethene, in which ethene molecules are linked into long chains. Note that polyethylene is the common name for the polymer produced, but the IUPAC preferred name is polyethene. Therefore, the name polyethene will be used when referring to this polymer.

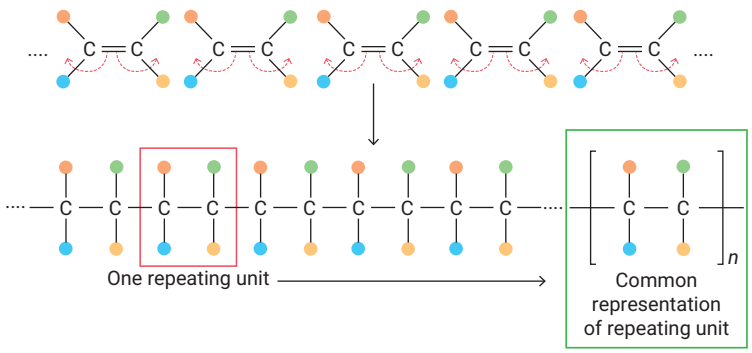


FIGURE 18.1.1 The formation of an addition polymer from an alkene

The production of polyethene is represented by the general equation:

$$n(CH_2{=}CH_2) \rightarrow -CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2-$$

During this addition polymerisation reaction, one of the bonds in each C=C double bond is broken, under the influence of a catalyst at high temperature and pressure. This leads to the formation of single covalent bonds between C atoms on adjacent monomers (ethene molecules) **(Figure 18.1.2)**.

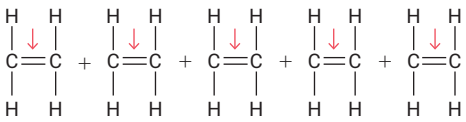


FIGURE 18.1.2 The double bonds break in the ethene monomers.

This frees up one electron on each C for further bonding, as shown in **Figure 18.1.3**.

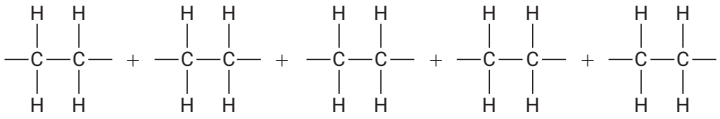


FIGURE 18.1.3 Each carbon is free to form bonds.

New carbon–carbon bonds form between adjacent molecules to give polymer chains, as shown in **Figure 18.1.4**.

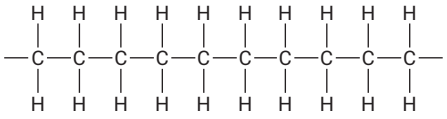
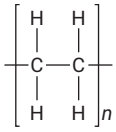


FIGURE 18.1.4 New C–C bonds form to give the polymer.

As can be seen, the polymer is made up of repeating CH_2–CH_2 units, so the structure of the polymer is often written in an abbreviated form $(–CH_2–CH_2–)_n$ or:



where n is the number of monomer units in the molecule.

As you have learnt, there are two types of polyethene: low-density polyethene (LDPE) and high-density polyethene (HDPE). They are produced by two different processes. Their different properties are a result of their different structures.

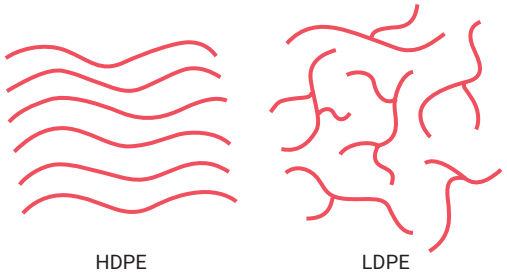
LDPE is produced by a gas-phase process using high temperature (300°C), high pressure (1000–3000 atm) and an initiator (to start the reaction) such as peroxide. As mentioned in Chapter 15, the branches in the structure of LDPE prevent the polymer chains packing closely together, resulting in fewer dispersion forces. As a result, LDPE has a lower density and melting point but greater flexibility.

Syllabus link
Chapter 15 introduces LDPE and HDPE.

The Ziegler–Natta process for the production of HDPE uses lower pressures (only a few atmospheres) and low temperatures (60°C) and a catalyst that is a mixture of titanium(III) chloride and trialkylaluminium compound (e.g. $(CH_3CH_2)_3Al$). As described in Chapter 15, HDPE is made up of unbranched chains that can pack closely together, allowing for more dispersion forces between the chains. As a result, it has a higher density and melting point but is less flexible than LDPE.

Figure 18.1.5 shows the difference between the chains of HDPE and LDPE.

Weblink
Polyethene



Smith et al. 2010 Chemistry in use. Book 2

FIGURE 18.1.5 The arrangements of polymer chains in HDPE and LDPE

Other addition polymers

As well as being used directly to produce polyethene, ethene is converted into a range of other useful monomers, which are, in turn, used to produce polymers.

The general reaction for the production of a polymer from an alkene was shown in Figure 18.1.1, where each coloured circle represented an H or a substituent group. This can also be represented by the general equation in **Figure 18.1.6**.

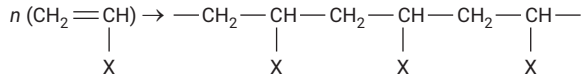
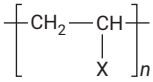


FIGURE 18.1.6 The general equation for the production of a polymer from an alkene. X may be hydrogen or a substituent group.

Substituting the hydrogen with different substituent groups, such as a halogen, a benzene ring or an alkyl group, produces polymers with different properties. As with polyethene, this can be abbreviated to:



One or more hydrogen atoms of the alkene may be replaced by a different substituent group.

Polypropene

Polypropene manufacture uses catalysts, including Ziegler–Natta catalysts, to convert propene to polypropene. The formation of polypropene and the abbreviated form of the polymer is shown in **Figure 18.1.7**.

Weblink
Polypropene

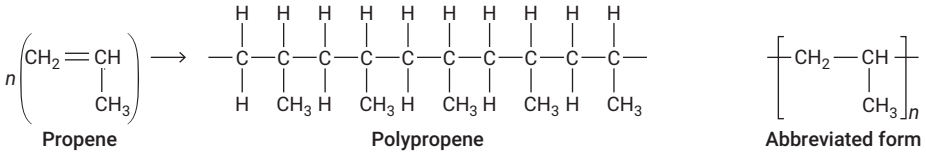


FIGURE 18.1.7 The formation of polypropene from propene, and the abbreviated form of the polymer

Polytetrafluoroethene (PTFE)

Polytetrafluoroethene (PTFE), commonly known as Teflon™, is a polymer formed from the monomer tetrafluoroethene, which has the formula $CF_2=CF_2$. All the hydrogen atoms have been replaced by fluorine atoms. The structure of the resulting polymer is shown in **Figure 18.1.8**.

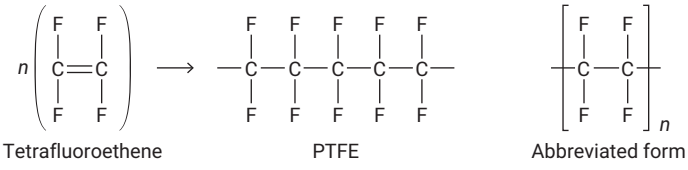


FIGURE 18.1.8 The formation of polytetrafluoroethene from tetrafluoroethene, and the abbreviated form of the polymer

LEARNING CHECK 18.1

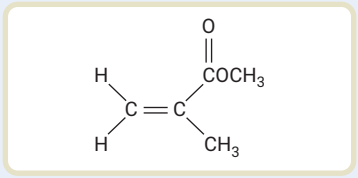
DESCRIBING

1 **a** **Describe** what is necessary in a monomer for addition polymerisation to occur.
b **Explain** the process of addition polymerisation.

2 Name the most common addition monomer and polymer.

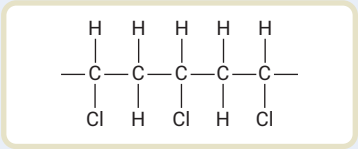
APPLYING

3 Perspex is made by addition polymerisation from the following monomer.



Sketch part of the polymer of Perspex (include at least three monomer units).

4 Given the following polymer, write the structural formula of the:
a repeating unit
b monomer.



18.2 Describing the production of synthetic condensation polymers

condensation polymer
a polymer that forms by the elimination of a small molecule (often water) when monomers join

Addition polymerisation requires that the monomer have a double bond. However, if organic molecules have a functional group at each end, the functional group can undergo a condensation reaction with a functional group on another molecule to form a **condensation polymer**. Condensation polymers are formed when two monomer molecules join together to eliminate a small molecule (often water). The process is called condensation polymerisation. Functional groups such as $-NH_2$, $-OH$, $-COOH$ and $-COCl$ are suitable for condensation polymerisation.

As you learnt in Chapter 14, esters and amides are formed by a condensation reaction so it follows that the synthetic polymers, polyesters and polyamides (nylons) are formed by condensation polymerisation. Polyesters and polyamides (nylons) are examples of synthetic condensation polymers; polypeptides (proteins) and polysaccharides (cellulose and starch) are examples of natural condensation polymers.

Weblink
Nylons

Polyesters

Polyesters are condensation polymers in which the monomers are joined by an ester link ($-COO-$). As you know, an ester and water are formed when a carboxylic acid reacts with an alcohol.

To form a polyester, the monomer molecules need to join at each end, which means they need to have either a carboxylic acid or an alcohol functional group at each end.

Polyesters can be produced from:

- a single monomer that has a hydroxyl (–OH) functional group at one end and a carboxyl (–COOH) functional group at the other **(Figure 18.2.1)**
- two different monomers – one monomer with hydroxyl groups at each end (a **diol**) and the other monomer with carboxyl functional groups at each end (a **dicarboxylic acid**) (Figure 18.2.2).

The general production of a polyester from a monomer is shown in Figure 18.2.1. The monomers must be aligned so the hydroxyl and carboxyl acid groups are next to each other.

Syllabus link
Chapter 14 describes the condensation reactions by which esters and amides are formed.

diol an alcohol molecule that has two hydroxyl (–OH) functional groups

dicarboxylic acid a molecule that has two carboxyl (–COOH) functional groups

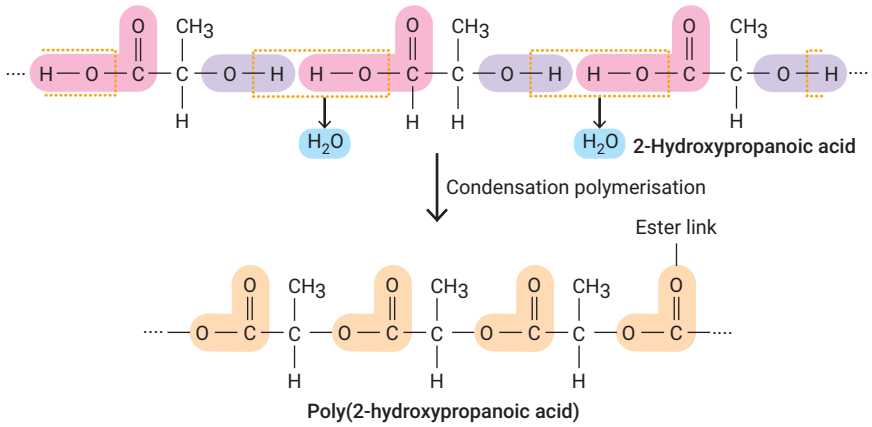


FIGURE 18.2.1 A general condensation reaction to form a polyester

As mentioned in Chapter 15, an example of a synthetic polyester is polyethylene terephthalate (PET or terylene). It is used to make fibres, clothing and beverage containers. PET is formed from the condensation polymerisation reaction of ethane-1,2-diol and benzene-1,4-dicarboxylic acid. The structures are shown in **Figure 18.2.2**.

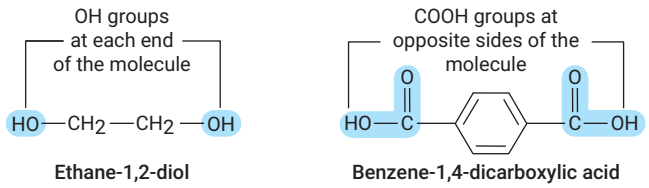


FIGURE 18.2.2 Ethane-1,2-diol has one OH group at each end of the molecule and benzene-1,4-dicarboxylic acid has COOH groups on opposite sides of the benzene ring.

The molecules can polymerise through an esterification reaction between the carboxyl group of one molecule and the hydroxyl group of another, to produce PET, or terylene **(Figure 18.2.3)**.

Weblink
Polyesters

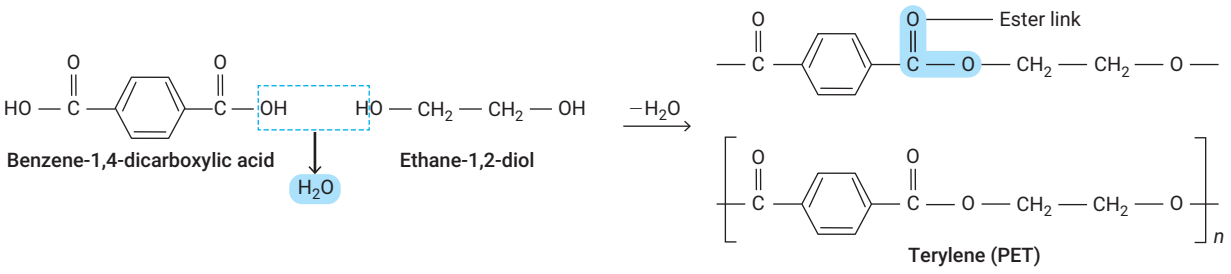


FIGURE 18.2.3 The polymerisation reaction to produce terylene (PET)

Polylactic acid (PLA) has also been mentioned previously. PLA is used to make biodegradable surgical sutures. Lactic acid (2-hydroxypropanoic acid) has a hydroxyl (–OH) functional group attached to the second carbon and a carboxyl (–COOH) functional group at the other. The structure of lactic acid is shown in **Figure 18.2.4**.

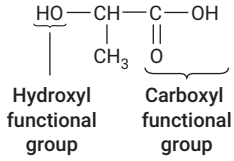


FIGURE 18.2.4 Lactic acid (2-hydroxypropanoic acid)

The molecules polymerise through an esterification reaction between the carboxyl group of one molecule and the hydroxyl group of another, as shown in **Figure 18.2.5**.

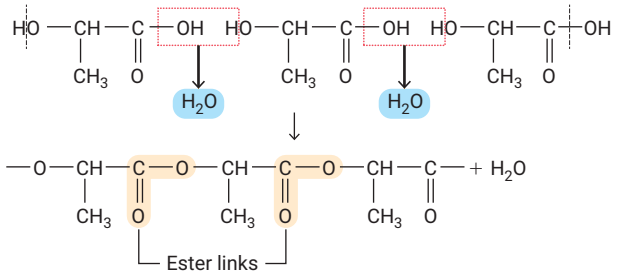


FIGURE 18.2.5 The polymerisation of lactic acid

The general formula for the polymer is shown in **Figure 18.2.6**.

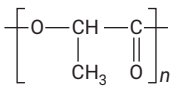


FIGURE 18.2.6 The general formula for polylactic acid (PLA)

One disadvantage of a polyester is that it is easily damaged by acids and alkalis. As was shown in Chapter 14, this results in the ester linkages being *hydrolysed* back to the acid and alcohol monomers. Therefore, polyester fabrics get holes in them if an acid or alkali is spilled on them.

PRACTICAL ACTIVITY 18.2.1

MAKING POLYLACTIC ACID

Introduction

Lactic acid is a versatile molecule that can be added to foods or be used to produce plastics such as polylactic acid (PLA). Lactic acid can be produced by the fermentation of sugars or obtained from milk. PLA can be used to make a variety of materials, including packaging materials and surgical threads.

Research question

How can polylactic acid (PLA) be synthesised from lactic acid in a laboratory setting?

Aim

To produce PLA through the polymerisation of lactic acid and observe the process and characteristics of the resulting polymer

Materials

- lactic acid
- 2 M hydrochloric acid
- test tube
- test-tube holder
- 10 mL measuring cylinder
- Bunsen burner and heatproof mat
- 2 anti-bumping granules
- Pasteur pipette
- petri dish
- timer/stop watch
- matches

What are the risks in doing this experiment?	How can you manage these risks to stay safe?

Copy and complete the risk assessment table. Add any risks you can think of, as well as ways to manage them. Ask your teacher to check your risk assessment before you proceed.

Procedure

1. Measure and add 4 mL lactic acid into the test tube.
2. Add 5 drops of hydrochloric acid and two anti-bumping granules into the test tube.
3. Hold the test tube near the top with the test-tube holder and begin to heat the tube over the Bunsen burner. Ensure the open end of the test tube is not pointed at anyone.
4. Keep the mixture gently boiling and gently shake the tube occasionally to mix.
5. After approximately 12 minutes, the mixture will begin to go a yellowish colour. Continue to heat for another minute or two.
6. Quickly pour the contents into a petri dish.
7. Leave the mixture to cool.

Results

Take a photo of the PLA that you have made.

Analysis of results

1 If you have successfully polymerised the lactic acid, what will have happened to the size of the molecules?

2 Look at the lactic acid you started with and your product. Describe the differences in properties between them. (Be careful: your product will be very sticky.)

Interpretation

3 Explain the change in properties in terms of the size of the molecules in the materials.

Polyamides (nylons)

polyamide a polymer formed by a condensation polymerisation reaction between an amine group and a carboxylic acid group

amidation a reaction between a carboxyl (–COOH) and an amine ($–NH_2$) group that forms an amide functional group

diamine a molecule that has two amino ($–NH_2$) functional groups

Weblink
Making nylon

Worksheet
Polymer formation

Practical
Making nylon

Nylon is the commercial name for a group of synthetic **polyamides** that are lightweight, very durable and stretchy. They are widely used in the fashion and textile industry in activewear, swimwear and other technical performance garments. The production of nylon relies on chemicals derived from fossil fuels, which are energy intensive to make and can shed microplastic fibres during production and use.

Polyamides are condensation polymers in which the repeating units are held together by amide links (–CO–NH–). The monomers of polyamides are joined together by **amidation**, a condensation reaction between a carboxylic acid (–COOH) and an amino ($–NH_2$) functional group. As with polyesters, the monomer molecules need to join at each end, which means they need to have either a carboxylic acid or an amino functional group at each end. Polyamides can be produced from a monomer with both an amino and a carboxylic functional group at either end. Alternatively, they can be produced from two different monomers, one with an amino group at each end, known as a **diamine**, and another with a carboxyl group at each end, known as a dicarboxylic acid. A water molecule is eliminated every time an amide link is formed.

The general production of a polyamide from two different monomers is shown in Figure 18.2.7.

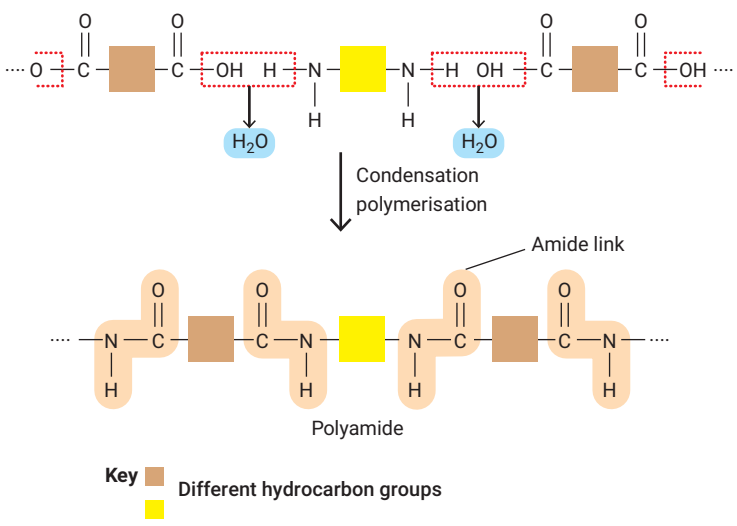


FIGURE 18.2.7 The general process involved in the production of a polyamide from two different monomers

There are different types of nylon depending on the monomers used. Nylon-6,6 is made from two monomers that each contain six carbon atoms – hence its name. One of the monomers is hexanedioic acid and the other is 1,6-diaminohexane (also known as hexane-1,6-diamine). When they first react, they form a salt due to the acidic nature of the carboxylic acid and the basic nature of the amine. This is then converted into nylon-6,6 by heating it under pressure at 350°C and with a nickel catalyst **(Figure 18.2.8)**.

Weblink
Condensation polymerisation

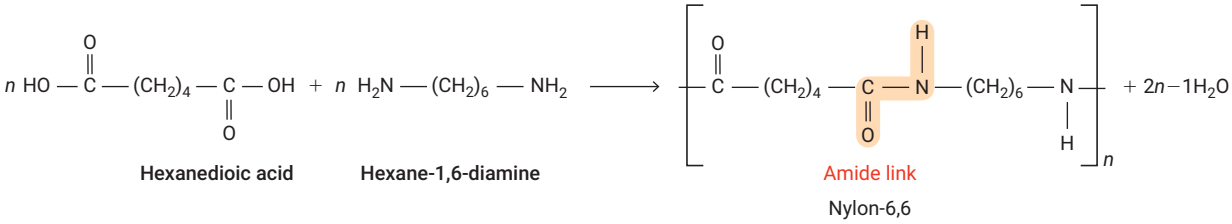


FIGURE 18.2.8 The formation of nylon-6,6

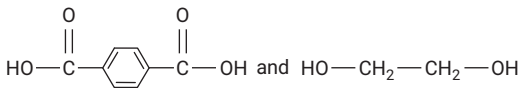
LEARNING CHECK 18.2

DESCRIBING

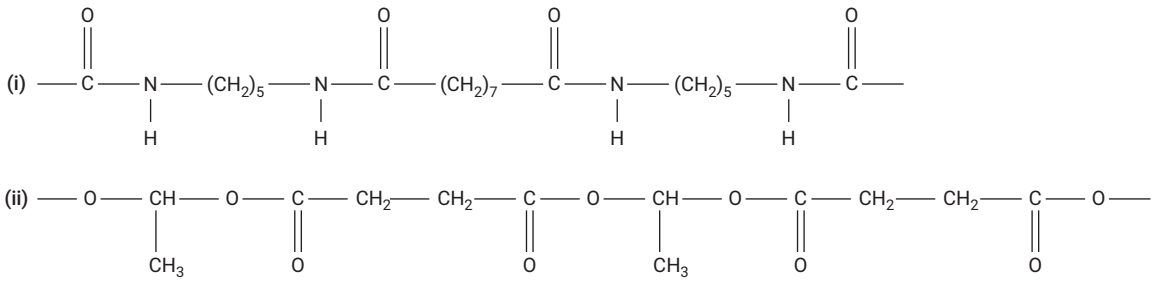
1 Name two examples of synthetic condensation polymers.
2 **Compare** condensation polymerisation and addition polymerisation.
3 **Sketch** the structure of an ester link.

APPLYING

4 **Sketch** two repeating segments of the structure of the polymer formed when the following react.



5 For the polymer in Question 4:
   a **identify** the type of polymer formed
   b name the functional groups in the monomers.
6 For each of the polymers i and ii:



   a **identify** the type of polymer
   b **sketch** the structure of the monomers.

18.3 Describing the formation of natural condensation polymers

Polypeptides (proteins)

FORMULA AND DATA BOOK

Polypeptides are an important class of naturally occurring condensation polymers. The monomers of polypeptides are amino acids. Polypeptides are also known as polyamides.

As you learnt in Chapter 15, amino acids have the amino ($-NH_2$) and carboxyl ($-COOH$) functional groups.

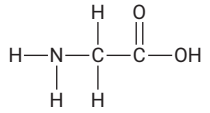


FIGURE 18.3.1 Glycine

The special structural features common to the 20 amino acid monomers that form proteins are:

- the amino and carboxyl functional groups are attached to the same carbon atom (the alpha-carbon)
- a hydrogen is attached to the alpha-carbon.

The simplest amino acid is glycine, which has the structure shown in Figure 18.3.1.

Joining amino acids

Amino acids undergo condensation polymerisation to form an amide. The bonds that hold amino acids together are covalent bonds. The link that joins two amino acids together is called a peptide bond or link. The compound formed when two amino acids join together is a dipeptide. When three amino acids join together, it is called a tripeptide. When long chains of amino acid units join, the result is a polypeptide. Unlike some other polymers, which have a regular repeating unit, polypeptides can have various combinations of amino acids.

For example, when glycine reacts with alanine, the result is the alanylglycine dipeptide (Figure 18.3.2).

Weblink
Protein formation

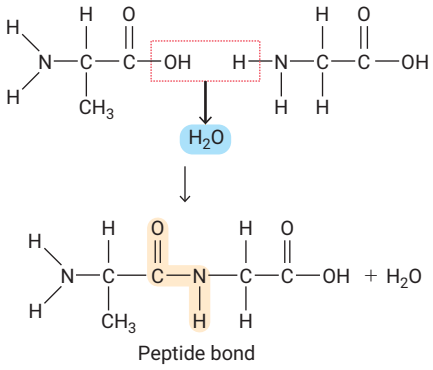


FIGURE 18.3.2 Formation of the dipeptide alanylglycine

FORMULA AND DATA BOOK

The resultant dipeptide has functional groups at each end so it can continue to react with other amino acids to produce a tripeptide. A peptide is named by listing its constituent amino acids from the amino functional group to the carboxyl functional group, with the last syllable changed to 'yl', except for the final carboxyl functional group at the end. For example, the dipeptide of alanine and glycine is alanylglycine, and the tripeptide of glycine, histidine and lysine is glycylhistidyllysine. Amino acids can also be represented by a three-letter abbreviation (e.g. Gly for glycine) (see the *Formula and Data Book*).

Figure 18.3.3 shows alanylglycine reacting with serine to produce alanylglycylserine tripeptide. Using the three-letter abbreviation system, this could also be named Ala–Gly–Ser.

A possible sequence of a peptide with eight amino acids is Lys–Cys–Asp–Cys–Gly–Val–Val–Thr. The biological function of a peptide is highly dependent on the sequence of its amino acids, so it is important to name the peptide correctly.

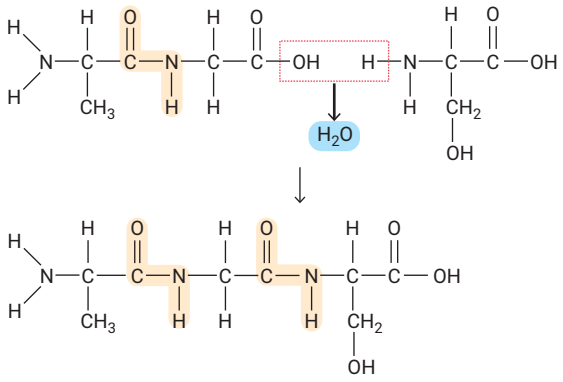


FIGURE 18.3.3 The tripeptide alanylglycylserine (Ala–Gly–Ser)

The resultant tripeptide still has functional groups at each end so it can continue to react with other amino acids to produce a polypeptide, as shown in **Figure 18.3.4**. When hundreds to thousands of amino acid units join together, the result is a protein. So, proteins are giant polypeptides. In the final protein, there is still an amino group at one end and a carboxyl group at the other.

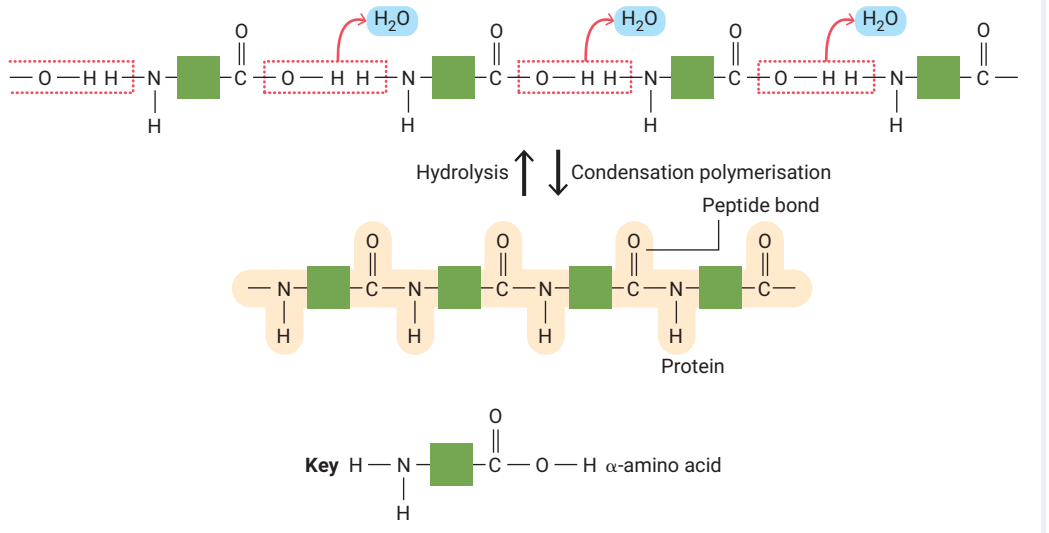


FIGURE 18.3.4 Forming a polypeptide and breaking it down again by hydrolysis

This condensation polymerisation reaction is reversible (Figure 18.3.4) – under certain conditions, such as in the presence of water and enzymes like proteases or at extreme pH or temperature, the peptide bonds undergo hydrolysis. This means that a water molecule can break the peptide bond, regenerating the original amino acids. The equilibrium between condensation (polymerisation) and hydrolysis (decomposition) highlights the dynamic nature of peptide formation and breakdown, which is crucial in biological systems for protein synthesis and degradation.

polysaccharide a carbohydrate molecule made from many monosaccharide units

Weblink
Peptide bond formation

Worksheet
Sugars and proteins

FORMULA AND DATA BOOK

Polysaccharides

Polysaccharides are an important class of naturally occurring condensation polymers. The monomers of polysaccharides are monosaccharides. Common monosaccharides are glucose, galactose and fructose. Glucose is the most important of these for human nutrition because sugar in this form is used by our bodies as an energy source.

The structure of α-glucose, an isomer of glucose, is shown in **Figure 18.3.5**.

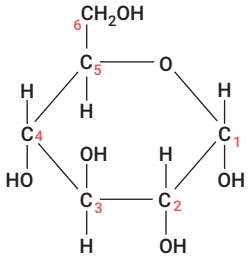


FIGURE 18.3.5 The structure of α-glucose

Joining monosaccharides

Monosaccharides undergo condensation polymerisation to form polysaccharides. A polysaccharide may contain one type of monomer or different types.

The link that joins two monosaccharides together is called a glycosidic link or glycosidic bond. The compound formed when two monosaccharides join is called a disaccharide and when long chains of monosaccharide units join, the result is a polysaccharide **(Figure 18.3.6)**.

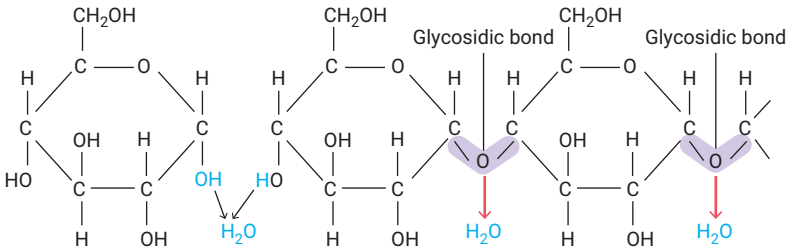


FIGURE 18.3.6 Forming the polysaccharide starch from α-glucose monomers

Disaccharides

As you already know, disaccharides consist of two monosaccharides joined together. Common disaccharides are sucrose from cane sugar, maltose from malt and lactose from milk.

The reaction that occurs to form the disaccharide is a condensation reaction because a water molecule is released. For example, the formation of maltose from two glucose monosaccharides can be written simply as:

$$2C_6H_{12}O_6 \rightarrow C_{12}H_{22}O_{11} + H_2O$$

Maltose is produced when two α-glucose monomers join, and lactose is produced when a β-glucose monomer and a β-galactose monomer join **(Figure 18.3.7)**. Sucrose is formed by linking the carbonyl carbons of α-glucose and β-fructose **(Figure 18.3.8)**.

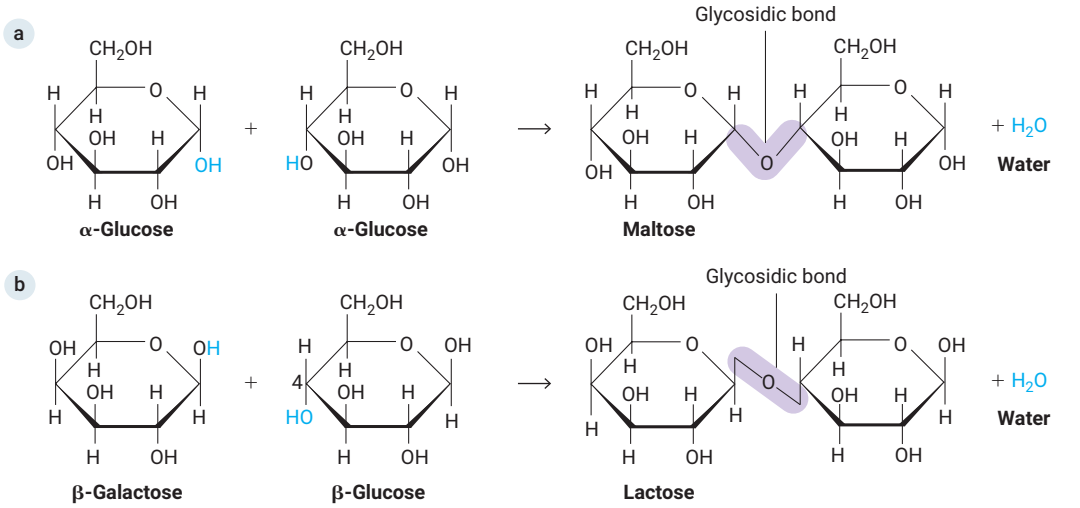
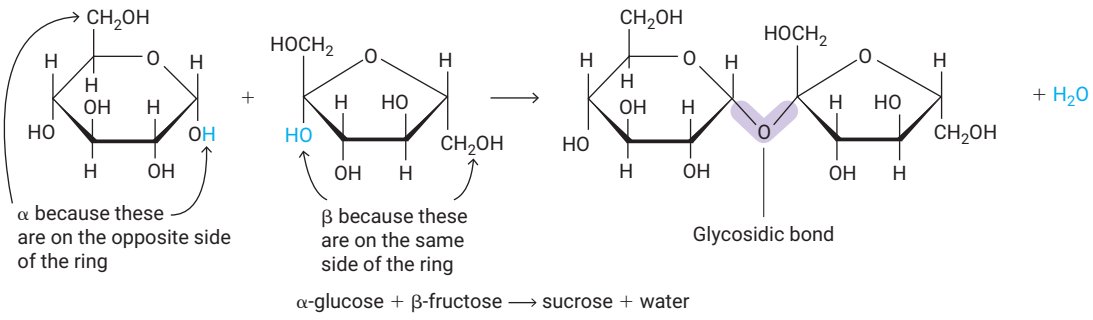


FIGURE 18.3.7 The formation of (a) maltose and (b) lactose



Smith et al. 2010 Chemistry in use, Book 2

FIGURE 18.3.8 The formation of sucrose from α-glucose and β-fructose

Similar to the formation of polypeptides, the condensation reaction that forms polysaccharides is reversible. Through hydrolysis (the addition of water), glycosidic bonds between monosaccharides can be broken, producing the original monosaccharides **(Figure 18.3.9)**. This process allows stored energy in polysaccharides to be accessed and metabolised, helping organisms regulate and manage their energy needs.

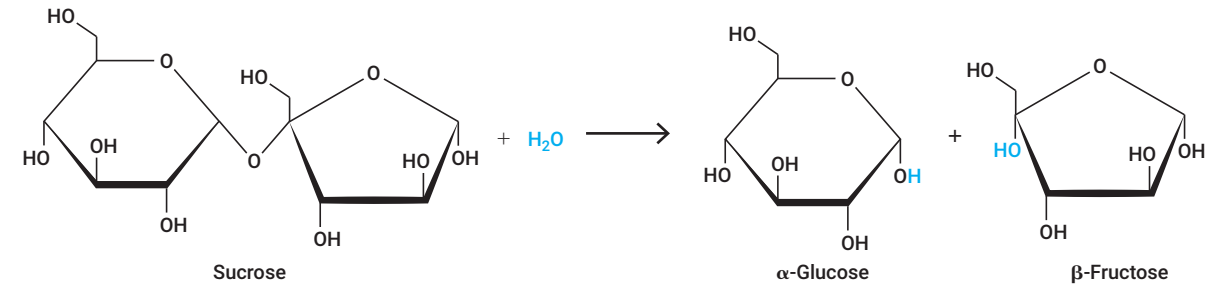


FIGURE 18.3.9 The hydrolysis of sucrose

Weblink
Carbohydrates

LEARNING CHECK 18.3

DESCRIBING

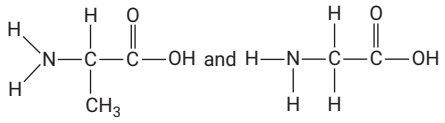
1 **Sketch** the structure of a:
   - **a** peptide bond
   - **b** glycosidic bond.

2 **Compare** an ester link and a peptide bond.

3 **Describe** the differences between monosaccharides and disaccharides.

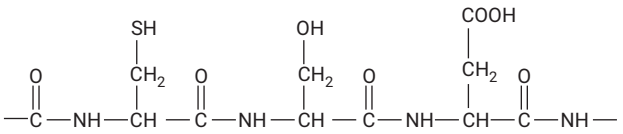
APPLYING

4 **Sketch** two repeating segments, showing the structure of the polymers formed when the following amino acids react.



5 Tripeptides can form between different amino acids.
   - **a** **Sketch** the structural formula of a tripeptide formed between:
     - **i** alanine, cysteine and asparagine
     - **ii** glycine, serine and phenylalanine.
   - **b** Name the tripeptides formed, using both the abbreviated and full names.

6 A section of a protein chain is shown.



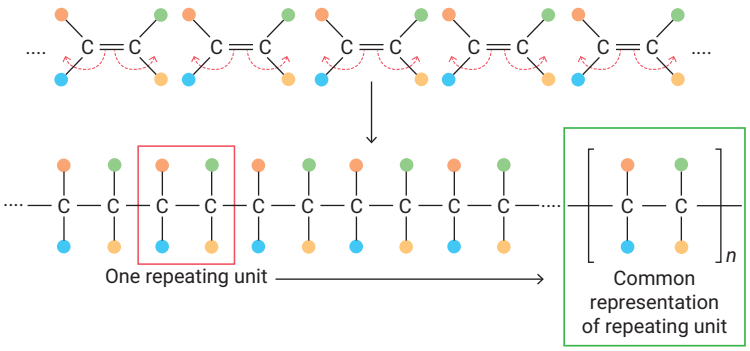
   - **a** **Determine** how many different amino acids reacted to produce this segment.
   - **b** **Sketch** the structure of the amino acids identified in part a.

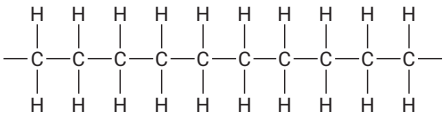
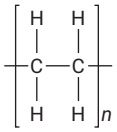
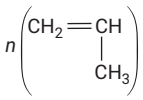
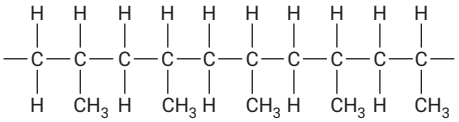
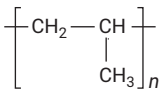
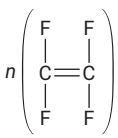
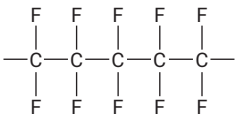
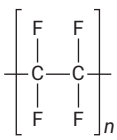
7 **a** **Explain** why the combined mass of the monosaccharides resulting from the hydrolysis of a disaccharide is greater than that of the disaccharide.
   - **b** Write the equation for the hydrolysis of sucrose.

CHAPTER SUMMARY

Addition polymerisation

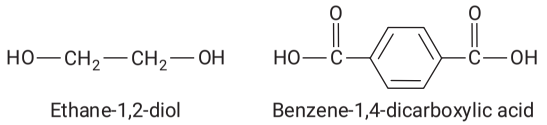
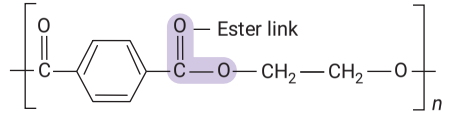
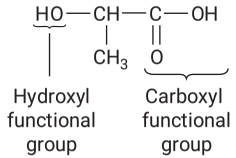
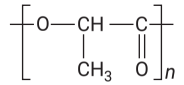
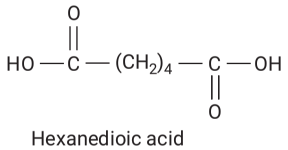
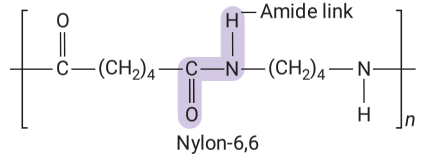
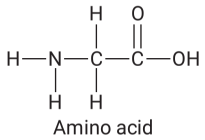
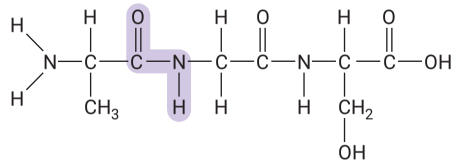
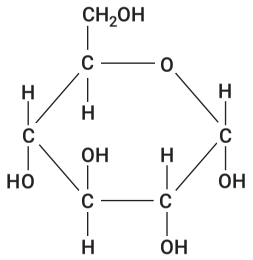
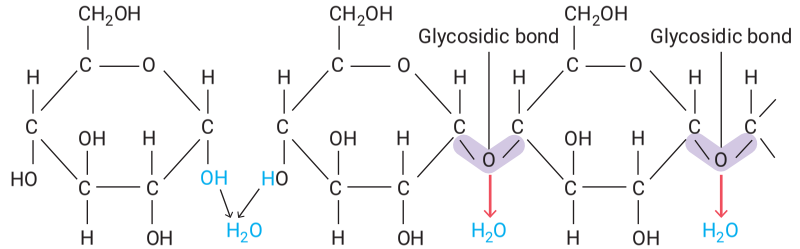
- Addition polymers form by adding together molecules without the loss of any atoms.
- The monomers must have a double bond between two carbon atoms for this to occur.



Macromolecule	Monomer	Polymer	Repeating unit
Polyethene	$n(CH_2{=}CH_2)$		
Polypropene			
Polytetrafluoroethene			

Condensation polymerisation

- Organic molecules with functional groups at each end can undergo a condensation reaction with a functional group on another molecule to form a condensation polymer.
- When two monomer molecules join together, a small molecule such as water is eliminated.
- Functional groups include $-NH_2$, $-OH$, $-COOH$ and $-COCl$.
- Examples of synthetic condensation polymers are polyesters and polyamides (nylons).
- Example of natural condensation polymers are polypeptides (proteins) and polysaccharides (carbohydrates).

Macromolecule	Monomer	Polymer
Polyethylene terephthalate (PET)		
Polylactic acid (PLA)		
Nylon		
Polypeptides (proteins)		
Polysaccharides (carbohydrates)		

9780170483544

MULTIPLE CHOICE

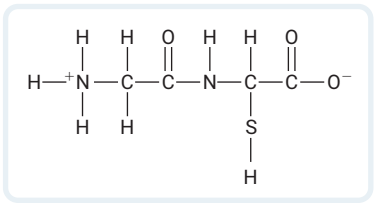
1. The monomers for addition polymerisation must be:

A alkanes.
B alkenes.
C alcohols.
D carboxylic acids.

2. Identify the two functional groups that are needed to form a polyester.

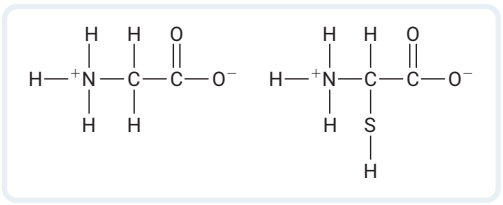
A Alcohol and amine
B Amine and aldehyde
C Alcohol and carboxylic acid
D Amine and carboxylic acid

3. The diagram shows the structure of a small section of a protein.

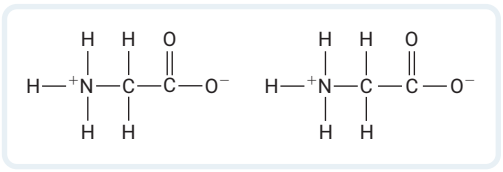


The amino acids used to form this are:

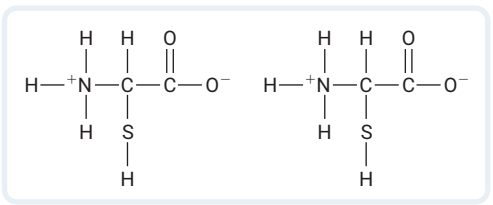
A



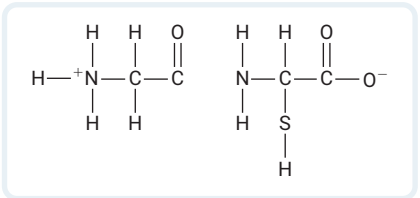
B



C



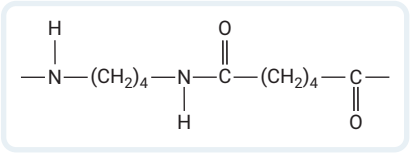
D



4. The bond that joins polylactic acid monomers together is:

A a peptide bond
B an ester bond
C an amide bond
D a glycosidic bond

5. Consider the following diagram.



Which of the following is true?

A It contains an ester link.
B The monomer used to produce this polymer is an amino acid.
C A monomer used to produce this polymer is a diamine.
D Water is consumed during the reaction.

6. When a polymer is formed by condensation polymerisation, the:

A mass of the polymer formed is less than the total mass of reactants.
B polymer must be linear.
C polymer must be cross-linked.
D polymer must be thermoplastic.

7. When sucrose is digested, it yields the two monosaccharides:

A glucose and lactose.
B glucose and maltose.
C glucose and glucose.
D glucose and fructose.

8. Which of the following compounds is an amino acid?

A Ethanoic acid
B Alanine
C Lactose
D DNA

9. Teflon is the polymer used to coat non-stick kitchenware. It is formed by reacting tetrafluoroethene in the presence of a catalyst. In this process:

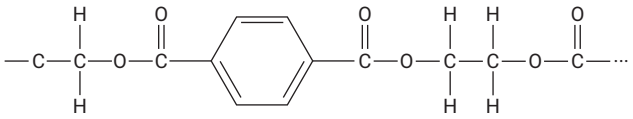
A a condensation reaction takes place, producing the polymer and water.
B a condensation reaction takes place, producing the polymer only.
C an addition reaction takes place, producing the polymer and water.
D an addition reaction takes place, producing the polymer only.

10. A functional group found in glucose, galactose and fructose is the:

A carboxyl group.
B amino group.
C hydroxyl group.
D halogen.

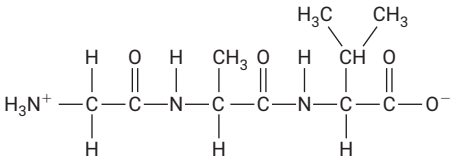
SHORT RESPONSE

11. PET, also known as terylene or Dacron™, is a common polymer used in a wide variety of applications from synthetic fabrics to soft-drink bottles. A section of the polymer is shown.



Sketch the structures of two monomers that this polymer could be made from.

12. Three amino acids glycine (Gly), alanine (Ala) and valine (Val) join to form the tripeptide glycylalanylvaline (Gly–Ala–Val), as shown.



Copy the diagram, and circle and name the bonds that join the three amino acids together.

13. Write an equation for the hydrolysis of maltose.

CROSS-CHAPTER QUESTION

14. Consider the hydrocarbon $CH_3CH{=}CHCH_3$, which can be polymerised.

- **a** Name the hydrocarbon.
- **b** Name the type of polymerisation involved between monomers of this hydrocarbon and **sketch** the repeating unit of the polymer.
- **c** **Sketch** the structures of the geometrical isomers of the above hydrocarbon. Name the geometrical isomers that you have sketched.
- **d** **Sketch** the structure of a structural isomer of the hydrocarbon that does not react with bromine water.
- **e** The hydrocarbon reacts with water. Construct a balanced chemical equation of this reaction. Name the product(s) formed and state the class.
- **f** State the functional group of the product(s) formed in part e.

DATA ANALYSIS

15. Interpret evidence

Unplasticised polyvinyl chloride (uPVC) is used to make door and window frames. PVC with a plasticiser added is used to make cling film for wrapping food. A plasticiser is a chemical compound that can be added during the polymerisation process.

A student investigated how the percentage of plasticiser added to PVC affected its flexibility. The student measured the bending of PVC samples when a mass was added. Their results are shown in the table below.

Sample of PVC	Percentage (%) of plasticiser	Bending of PVC sample (mm)			
		Trial 1	Trial 2	Trial 3	Trial 4
A	0	2	3	3	4
B	5	22	15	23	24
C	10	27	27	29	29
D	15	34	35	35	36

a Each PVC sample should be the same size to make it a fair test. **Deduce** why.

b The student repeated the test so that there were four trials for each sample. **Deduce** why.

c **Calculate** the mean value for Sample B.

d Each of the samples bent the most in Trial 4. **Draw a conclusion** for why this occurred.

e Suggest why uPVC is used to make door and window frames.

SCIENCE AS A HUMAN ENDEAVOUR

Syllabus dot point

- Consider that molecular manufacturing processes involve the positioning of molecules to facilitate a specific chemical reaction; such methods have the potential to synthesise specialised products, including proteins, carbon nanotubes, nanorobots and chemical sensors used in medicine.

Molecular manufacturing to the rescue!

Molecular manufacturing is the production of molecules, crystals and other chemical structures that have been designed to have a specific shape or chemical composition. These materials are incorporated into fabrics, batteries, medical devices and many other products.

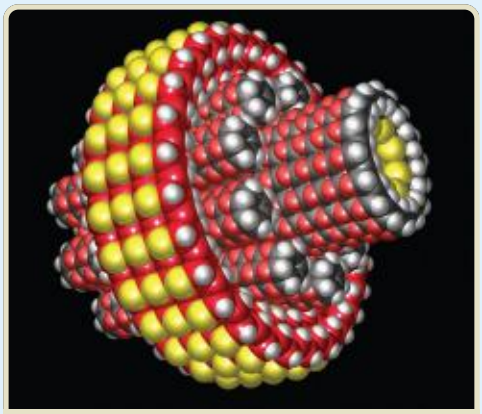
Devices and applications that incorporate these manufactured molecules have many advantages over conventional versions. Molecular manufacturing has also allowed researchers to develop innovative technology such as specialised drug delivery systems that can target disease in the body. This has made treatment more effective, and patients suffer fewer side effects.

How is molecular manufacturing done?

Molecular manufacturing can be carried out in many ways.

Method 1: The orientation effect

This is also referred to as mechanosynthesis and involves positioning molecules so that the desired functional groups line up, all reactions are efficient and there is less waste and fewer undesired products forming. Specifically manufactured proteins can be built in the form of a molecular machine called a nanomachine. Nanomachines can manufacture molecules, as suggested in Figure 1.



Alfred Pasieka/Science Photo Library

FIGURE 1 An artist's impression of a nanomachine. This is a molecule created to perform a very specific task such as building a larger molecule like a protein.

Method 2: Manipulation of structures at the atomic or molecular level

This method is done in two ways:

1. The bonding between atoms, ions and molecules can be altered, manipulated or controlled. If the bonds that form can be controlled, then specific properties can be given to the final structure.
2. Substances can be built by adding or substituting specific atoms in a structure, as shown in Figure 2. This also gives the final structure very specific properties. In this manner, chemicals and materials can be tailored for a specific purpose, as can be seen in Figure 3.

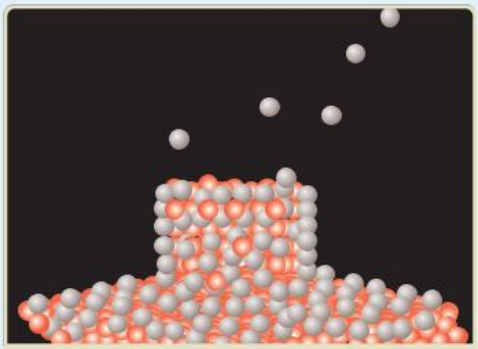


FIGURE 2 Atoms being added individually to a structure to create a very specific final molecule

Horia Bogdan/Shutterstock.com

FIGURE 3 This nanofabric does not absorb water or other liquids. The properties of the fabric have been changed so that the water beads rather than being absorbed.

Method 3: Use of protecting groups

Large molecules often have many reactive sites and/or functional groups. Sometimes a different functional group reacts rather than the one that has been targeted, and an unwanted product is formed. This is wasteful and reduces the yield of the desired product. These functional groups can be prevented from reacting by adding a protecting group.

Chemical sensors used in medicine

A biosensor is a structure that can detect a change in a biological component such as a particular chemical. Biosensors can detect when a particular chemical is present in the blood or body. Specific chemicals can indicate when a particular disease is present.

For example, cancer cells produce specific chemicals that indicate that a tumour is present. Bacteria and viruses do the same. A biosensor can detect these chemicals. One of the major advantages of a biosensor over conventional tests is that the patient can be assessed and the problem detected much earlier. This reduces risk because the disease can be treated much earlier than usual.

An example of better monitoring reducing patient risk is in the assessment of patients with diabetes mellitus. People with diabetes produce ketones as their blood insulin decreases. Propanone (acetone) is one of these ketones and is usually detected in the patient's urine. A nanosensor called a cantilever, seen in **Figure 4**, has a particular structure that will bind with the propanone in the air as a patient breathes out. The cantilever structure is covered with molecules that recognise and bond to the ketone molecules produced by a patient with diabetes mellitus.

Sharwood et al. 2008 Nelson VCE Chemistry units 3 and 4

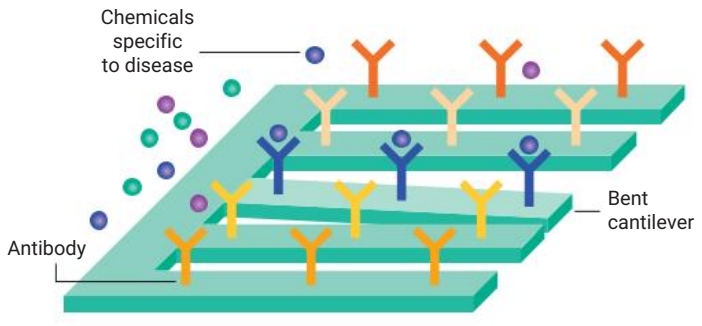


FIGURE 4 A bent cantilever due to bonding of particles to the antibodies on the surface

When the cantilever binds to the propanone, the structure changes because of the extra molecules now bound to the surface. As the cantilever changes shape, it generates a small electrical charge that can be measured and used to determine the concentration of propanone present. The more molecules present, the more the cantilever is bent out of shape, and the larger the electrical charge generated. In this way, the amount of molecules present can be measured.

This cantilever has several advantages over conventional detection of ketones. First, the patient only needs to breathe on the sensor rather than provide a urine sample. Second, the cantilever can detect propanone in much smaller amounts than conventional tests. This allows doctors to identify anomalies in blood glucose much earlier, reducing the overall risk to the patient, who can adjust their blood glucose concentration before symptoms appear.

ANSWERS

CHAPTER 1 CHEMICAL EQUILIBRIUM

LEARNING CHECK 1.1

DESCRIBING

1 The difference between a forward and a reverse reaction lies in the direction of the reaction. In a forward reaction, reactants are converted into products. In contrast, in a reverse reaction, the products are converted back into the original reactants.

2 A closed system means that the reaction occurs in a contained environment: the reactants and products cannot escape and other substances cannot enter or leave the system.

3 Not all reactions are reversible. Many reactions tend to proceed in one direction until one of the reactants is depleted, resulting in irreversible changes.

4 Double arrows are used in equations for reversible reactions to indicate that the reaction can proceed in both directions. The double arrows (⇌) signify that the forward reaction and the reverse reaction can both occur.

5 The difference between a chemical change and a physical change lies in the nature of the substances involved. A chemical change results in the formation of new substances with different chemical properties, but a physical change involves alterations in physical properties (such as state, shape or size) without changing the chemical composition of the substance.

APPLYING

6 **a** $H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$

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

c The double arrows (⇌) show that the reaction can proceed in both the forward and reverse directions.

LEARNING CHECK 1.2

DESCRIBING

1 **a** Equilibrium occurs when the rates of the forward and reverse reactions are equal, leading to constant concentrations of reactants and products.

b Dynamic equilibrium is the state in which the forward and reverse reactions continue to occur at equal rates, but there is no net change in the concentrations of reactants and products. The system is in constant motion at the molecular level, even though it appears static.

c Steady state is the continuous input and output of materials and energy, even though the system may not be at equilibrium.

2 **a** False. A chemical system will not reach equilibrium if it is an open system.

b True. A chemical system will reach equilibrium if it involves a reversible reaction, as long as it is in a closed system where no reactants or products can enter or leave.

c True. At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction.

d False. At equilibrium, the concentrations of the reactants and products remain constant, though they are not necessarily equal.

e False. At equilibrium, macroscopic (large-scale) properties, such as concentration remain constant because the rates of the forward and reverse reactions are balanced.

APPLYING

3 Figure 1.2.1 shows how the concentration of reactants decreases while the concentration of products increases over time until the concentrations become constant. Figure 1.2.2 shows how, as time progresses, the rates of the forward and reverse reactions equalise, indicating that equilibrium has been achieved.

4 The initial rates of the forward reaction are higher than the reverse reaction when one reactant decomposes into two products because, initially, the concentration of the reactant is high while the concentration of the products are low or zero.

5 The trend indicating that equilibrium has been achieved would show the rates of the forward and reverse becoming the same.

LEARNING CHECK 1.3

DESCRIBING

1 Activation energy is the minimum energy required for a reaction to occur.

2 An activated complex is a temporary, unstable structure formed during the transition from reactants to products.

3 Reversibility of reactions depends on the activation energies of both forward and reverse reactions.

APPLYING

4 The reaction will quickly reach equilibrium, with both reactions occurring at similar rates.

5 Reversible reactions have low activation energies in both directions, allowing equilibrium, whereas non-reversible reactions have high reverse reaction activation energies, making them go in only one direction.

6 The Haber process is reversible because of the low activation energies in both directions. Petrol combustion is not reversible because it releases too much energy, making the reverse reaction unlikely.

LEARNING CHECK 1.4

DESCRIBING

1 A plateau indicates that the concentrations of reactants and products have become constant, signifying that the system has reached dynamic equilibrium.

APPLYING

2 Equilibrium is reached when the concentrations of reactants and products stop changing and remain constant over time.

3 When the rates of the forward and reverse reactions become equal, equilibrium has been reached. Monitoring the reaction rates can show when this balance occurs.

4 At the beginning of a reaction, the forward reaction is faster than the reverse reaction due to the higher concentration of reactants. At equilibrium, the forward and reverse reactions occur at the same rate.

CHAPTER EXAM

MULTIPLE CHOICE

1 C

2 B

3 B

4 A

5 D

6 A

7 D

8 D

9 A

10 A

SHORT RESPONSE

11 The statement is incorrect because equilibrium does not require equal concentrations of reactants and products. Instead, it refers to a state where the rates of the forward and reverse reactions are equal, resulting in constant concentrations over time. The specific concentrations at equilibrium depend on the reaction and the conditions, meaning that the amounts of reactants and products can vary widely while still maintaining equilibrium.

12 An open system can never reach equilibrium because matter and energy continuously exchange with the surroundings. This means reactants can be added or removed, and products can escape into the environment. In contrast, a closed system isolates the reaction, enabling it to reach a stable state where the rates of the forward and reverse reactions are equal.

CROSS-CHAPTER QUESTION

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

b Carbon monoxide (CO) and oxygen (O_2)

c Carbon dioxide (CO_2)

d The concentration of carbon dioxide (CO_2) would initially increase as CO and O_2 react to form CO_2. As the reaction approaches equilibrium, the rate of formation of CO_2 will decrease, and its concentration will stabilise at a certain value, while the concentrations of CO and O_2 decrease and stabilise at the same time as CO_2.

DATA ANALYSIS

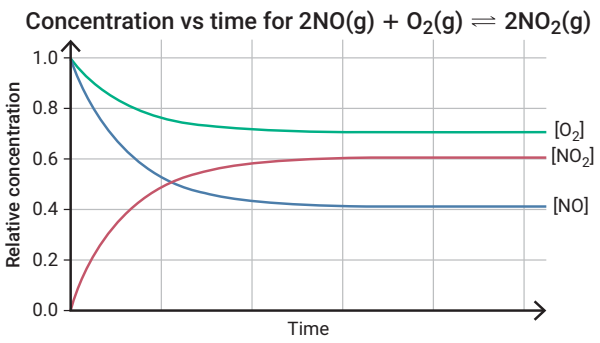
14 a Initially, the concentration of N_2O_4 is 5 mol L^{-1} and that of NO_2 is 0 mol L^{-1}.

b The plateau lines indicate that the system was at equilibrium.

c 9 minutes

d The line indicates N_2O_4 dropped sharply in the initial stages of the reaction because it was consumed rapidly to form NO_2 as the reaction proceeded. The forward reaction occurred quickly at the start when reactant concentrations were higher, resulting in a significant decrease in N_2O_4.

15



Initially, the concentrations of NO and O_2 will be high, while NO_2 will be at zero. As the reaction progresses, the concentrations of NO and O_2 will decrease while the concentration of NO_2 will increase. The graph will show the concentrations of NO and O_2 decreasing, while the concentration of NO_2 increases until all three concentrations level off at the same time, indicating equilibrium.

CHAPTER 2 FACTORS THAT AFFECT EQUILIBRIUM

LEARNING CHECK 2.1

DESCRIBING

1 **a** endothermic

b exothermic

c endothermic, exothermic

2 **a** The system favours the endothermic reaction, so the equilibrium will shift to the left, reducing the yield of ammonia.

b The position of equilibrium shifts to the left (towards the reactants) if the change causes a decrease in the amount of products formed.

APPLYING

3 Raising the temperature increases the kinetic energy of particles, leading to more frequent and successful collisions, thus increasing the rate of an endothermic reaction more than an exothermic reaction due to a greater increase in the proportion of particles with enough energy to react successfully.

4 When temperature changes, the rate of reaction changes gradually as the concentrations of reactants and products respond to the change. This is indicated on the graph as a slow shift, instead of an immediate shift.

LEARNING CHECK 2.2

DESCRIBING

1 An increase in concentration means that there is an increase in the number of particles of a substance in a given volume (either gases or aqueous solutions).

2 According to collision theory, the rate of a reaction depends on the frequency of successful collisions between reactant particles. When the concentration is increased, there are more particles in a given volume, leading to more frequent collisions and an increase in reaction rate because there are more frequent opportunities for particles to collide with enough energy and proper orientation to react.

APPLYING

3 In a system at equilibrium, increasing the concentration of one reactant disturbs the equilibrium. If the concentration of a reactant is increased, the rate of the forward reaction will increase as more collisions occur. This will lead to a shift in equilibrium position to the right.

4 If C is suddenly removed from the system, the equilibrium will shift to the right (towards the products) because the reverse reaction cannot occur. This shift will cause an increase in the consumption of A and B, leading to a decrease in their concentrations as more of them react to form C.

LEARNING CHECK 2.3

DESCRIBING

1 **a** Reducing the volume would favour the side with fewer gas molecules (3 mol of reactants → 2 mol of products) so it would shift to the right (towards products).

b Reducing the volume will favour the side with fewer gas molecules (3 mol of reactants → 2 mol of products) so it would shift to the right (towards products).

c This reaction will not be affected by a reduction in volume because the number of moles of gas is the same on both sides (1 mol of N_2 + 1 mol of O_2 = 2 mol of NO) so the equilibrium will not shift.

APPLYING

2 In a gaseous system at equilibrium, changing the volume alters the pressure of the system. When the volume decreases (increasing pressure), the equilibrium will shift towards the side with fewer gas molecules to reduce pressure. When the volume increases (decreasing pressure), the equilibrium will shift towards the side with more gas molecules to increase pressure.

3 Diluting an aqueous system reduces the concentration of all species in the solution, just as increasing the volume of a gaseous system decreases the concentration (pressure) of the gases. The reaction that produces the greater proportion of aqueous particles will be favoured.

LEARNING CHECK 2.4

DESCRIBING

1 a Endothermic reaction: A chemical reaction that absorbs energy (heat) from its surroundings, as the products of an endothermic reaction have higher energy than the reactants.

b Le Châtelier's principle: If a dynamic equilibrium system is disturbed by changing the conditions (concentration, pressure, temperature), the system will adjust to partially counteract the disturbance and restore equilibrium.

2 a According to Le Châtelier's principle, adding more CO_2 will shift the equilibrium to the right (towards the formation of more H_2CO_3) to reduce the concentration of CO_2.

b Removing H_2CO_3 (carbonic acid) will shift the equilibrium to the right (towards the products) to produce more H_2CO_3.

c Since the reaction is exothermic ($\Delta H = -15$ kJ mol^{-1}), cooling the system will shift the equilibrium to the right (towards more H_2CO_3 formation) because the system releases heat as a product, and cooling favours heat-producing reactions.

APPLYING

3 • Increase the concentration of carbonate ions (CO_3^{2-}): adding more CO_3^{2-} will shift the equilibrium to the right, promoting the formation of more solid Ag_2CO_3 and removing silver ions from the solution.

• Evaporate some of the water which would cause the concentration of ions present to increase. The silver and carbonate ions would react to reduce their concentration.

4 a Adding more sodium hypochlorite pellets would result in an increase in the concentration of ClO^- as the pellets dissolve. An increase in ClO^- will cause equilibrium will shift to the right, producing more HClO and releasing heat.

b Adding sodium hydroxide: sodium hydroxide (NaOH) is a base that adds OH^- ions, which neutralise H^+ ions (forming water in a neutralisation reaction). This decreases the concentration of H^+ ions, shifting the equilibrium to the left (towards the reactants) to produce more H^+.

c Since the reaction produces heat (exothermic), an increase in temperature will shift the equilibrium to the left to absorb the added heat, resulting in further break down of HClO to ClO^- and H^+ ions.

5 At the time when the change was made, the concentration of both N_2O_4 and NO_2 increases instantaneously. This suggests that the volume of the system was decreased. According to Le Châtelier's principle, the system will favour the reaction with fewer particles to decrease the concentration. As a result, the reverse reaction is favoured, increasing the concentration of N_2O_4 and decreasing the concentration of NO_2. The extent of the change of each substance reflects the molar ratio as per the balanced equation, where the change is twice as much in NO_2 than in N_2O_4.

CHAPTER EXAM

MULTIPLE CHOICE

1 C
2 D
3 B
4 A
5 C
6 C
7 A
8 B
9 D
10 D

SHORT RESPONSE

11 a The reaction occurs in a closed system. This is indicated by the mention of a 'sealed container', which prevents the escape of gases and allows for the establishment of equilibrium.

b Once equilibrium is established, the rate of the forward reaction (decomposition of HgO into Hg and O_2) equals the rate of the reverse reaction. As a result, the concentrations of the reactants and products remain constant, so the proportions of the colours in the system do not change, maintaining a consistent appearance.

c Orangey/silver: If the equilibrium shifts to the left, more HgO is formed; however, there would still be a small amount of Hg (silver).

12 a Adding N_2O_4 shifts the equilibrium to the right to produce more NO_2 in order to reduce the concentration of the added reactant.

b Adding NO_2 shifts the equilibrium to the left to produce more N_2O_4 in order to counteract the increase in the product concentration.

c Adding heat shifts the equilibrium to the right since the reaction is endothermic (ΔH is positive), favouring the formation of more NO_2.

d Removing N_2O_4 shifts the equilibrium to the left to produce more N_2O_4 in order to replace the removed reactant.

e Increasing the pressure shifts the equilibrium to the left to favour the side of the reaction with fewer moles of gas (1 mol of N_2O_4 as compared to 2 mol of NO_2).

CROSS-CHAPTER QUESTION

13 a According to Le Châtelier's principle, an increase in temperature of an exothermic reaction will shift the reaction in the direction that absorbs heat to counteract the change. In this case, an increase in temperature will shift the equilibrium to the left (towards the reactants) to decrease the concentration of NH_3 and absorb the added heat, thereby favouring the formation of N_2 and H_2.

b The forward reaction is exothermic. In the energy profile diagram, the reactants (N_2 and H_2) will have higher energy than the products (NH_3), and the difference in energy corresponds to the enthalpy change. In an exothermic reaction, the activation energy (energy barrier) is typically higher than the overall enthalpy change since energy is released as the reaction proceeds to products. This must be overcome for the reactants to convert to products.

c At a lower temperature, the equilibrium may shift to the right (according to Le Châtelier's principle). However, a lower temperature generally decreases the reaction rate because there is less kinetic energy and fewer effective collisions between reactant molecules. Thus, while the yield of NH_3 could potentially increase, the rate of formation of NH_3 would be slower at lower temperatures because of the slower rate of reaction.

DATA ANALYSIS

14 a $SO_2(g)$ 0.8 mol L^{-1}, $Cl_2(g)$ 0.6 mol L^{-1}, $SO_2Cl_2(g)$ 0.0 mol L^{-1}

b At t_2, the volume must have decreased causing the concentration of all species to increase. The decrease in volume also resulted in an increase in pressure.

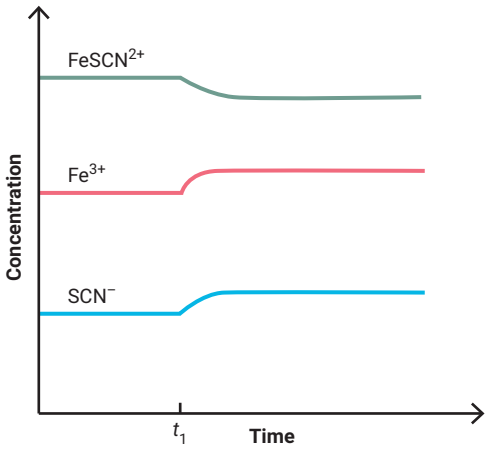
c From t_2 to t_3, Cl_2 decreased by 0.5 mol L^{-1}, stabilising at 0.45 mol L^{-1}, whereas the concentration of SO_2Cl_2 increased by 0.5 mol L^{-1} stabilising at 0.35 mol L^{-1}. This shows that the system shifted to the right to counteract the increase in pressure and re-established a new equilibrium position.

d Since the reaction is exothermic ($\Delta H = -67$ kJ mol^{-1}), an increase in temperature would drive the system to the left. There would be a gradual increase in Cl_2 and SO_2, while there would also be a gradual decrease in SO_2Cl_2 after t_4 until equilibrium is established.

15 a

Change	Shift in equilibrium position (left, right or no change)	Rate of forward reaction compared to original rate (increase, decrease or no change)	Colour of reaction mixture
The reaction mixture is heated	Left	Increase	(More) brown/ orange/pale brown
A few crystals of $FeCl_3$ are added	Right	Increase	(More) red/ deeper red
Water is added to the reaction mixture	Left	Decrease	(Very) pale brown
A few drops of concentrated Na_3PO_4 are added	Left	Decrease	(Very) pale brown

b



CHAPTER 3 EQUILIBRIUM CONSTANTS

LEARNING CHECK 3.1

DESCRIBING

1 a An equilibrium expression is a mathematical representation that shows the ratio of the concentrations of the products to the reactants, each raised to the power of their coefficients in the balanced chemical equation, at equilibrium.

The general form for reaction $aA + bB \rightleftharpoons cC + dD$ is:

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

b An equilibrium constant is a numerical value (K_c) that expresses the ratio of the concentrations of products to reactants at equilibrium for a given reaction at a specific temperature.

c A homogenous system is a system in which all reactants and products are in the same phase (e.g. all gases or all solutions).

d A heterogeneous expression is a system in which reactants and products exist in more than one phase (e.g. solids, liquids and gases); therefore, the concentrations of solids and liquids are considered to be constant and are not included in the equilibrium expression.

2 a $K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]}$

b Carbon is a solid, so it is not included in the equilibrium expression:

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

c Both $CaCO_3$ and CaO are solids, so they are not included in the expression:

$K_c = [CO_2]$

d Water is a liquid and not included in the equilibrium expression:

$$K_c = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]}$$

e Water is a liquid and not included in the equilibrium expression:

$$K_c = \frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2 [H^+]^2}$$

APPLYING

3 a $K_c = \frac{(0.17)(0.17)}{(2.00)(3.00)}$

$= 0.0048$

b $K_c = \frac{(7.0 \times 10^{-3})^2 (3.5 \times 10^{-3})}{(0.2)^2}$

$= 4 \times 10^{-6}$

c $K_c = \frac{(1.70)^2}{(0.75)^2 (0.62)}$

$= 8.3$

d $K_c = \frac{(2.00)^2}{(1.25)(1.70)}$

$= 1.88$

LEARNING CHECK 3.2

DESCRIBING

1 a The reaction is at equilibrium. Neither the forward nor reverse reaction is favoured.

b The concentration of reactants is higher than the concentration of the products compared to at equilibrium. The forward reaction is favoured, meaning the system will shift to the right.

c The concentration of products is higher than the concentration of the reactants compared to at equilibrium. The reverse reaction is favoured, meaning the system will shift to the left.

2 A K_c value close to 1 means at equilibrium, the concentrations of reactants and products are similar. Neither the reactants nor the products are significantly favoured, and both are present in comparable amounts.

3 A very high K_c value of 2.4×10^{47} indicates that the reaction proceeds almost entirely towards the formation of products (in this case, steam). This high K_c value suggests that, at equilibrium, the concentration of water (the product) is extremely high, while the concentrations of hydrogen and oxygen (the reactants) are very low. The reaction occurs to a large extent and highly favours the product.

APPLYING

4 Since $Q < K_c$, the system has more reactants than it would at equilibrium. This indicates that the forward reaction is favoured, meaning the system will shift towards the right (towards products) in order to reach equilibrium. $Q = 15$ is less than $K_c = 22$ so the forward reaction is favoured until equilibrium is reached.

5 a $Q = \frac{[CH_3OH]}{[CO][H_2]^2}$

$= \frac{18.0}{(0.5)(1.0)^2}$

$= 36.0$

b Since $Q = 36.0$ and $K_c = 14.5$, $Q > K_c$, meaning the system has too many products. Therefore, the reverse reaction is favoured, and the system will shift to the left (towards reactants) in order to reach equilibrium.

LEARNING CHECK 3.3

DESCRIBING

1 The equilibrium constant K_c indicates the relative concentrations of products and reactants at equilibrium.

- If $K_c > 1$, the equilibrium favours the formation of products, meaning that at equilibrium, the concentration of products is greater than that of reactants.
- If $K_c < 1$, the equilibrium favours the reactants, meaning that at equilibrium, the concentration of reactants is greater than that of products.
- If $K_c \approx 1$, the concentrations of reactants and products are comparable, and neither side of the reaction is strongly favoured.

2 This assumption is typically valid when the initial concentration of reactants is large relative to the change in concentration at equilibrium (x), which happens when the equilibrium constant K_c is very small. In such cases, x represents a small shift in concentration, so subtracting x from the initial concentration has a negligible effect, simplifying the calculations.

APPLYING

3 a

R	$N_2(g)$	$O_2(g)$	2NO(g)
I	1 mol in 2 L	1 mol in 2 L	0 mol in 2 L
C	$-x$ (1 − 0.25 = 0.75 mol)	$-x$ (0.75 mol)	$+2x$ ($2 \times 0.75 =$ 1.50 mol)
E	0.25 mol $[N_2]_{eq} = \frac{0.25\text{ mol}}{2\text{ L}} = 0.125\text{ mol L}^{-1}$	0.25 mol $[O_2]_{eq} = \frac{0.25\text{ mol}}{2\text{ L}} = 0.125\text{ mol L}^{-1}$	$[NO]_{eq} = \frac{1.5\text{ mol}}{2\text{ L}} = 0.75\text{ mol L}^{-1}$

b $K_c = \frac{[NO]^2}{[NO_2][O_2]}$

$= \frac{(0.75)^2}{(0.125)(0.125)}$

$= 36.0$

4 a

R	2HI(g)	$H_2(g)$	$I_2(g)$
I	1.5 M	0.0 M	0.0 M
C	$-2x$	$+x$	$+x$
E	$1.5 - 2x$	x	x

$K_c = \frac{[H_2][I_2]}{[HI]^2} = 53.25$

$53.25 = \frac{x^2}{(1.5-2x)^2}$

$\sqrt{53.25} = \frac{x}{1.5-2x}$

$10.95 - 14.6x = x$

$10.95 = 15.6x$

$x = 0.701$

Therefore:

$[HI] = 0.098\text{ mol L}^{-1}$

$[H_2] = 0.701\text{ mol L}^{-1}$

$[I_2] = 0.701\text{ mol L}^{-1}$

b

R	HCN(aq)	$CN^-(aq)$	$H^+(aq)$
I	1.25 M	0.0 M	0.0 M
C	$-x$	$+x$	$+x$
E	1.25 - x Assume x is negligible since K_c is small	$+x$	$+x$

$K_c = \frac{[CN^-][H^+]}{[HCN]}$

$= \frac{x^2}{1.25-x}$

$= 4.97 \times 10^{-10}$

$4.97 \times 10^{-10} = \frac{x^2}{1.25}$

$x^2 = 6.21 \times 10^{-10}$

$x = 2.49 \times 10^{-5}$

$[CN^-] = 2.49 \times 10^{-5}\text{ mol L}^{-1}$

$[H^+] = 2.49 \times 10^{-5}\text{ mol L}^{-1}$

$[HCN] = 1.25\text{ mol L}^{-1}$

5 a Since 1 mol of Cl_2 is formed with 1 mol of PCl_3 from 1 mol of PCl_5, the number of moles of PCl_3 at equilibrium is 0.25 mol, and the number of moles of PCl_5 consumed is 0.25 mol.

PCl_5 at equilibrium = 0.40 − 0.25 = 0.15 mol

b

R	$[PCl_5]$	$[PCl_3]$	$[Cl_2]$
I	0.40 M	0.00 M	0.00 M
C	$-x$	$+x$	$+x$
E	0.40 − 0.25 = 0.15 mol in 10 L = 0.015 M	0.25 mol in 10 L = 0.025 M	0.25 mol in 10 L = 0.025 M

c $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

$= \frac{(0.025)(0.025)}{0.015}$

$= 0.0417\text{ M}$

LEARNING CHECK 3.4

DESCRIBING

1 The solubility product constant (K_{sp}) is a measure of the extent to which a compound can dissolve in water. A larger K_{sp} value indicates that the substance is more soluble in water, meaning more of the solid dissociates into its ions in solution. Conversely, a smaller K_{sp} value indicates that the substance is less soluble, meaning fewer ions dissociate from the solid at equilibrium.

2 The solubility product constant (K_{sp}) is temperature dependent. Therefore, when reporting the K_{sp} value, it is crucial to include the temperature to ensure accurate interpretation of solubility under specific conditions.

APPLYING

3 a CuS is less soluble because it has a smaller K_{sp}.

b CaF_2 is less soluble because it has a smaller K_{sp}.

c Copper (II) sulfide is less soluble because it has a smaller K_{sp}.

d Copper (II) sulfide is less soluble because it has a smaller K_{sp}.

4 $AgI(s) \rightarrow Ag^+(aq) + I^-(aq)$

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

$K_{sp} = (9 \times 10^{-9})(9 \times 10^{-9}) = 8.1 \times 10^{-17}$

5 $CuS(s) \rightarrow Cu^{2+}(aq) + S^{2-}(aq)$

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

$K_{sp} = x \times x = x^2$

$x^2 = 8.0 \times 10^{-37}$

$x = \sqrt{(8.0 \times 10^{-37})}$

$= 8.9 \times 10^{-19}$

CHAPTER EXAM

MULTIPLE CHOICE

1 A

2 D

3 C

4 D

5 C

6 B

7 B

8 C

9 C

10 C

SHORT REPSONSE

11 $K_{sp} = (6.13 \times 6.13)$

$= 37.6$

12 a The reaction occurred in a closed system; therefore, matter is not exchanged with the surroundings. This means the system can reach a steady state where the rate of the forward reaction (conversion of reactants to products) equals the rate of the reverse reaction (products are converted back into reactants) to establish a state of dynamic equilibrium.

b $K_c = \dfrac{[XA_3]^2}{[A_2]^3[X_2]}$

$= \dfrac{4.2^2}{3.4^3 \times 1.8}$

$= 0.25$

$K_c < 1$; therefore, equilibrium lies to the left.

CROSS-CHAPTER QUESTION

13 a $[Cl_2] = 0.12$ M, $[CO] = 0.06$ M, $[COCl_2] = 0.03$ M

b $K_c = \dfrac{[Cl_2][CO]}{[COCl_2]} = \dfrac{(0.12)(0.06)}{(0.03)} = 0.24$

c $[COCl_2]$ decreased, and $[CO]$ and $[Cl_2]$ increased; therefore, the reaction moved in the forward direction (to the right).

d $K_c = \dfrac{[Cl_2][CO]}{[COCl_2]}$

$= \dfrac{(0.11)(0.085)}{0.04}$

$= 0.23$

DATA ANALYSIS

14 a Exothermic: Increasing temperature decreases K_c, indicating that the equilibrium shifts towards the reactants (endothermic) direction.

b $8.61 \times 10^{11} = \dfrac{[SO_3]^2}{(0.860)^2(0.330)}$

$[SO_3]^2 = (0.7396)(0.330)(8.61 \times 10^{11}) = 2.10 \times 10^{11}$

$[SO_3] = 4.58 \times 10^5$ M

c Halving the volume would double the pressure. To reduce the pressure, the equilibrium would shift towards the product to reduce the number of molecules present. However, because the reactant concentration decreases, the equilibrium constant remains unchanged.

15 a $[HI] = 0.06$ M, $[I_2] = 0.01$ M

b $K_c = \dfrac{[H_2][I_2]}{[HI]^2} = \dfrac{0.03^2}{0.06^2} = 0.25$

c The temperature was higher for Experiment 2. The K_c value was larger for Experiment 2, indicating that the equilibrium shifted towards the products (endothermic direction) to compensate for the increase in temperature.

CHAPTER 4 ACIDS, BASES AND pH

LEARNING CHECK 4.1

DESCRIBING

1 a An acid is a substance that can donate a proton (H^+ ion).

b A base is a substance that releases hydroxide ions (OH^-) into solution.

c A hydronium ion is the ion that forms when a proton is donated to a water molecule (H_3O^+).

d A monoprotic acid is a substance that can donate one proton.

e A diprotic acid is a substance that can donate two protons.

f A triprotic acid is a substance that can donate three protons.

APPLYING

2 a $H_2CO_3(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + H_3O^+(aq)$

$HCO_3^-(aq) + H_2O(l) \rightarrow CO_3^{2-}(aq) + H_3O^+(aq)$

b $C_6H_8O_7(aq) + H_2O(l) \rightarrow C_6H_7O_7^-(aq) + H_3O^+(aq)$

$C_6H_7O_7^-(aq) + H_2O(l) \rightarrow C_6H_6O_7^{2-}(aq) + H_3O^+(aq)$

$C_6H_6O_7^{2-}(aq) + H_2O(l) \rightarrow C_6H_5O_7^{3-}(aq) + H_3O^+(aq)$

3 Potassium hydrogen phthalate is a monoprotic acid. The only H atom it can donate is the one bonded to the oxygen atom.

$KC_8H_5O_4 + H_2O(l) \rightarrow KC_8H_4O_4^-(aq) + H_3O^+(aq)$

LEARNING CHECK 4.2

DESCRIBING

1 a A strong acid is an acid that readily donates a proton to water.

b A weak acid is an acid in which only a small proportion of the molecules will donate their proton.

c A concentrated acid is a solution in which there is a large number of H_3O^+ ions per unit volume of water.

d A dilute acid is a solution in which there is a small number of H_3O^+ ions per unit volume of water.

APPLYING

2 a $HNO_3(l) + H_2O(l) \rightarrow NO_3^-(aq) + H_3O^+(aq)$

b $H_2C_2O_4(l) + H_2O(l) \rightleftharpoons HC_2O_4^-(aq) + H_3O^+(aq)$

$HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons C_2O_4^{2-}(aq) + H_3O^+(aq)$

c $Ba(OH)_2(s) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$

d $CH_3CH_2CH_2NH_2(l) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2NH_3^+(aq) + OH^-(aq)$

ANALYSING

3 Sulfuric acid has the highest conductivity. It is a strong diprotic acid, whereas carbonic acid is a weak diprotic acid:

$H_2SO_4(aq) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$

$HSO_4^-(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + H_3O^+(aq)$

Carbonic acid is a weak diprotic acid. Very few carbonic acid molecules or hydrogencarbonate ions dissociate to produce H_3O^+ ions:

$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$

Since all H_2SO_4 dissociates, it produces more ions in solution, resulting in greater electrical conductivity.

4 Base X would be a strong base because it has a higher pH than base Y. Base Y is a weak base. This is further supported by the electrical conductivity; because base X is a strong base, all particles will dissociate in water and will have the most ions to produce the highest conductivity.

5 B = H_2SO_4 = strong, diprotic acid = largest conductivity

E = HCl = strong monoprotic acid = large conductivity

D = H_3PO_4 = weak triprotic acid = relatively large number of H_3O^+

C = H_2CO_3 = weak diprotic acid

A = CH_3COOH = weak monoprotic acid

LEARNING CHECK 4.3

DESCRIBING

1 a An ionisation reaction that takes place in pure water or aqueous solution in which a water molecule loses a hydrogen ion to become a hydroxide ion. The hydrogen ion immediately attaches to another water molecule to produce the hydronium ion.

b K_w is the equilibrium constant representing the equilibrium expression that shows water ionising into hydroxide and hydronium ions.

APPLYING

2 a $[H_3O^+] = 1.45\ M$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{1.45} = 6.90 \times 10^{-15}\ M$$

b $[OH^-] = 0.89\ M$

$$[H_3O^+] = \frac{1.00 \times 10^{-14}}{0.89} = 1.12 \times 10^{-14}\ M$$

c $[H_3O^+] = 1.5 \times 2 = 3.00\ M$

$[OH^-] = \frac{1.00 \times 10^{-14}}{3.00} = 3.33 \times 10^{-15}$ M

d $[OH^-] = 2 \times 0.89 = 1.78$ M

$[H_3O^+] = \frac{1.00 \times 10^{-14}}{1.78} = 5.62 \times 10^{-15}$ M

e $n(KOH) = \frac{25}{56.11} = 0.45$ mol

$c(KOH) = \frac{0.45}{0.05} = 9$ M

$[OH^-] = 9$ M

$[H_3O^+] = \frac{1.00 \times 10^{-14}}{9} = 1.11 \times 10^{-15}$ M

f $n(HCl) = \frac{2.76}{36.46} = 0.076$ mol

$c(HCl) = \frac{0.076}{0.125} = 0.61$ M

$[H_3O^+] = 0.61$ M

$[OH^-] = \frac{1.00 \times 10^{-14}}{0.61} = 1.64 \times 10^{-14}$ M

LEARNING CHECK 4.4

APPLYING

1 **a** $pH = -\log 0.001 = 3$

b $pH = -\log(1.2 \times 10^{-5}) = 4.9$

2 $[OH^-] = 2 \times 0.02 = 0.04$ M

$pOH = -\log 0.04 = 1.4$

$pH = 14 - 1.4 = 12.6$

3 $[H_3O^+] = 10^{-9.5} = 3.2 \times 10^{-10}$ M

$[OH^-] = \frac{1.00 \times 10^{-14}}{3.2 \times 10^{-10}}$

$[NaOH] = 3.2 \times 10^{-5}$ M

4 **a** $pOH = -\log 0.0001 = 4$

b $pOH = -\log(6.5 \times 10^{-5}) = 4.2$

5 **a** $[H_3O^+] = 10^{-5}$ M, $[OH^-] = 10^{-9}$ M

b $[H_3O^+] = 10^{-14}$ M, $[OH^-] = 10^{0}$ M

c $[H_3O^+] = 10^{-2.5}$ M, $[OH^-] = 3.2 \times 10^{-12}$ M

d $[H_3O^+] = 10^{-5.8}$ M, $[OH^-] = 6.3 \times 10^{-9}$ M

6 **a** $n(NaOH) = 0.100 \times 0.025 = 2.5 \times 10^{-3}$ mol

$c(NaOH) = \frac{2.5 \times 10^{-3}}{0.125} = 0.02$ M

$[OH^-] = 0.02$ M

$[H^+] = \frac{1.00 \times 10^{-14}}{0.02} = 5 \times 10^{-13}$ M

$pH = -\log(5 \times 10^{-13}) = 12.3$

b $n(Ba(OH)_2) = 0.100 \times 0.100 = 0.01$ mol $\times 2 = 0.02$ mol

$c(Ba(OH)_2) = \frac{0.02}{0.125} = 0.160$ M

$[H^+] = \frac{1.00 \times 10^{-14}}{0.160} = 6.25 \times 10^{-14}$ M

$pH = -\log(6.25 \times 10^{-14}) = 13.2$

7 **a** $n(NaOH) = 0.1 \times 0.050 = 0.0050$ mol

$n(HCl) = 0.1 \times 0.100 = 0.0100$ mol

NaOH is the limiting reactant.

All 0.0050 mol NaOH will neutralise 0.0050 mol HCl remaining $n(HCl) = 0.0100 - 0.0050 = 0.0050$ mol

$[H^+] = \frac{0.0050}{0.150} = 0.033$ M

$pH = -\log 0.033 = 1.5$

b $n(HCl) = 0.2 \times 0.05 = 0.01$ mol

$n(NaOH) = 0.1 \times 0.1 = 0.01$ mol

$pH = 7$ because $[H^+] = [OH^-]$

c $[H^+] = 10^{-6}$ M

New $[H^+] = \frac{10^{-6}}{2} = 5 \times 10^{-7}$ M (dilution halves the concentration)

$pH = -\log(5 \times 10^{-7}) = 6.3$

8 $n(HNO_3) = 0.2 \times 0.5 = 0.1$ mol

$n(Ba(OH)_2) = \frac{0.1}{2} = 0.05$ mol (according to balanced equation)

$m(Ba(OH)_2) = 0.05 \times 171.35 = 8.6$ g

9 $n(HCl) = 0.277 \times 0.1 = 0.0277$ mol

$n(NaOH) = 0.0277$ mol (according to balanced equation)

$V(NaOH) = \frac{0.0277}{0.1} = 0.277$ L or 277 mL

10 $n(Ba(OH)_2) = 0.108 \times 0.038\,95 = 4.2 \times 10^{-3}$ mol

$n(OH^-) = 2 \times 4.2 \times 10^{-3} = 8.4 \times 10^{-3}$ mol

$n(HNO_3) = 0.116 \times 0.044\,86 = 5.2 \times 10^{-3}$ mol

Excess $OH^- = 8.4 \times 10^{-3} - 5.2 \times 10^{-3} = 3.2 \times 10^{-3}$ mol

$c(OH^-) = \frac{3.2 \times 10^{-3}}{0.038\,95 + 0.04\,486} = 0.038$ M

$pOH = -\log_{10} 0.038 = 1.42$

$pH = 14 - 1.42 = 12.58$

11 $n(HCl) = 1.087 \times 0.025 = 0.027$ mol in 25 mL

$c(HCl) = \frac{0.027}{0.25} = 0.1087$ M in 250 mL

$n(HCl) = 0.1087 \times 0.020 = 2.174 \times 10^{-3}$ mol in 20 mL

$c(HCl) = \frac{2.174 \times 10^{-3}}{0.1} = 0.021\,74$ M in 100 mL

$[H^+] = 0.021\,74$ M

$pH = -\log_{10} 0.021\,74 = 1.66$

$pOH = 14 - 1.66 = 12.34$

12 $[H^+] = 10^{-1.00} = 0.1$ M; $[H^+] = 10^{-2.00} = 0.01$ M

$n(H^+) = 0.1 \times 0.5 = 0.05$ mol at pH 1.00

$V(H_2O) = \frac{0.05}{0.01} = 5$ L

Therefore, 4.5 L of water needs to be added to the 500 mL of solution with a pH of 1.00 to make the pH 2.00.

CHAPTER EXAM

MULTIPLE CHOICE

1 C
2 C
3 D
4 D
5 D
6 C
7 C
8 D
9 A
10 A

SHORT RESPONSE

11 Both are strong acids because they are 100% dissociated. X must be diprotic and Y must be monoprotic. Therefore, X = H_2SO_4 and Y = HCl (or HNO_3).

12 a For pOH = 6: 1×10^{-6} M

b For pOH = 11.7: 2×10^{-12} M

13 a 2

b 12

c 13

d 2

CROSS-CHAPTER QUESTION

14 a i $[H^+] = 5.5 \times 10^{-8}$ M; pH = 7.3

ii $[H^+] = 1.7 \times 10^{-7}$ M; pH = 6.8

b As the temperature increases, K_w increases, resulting in an increase in $[H^+]$ or a decrease in pH. This indicates that the self-ionisation of water is an endothermic process. As the temperature increases, the products side is favoured.

c Adding NaOH increases $[OH^-]$. This results in the reactants being favoured. $[H^+]$ will decrease and the pH will increase.

d Adding $AgNO_3$ will cause OH^- to precipitate out as AgOH(s), reducing $[OH^-]$. The system will respond by favouring the production of OH^-. Production of OH^- also means production of H^+.

Overall the change will only be partially counteracted, so $[OH^-]$ will be less than before addition, $[H^+]$ will be greater than before addition and pH will decrease

e If the pH falls as temperature increases, this does *not* mean that water becomes more acidic at higher temperatures. A solution is acidic if there is an *excess* of hydrogen ions over hydroxide ions. In the case of pure water, there are always the same concentration of hydrogen ions and hydroxide ions, and hence the water is still neutral – even if its K_w changes.

DATA ANALYSIS

15 Calculate pH for all acids to be able to compare them.

A: $[H^+] = \frac{1.00 \times 10^{-14}}{5.0 \times 10^{-11}} = 2.0 \times 10^{-4}$ M

$pH = -\log(2.0 \times 10^{-4}) = 3.70$

B: $pH = -\log 0.20 = 0.70$

C: $pH = 14 - 11.30 = 2.70$

D: pH = 1.20

In order of decreasing acidity means from most acidic (lowest pH) to least acidic (highest pH) — B, D, C, A.

CHAPTER 5 BRØNSTED–LOWRY MODEL

LEARNING CHECK 5.1

DESCRIBING

1 The Arrhenius definition: acids produce H^+ ions in solution; bases produce OH^- ions in solution.

2 a A Brønsted–Lowry acid is a substance that donates one or more protons or hydrogen ions (H^+).

b A Brønsted–Lowry base is a substance that accepts one or more protons.

c A conjugate acid–base pair is a pair in a reaction that differs from each other by one proton.

d A conjugate acid is the acid that is formed when a base accepts a proton from an acid.

e A conjugate base is the base that is formed when an acid donates a proton to a base.

3 According to the Arrhenius theory of acids and bases, the carbonate ion (CO_3^{2-}) should not have any basic properties because it is unable to produce hydroxide ions OH^- in solution. However, carbonate compounds exhibit basic properties – high pH, reactions with acids and so on. The Brønsted–Lowry definition can explain the basic properties of carbonates by defining a base as a substance that can accept one or more H^+ ions from an acid.

APPLYING

4 a HF/F^-; H_2O/H_3O^+

b NH_4^+/NH_3; H_2O/H_3O^+

c HSO_4^-/SO_4^{2-}; O^{2-}/OH^-

d $H_2PO_4^-/HPO_4^{2-}$; CO_3^{2-}/HCO_3^-

e $HC_2H_3O_2/C_2H_3O_2^-$; HS^-/H_2S

5 **a** H_2CO_3
b H_2O
c $H_2PO_4^-$
d $(CH_3)_2NH_2^+$
e H_3O^+

6 **a** F^-
b HSO_4^-
c $H_2PO_4^-$
d CH_3COO^-
e OH^-

7 Only a, d, e contain acid–base conjugate pairs.

LEARRNING CHECK 5.2

DESCRIBING

1 An amphiprotic substance is a molecule that contains a proton that can be donated as well as being able to accept an additional proton.

APPLYING

2 HCO_3^- is amphiprotic because it can act as an acid or a base.

As an acid: $HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$

As a base: $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

3 HSO_4^- is amphiprotic because it can act as an acid or a base.

As an acid: $HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$

As a base: $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_2SO_4(aq) + OH^-(aq)$

LEARNING CHECK 5.3

DESCRIBING

1 A buffer is a solution that resists changes in pH when acid or alkali is added to it.

2 A solution of ammonia and ammonium chloride.

APPLYING

3 Only b can be used to make an acidic buffer solution.

4 Sodium methanoate, CH_3ONa

5 **a** This is a solution of a weak base in equilibrium with its conjugate acid. The pH will depend on the relative amounts of these substances but will be about 8–9.

b $CH_3CH_2NH_2(aq) + H_2O(l) \rightarrow CH_3CH_2NH_3^+(aq) + OH^-(aq)$

The Cl^- is a spectator ion and plays no part in the system.

c Initially, pH drops due to H_3O^+ from the HCl. Then, more $CH_3CH_2NH_2$ reacts, producing more OH^- ions, which neutralise the excess H_3O^+. The pH returns to close to its original value:

$CH_3CH_2NH_2(aq) + H_2O(l) \rightarrow CH_3CH_2NH_3^+(aq) + OH^-(aq)$

The conjugate acid ($CH_3CH_2NH_3^+$) reacts with the excess OH^- ions.

The equilibrium is restored and the pH decreases to close to its original value.

CHAPTER EXAM

MULTIPLE CHOICE

1 A
2 C
3 A
4 C
5 D
6 D
7 B
8 D
9 C
10 A

SHORT RESPONSE

11 $NH_4^+(s) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

12 Amphiprotic substance

13 $HCOO^-/HCOOH$ is a conjugate weak base/acid pair. Any acid that is added to the buffer system will react with $HCOO^-$, thus maintaining the pH by removing H_3O^+: $HCOO^- + H_3O^+ \rightarrow HCOOH + H_2O$. Any base that is added to the buffer system will react with the HCOOH, thus maintaining the pH by removing the OH^-: $HCOOH + OH^- \rightarrow HCOO^- + H_2O$.

CROSS-CHAPTER QUESTION

14 **a** Acid H_3O^+ and conjugate base H_2O. Base HCO_3^- and conjugate acid H_2CO_3.

b $K_c = \dfrac{[H_2CO_3]}{[H_3O^+][HCO_3^-]}$

c $H_3O^+(aq) + HCO_3^-(aq) \rightleftharpoons CO_2(aq) + 2H_2O(l)$

d i Removing CO_2 will cause the reaction to favour the forward reaction, decreasing the concentration of H^+. This causes an increase in pH

ii Removing hydrogencarbonate ions causes the reaction to favour the backwards reaction. This increases the concentration of H^+, decreasing the pH.

e $[H^+] = 10^{-7.4} = 4.0 \times 10^{-8}$ M

DATA ANALYSIS

15 **a** Brønsted–Lowry acid: CH_3COOH.
Brønsted–Lowry base: CH_3COO^-

b Solution A: pOH = 14 − 4.76 = 9.24
Solution B: pOH = 14 − 2.87 = 11.13

c Solution A contains both CH_3COOH and CH_3COO^-, which form a buffer. When HCl is added, the extra H^+ ions are removed by CH_3COO^- through proton transfer, forming CH_3COOH. This limits the pH change. In contrast, Solution B contains only CH_3COOH and no conjugate base to absorb added H^+, so the pH drops more sharply.

d In Solution A, CH_3COOH donates protons to react with added OH^-, forming water and CH_3COO^-. This minimises the pH increase.

Solution B lacks a conjugate base–acid pair, so OH^- is not neutralised effectively, resulting in a large increase in pH.

e Solution A is a buffer. It shows only small pH changes after acid or base is added (4.76 → 4.68 or 4.83), unlike Solution B, which has large pH changes (2.87 → 1.92 or 5.27).

CHAPTER 6 DISSOCIATION CONSTANTS

LEARNING CHECK 6.1

DESCRIBING

1 The equilibrium expression of a weak acid or a weak base

APPLYING

2 **a** $H_2CO_3(aq) + 2H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + 2H_3O^+(aq)$

$$K_a = \frac{[CO_3^{2-}][H_3O^+]^2}{[H_2CO_3]}$$

b $NH_2OH(aq) + H_2O(l) \rightleftharpoons NH_3OH^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_3OH^+][OH^-]}{[NH_2OH]}$$

c $HOCl(aq) + H_2O(l) \rightleftharpoons OCl^-(aq) + H_3O^+(aq)$

$$K_a = \frac{[OCl^-][H_3O^+]}{[HOCl]}$$

3 Hydrofluoric, methanoic, lactic, ethanoic, ammonium ion and hydrocyanic acid

4 Phosphine, phenylamine, hydrazine, ammonia, methylamine, ethylamine

5 **a** $C_6H_7O_6^-(aq) + H_2O(l) \rightarrow C_6H_8O_6(l) + OH^-(aq)$

b $K_a \times K_b = K_w$

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{7.9 \times 10^{-5}}$$

$$= 1.3 \times 10^{-10}$$

6 **a** $C_5H_6N^+(aq) + H_2O(l) \rightarrow C_5H_5N(aq) + H_3O^+(aq)$

b $K_a \times K_b = K_w$

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times -14^{-14}}{1.7 \times 10^{-9}}$$

$$= 5.9 \times 10^{-6}$$

7 $pK_a = -\log(1.38 \times 10^{-4}) = 3.86$.
$pK_b = 14 - 3.86 = 10.14$
$K_b = 10^{-10.14} = 7.24 \times 10^{-11}$

8 $pK_b = -\log(1.3 \times 10^{-6}) = 5.9$.
$pK_a = 14 - 5.9 = 8.1$
$K_a = 10^{-8.1} = 7.9 \times 10^{-9}$

LEARNING CHECK 6.2

APPLYING

1 **a** $[H^+] = 10^{-2.37} = 4.3 \times 10^{-3}$ M

b $[HCOO^-] = 4.3 \times 10^{-3}$ M

c $[HCOOH]_{eq} = 0.1 - 4.3 \times 10^{-3} = 0.0957$

$$K_a = \frac{(4.3 \times 10^{-3})^2}{0.0957} = 1.93 \times 10^{-4}$$

d $$\% \text{ ionisation} = \frac{4.3 \times 10^{-3}}{0.1} \times 100 = 4.3\%$$

2 **a** $[OH^-] = 1.26 \times 10^{-3}$ M

b $[NH_4^+] = 1.26 \times 10^{-3}$ M

c $[NH_3]_{eq} = 0.1 - 1.26 \times 10^{-3} = 0.0987$

$$K_a = \frac{(1.26 \times 10^{-3})^2}{0.0987} = 1.6 \times 10^{-5}$$

d $$\% \text{ ionisation} = \frac{1.26 \times 10^{-3}}{0.1} \times 100 = 1.26\%$$

3 $[H_3O^+] = 10^{-2.96} = 1.10 \times 10^{-3}$ M

$$\% \text{ ionisation} = \frac{1.10 \times 10^{-3}}{0.30} \times 100 = 0.37\%$$

4 $[H_3O^+] = 10^{-2.22} = 6.03 \times 10^{-3}$ M

$[HNO_2]_{eq} = 0.050 - 6.03 \times 10^{-3}$

$= 0.04397$

$$K_a = \frac{(6.03 \times 10^{-3})^2}{0.043\,97} = 8.27 \times 10^{-4}$$

5 $$K_b = \frac{[OH^-]^2}{0.2} = 5.4 \times 10^{-4}$$

$[OH^-] = 1.04 \times 10^{-2}$ M

$pOH = -\log(1.04 \times 10^{-2}) = 1.98$

$pH = 14 - 1.98 = 12.02$

6 $$K_a = \frac{[H^+]^2}{0.2} = 1.7 \times 10^{-5}$$

$[H^+] = 1.84 \times 10^{-3}$ M

$pH = -\log(1.84 \times 10^{-3}) = 2.7$

7 a $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$

b $K_{a1} = \dfrac{[HCO_3^-][H_3O^+]}{[H_2CO_3]}$

$K_{a2} = \dfrac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]}$

c $K_b = 2.1 \times 10^{-4}$

CHAPTER EXAM

MULTIPLE CHOICE

1 A
2 D
3 B
4 A
5 B
6 D
7 C
8 B
9 C
10 B

SHORT RESPONSE

11 $K_a = \dfrac{1.00 \times 10^{-14}}{4.3 \times 10^{-5}} = 2.33 \times 10^{-5}$

12 a $H_3PO_4(aq) + H_2O(l) \rightarrow H_2PO_4^-(aq) + H_3O^+(aq)$

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

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

b The strongest conjugate base would be from the third dissociation, find K_b for PO_4^{3-}:

$K_b = \dfrac{1.00 \times 10^{-14}}{4.5 \times 10^{-13}} = 2.2 \times 10^{-2}$

c pH = 4.1. Assumptions made: At equilibrium, $[H_2PO_4^-]$ is the same as the initial concentration; the weak acid only ionises to a small degree in water.

13 % ionisation $= 1.6 \times 10^{-3}\%$

CROSS-CHAPTER QUESTION

14 a $K_a = \dfrac{[H_3O^+]^2}{[HA]}$

$= \dfrac{(9.70 \times 10^{-5})^2}{0.200}$

$= 4.70 \times 10^{-8}$

Acid A is a weaker acid than acid B, because acid A has a lower K_a value than acid B.

b $C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^-(aq) + H_3O^+(aq)$

c The conjugate base ($C_6H_5COO^-$) is not amphiprotic because it can accept a H^+, but it cannot donate one.

d $C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$

$K_a = \dfrac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]}$

$= \dfrac{[H^+]^2}{[C_6H_5COOH]}$

$6.3 \times 10^{-5} = \dfrac{[H^+]^2}{0.100}$

$[H^+]^2 = 6.3 \times 10^{-6}$

$[H^+] = \sqrt{6.3 \times 10^{-6}}$

$[H^+] = 2.51 \times 10^{-3}$ M

$pH = -\log(2.51 \times 10^{-3})$

$= 2.60$

e Because $[H^+]$ is 10 times greater at a pH of 2 than a pH of 3, the final volume would need to be:
0.100 00 × 10 = 1.000 L
Therefore an additional
900 mL is needed.

DATA ANALYSIS

15 a 25°C: pOH = 14 − 10.44 = 3.56

$[OH^-] = 10^{-3.56} = 2.75 \times 10^{-4}$ M

35°C: pOH = 14 − 10.29 = 3.71

$[OH^-] = 10^{-3.71} = 1.95 \times 10^{-4}$ M

b 25°C: $K_b = 3.78 \times 10^{-7}$. 35°C: $K_b = 1.90 \times 10^{-7}$

c Similarity: Both values of K_b are small, indicating that ammonia is weak at both temperatures. Differences: K_b decreases as the temperature increases.

d The results show a decrease in K_b with increasing temperature, suggesting that the dissociation of ammonia is likely exothermic. As a result, raising the temperature reduces the extent of dissociation, which is consistent with exothermic equilibrium behaviour. According to Le Châtelier's principle, the formation of reactants is favoured.

e Inaccurate pH readings: pH meters might have been improperly calibrated leading to errors in the $[OH^-]$.

Temperature fluctuations in the classroom: Maintaining a constant temperature during the experiment is challenging; this can cause variations in the dissociation.
Concentration inconsistencies: The ammonia solutions might not be the correct concentration affecting the dissociation constant.
Assumption of negligible $[OH^-]$ loss: The assumption that $[OH^-]$ does not significantly reduce $[NH_3]$, but at higher concentrations, this assumption might not be correct, leading to minor inaccuracies.

f % error (25°C) = 97.9%. At 35°C, the experimental K_b continues to decrease, showing that the error persists at higher temperatures. The experimental K_b is significantly lower than the literature value. This suggests that the experimental conditions may not have been the ideal conditions under which the literature value was determined. The experimental set-up needs to be refined to improve the accuracy.

CHAPTER 7 TITRATIONS

LEARNING CHECK 7.1

DESCRIBING

1 a Indicator: a substance that changes colour in solution depending on whether the solution is acidic or basic.

b Indicator (acid form): the form of the indicator that can donate a proton to a base.

c Indicator (basic form): the form of the indicator that can accept a proton from an acid.

2 $HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$

3 $K_a = \dfrac{[In^-][H_3O^+]}{[HIn]}, K_b = \dfrac{[HIn]}{[In^-][H_3O^+]}$

APPLYING

4 Colour change occurs when pH of the solution = pK_a.
Useful pH range = pH ± 1 = 5.2 − 7.2

5 pH at end point = pK_a (indicator)

$$= -\log_{10}(7.9 \times 10^{-5}) = 4.1$$

6 Since:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{[H^+]^2}{1.0}$$

$$[H^+] = \sqrt{K_a \times 1.0}$$

And pH = $-\log[H^+]$

Bromoacetic acid:

$$[H^+] = \sqrt{1.4 \times 10^{-3} \times 1.0}$$
$$= 0.0347$$
$$pH = -\log(0.0347) = 1.43$$

Hypochlorous acid:

$$[H^+] = \sqrt{3.0 \times 10^{-8} \times 1.0}$$
$$= 5.48 \times 10^{-5}$$
$$pH = -\log(5.48 \times 10^{-5}) = 4.26$$

Hypoiodous acid:

$$[H^+] = \sqrt{2.3 \times 10^{-11} \times 1.0}$$
$$= 4.8 \times 10^{-6}$$
$$pH = -\log(4.8 \times 10^{-6}) = 5.32$$

Methyl red turns red in a pH of < 4 and yellow at a pH >5

m-cresol purple turns red in a pH <1 and yellow at pH >3

Alizarin red s turns yellow at pH <4 and red at pH >5

Therefore according to the results, Solution A is hypochlorous acid. Solution B is bromoacetic acid. Solution C is hypoiodous acid.

LEARNING CHECK 7.2

DESCRIBING

1 a End point: the pH of an acid–base titration at which the chosen indicator changes colour

b Equivalence point: the point when the reactants are present in the ratio shown by the mole ratio in the balanced chemical equation for the reaction

APPLYING

2

Acid	Base	Products	Equivalence point	Indicator
Propanoic	Sodium hydroxide	Sodium propanoate	9	Phenolphthalein
Nitric acid	Ammonia	Ammonium nitrate	4–5	Methyl orange
Hydrochloric	Potassium hydroxide	Potassium chloride	7	Bromothymol blue
Ethanoic	Ammonia	Ammonium acetate	None visible	NA

3 a Bromophenol blue

b Phenolphthalein

4 a Yellow to blue: The base form is yellow, so when equivalence point is reached, the acid form of the indicator is dominant, which is blue.

b Weak acid/strong base

LEARNING CHECK 7.3

ANALYSING

1 $n((COOH)_2.2H_2O) = \dfrac{0.291}{126.08} = 2.31 \times 10^{-3}$ mol

$n(KOH) = 2.31 \times 10^{-3} \times 2 = 4.62 \times 10^{-3}$

$[KOH] = \dfrac{4.62 \times 10^{-3}}{0.018\,12} = 0.254$ mol L^{-1}

2 a $n(Na_2CO_3) = \dfrac{5.267}{105.99} = 0.049\,69$ mol

$[Na_2CO_3] = \dfrac{0.049\,69}{0.250} = 0.1988$ mol L^{-1}

$n(Na_2CO_3)$ in 10 mL = 0.1988×0.010
$= 1.988 \times 10^{-3}$ mol

$n(HCl) = 1.988 \times 10^{-3} \times 2 = 3.976 \times 10^{-3}$ mol

$[HCl] = \dfrac{3.96 \times 10^{-3}}{0.0213} = 0.187$ mol L^{-1}

b $n(HCl) = 0.187 \times 0.0271 = 5.04 \times 10^{3}$ mol

$n(Ba(OH)_2) = \dfrac{5.10 \times 10^{-3}}{2} = 2.55 \times 10^{-3}$ mol

$[Ba(OH)_2] = \dfrac{2.55 \times 10^{-3}}{0.025} = 0.102$ mol L^{-1}

c $m(Ba(OH)_2) = 0.102 \times 171.35 = 17.5$ g L^{-1}

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

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

c $n(HCl) = 0.015\,14 \times 0.038\,83 = 5.881 \times 10^{-4}$ mol

$n(OH^-) = 5.881 \times 10^{-4}$ mol

$[OH^-] = \dfrac{5.881 \times 10^{-4}}{0.02500} = 0.023\,52$ mol L^{-1}

d $[Ca^{2+}] = \dfrac{[OH^-]}{2} = \dfrac{0.023\,52}{2}$

$= 0.01176$ mol L^{-1}

e $K_{sp} = [Ca^{2+}][OH^-]^2 = (0.011\,76)(0.023\,52)^2$

$= 6.50 \times 10^{-6}$

LEARNING CHECK 7.4

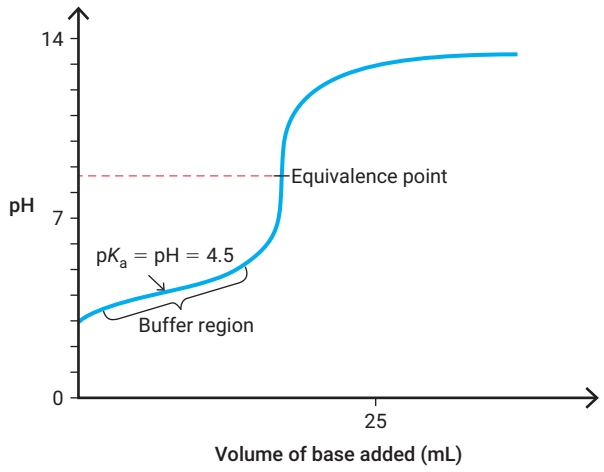
DESCRIBING

1 a Titration curve: A graphical representation of a titration with the *x*-axis being the volume of titrant added and the *y*-axis being the pH of the solution.

b Buffer region: The part of a titration curve during which the pH changes little as titrant is added. Occurs when one of the reagents is a weak acid or a base and is the result of a buffer solution being set up.

c Half-equivalence point: The point at which exactly half of the acid in the buffer solution has reacted with the titrant.

2



APPLYING

3 $n(KOH) = 0.100 \times 0.020\,00 = 0.002\,00$ mol

Volume of propanoic acid required to reach equivalence point is 12 mL. Since the ratio is a 1:1

$c(CH_3CH_2COOH) = \dfrac{0.00200}{0.012}$

$= 0.167$ mol L^{-1}

4 a HCl/NH_3 – high conductivity initially, indicating strong acid (HCl). Conductivity decreases gradually to the neutralisation point, after which conductivity rises gradually to a low maximum conductivity, indicating a weak base (NH_3).

b HCl/KOH – high conductivity initially, indicating strong acid (HCl). Conductivity decreases rapidly to the neutralisation point, after which the conductivity increases rapidly, indicating a strong base (KOH).

c CH_3COOH/KOH – low conductivity initially, indicating weak acid (CH_3COOH). Conductivity decreases after which conductivity rises slowly towards the equivalence point. After the equivalence point, there is excess OH^- which are very conductive, therefore theres a sharp increase in conductivity.

CHAPTER EXAM

MULTIPLE CHOICE

1 C
2 B
3 C
4 D
5 B
6 C
7 D
8 B
9 A
10 B

SHORT RESPONSE

11 Analyte

12 a $Ca(OH)_2(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$

$n(HCl) = 0.100 \times 0.038\,50$

$= 3.85 \times 10^{-3}$ mol

$n(Ca(OH)_2)$: $n(HCl)$ is a 1:2, therefore:

$n(Ca(OH)_2) = \dfrac{1}{2} \times 3.85 \times 10^{-3}$

$= 1.925 \times 10^{-3}$

$c(Ca(OH)_2) = \dfrac{1.25 \times 10^{-3}}{0.025\,00}$

$= 0.0770$ M

Therefore the solubility is 0.0770 mol L^{-1}

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

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

Since $[Ca^{2+}] = 0.0770$ M

$[OH^-] = 2 \times 0.0770 = 0.154$ M

$K_{sp} = (0.0770)(0.154)^2$

$= 1.82 \times 10^{-3}$

13 Citric acid

14 $n(HNO_3) = 0.151 \times 0.0262 = 0.003\,96$ mol

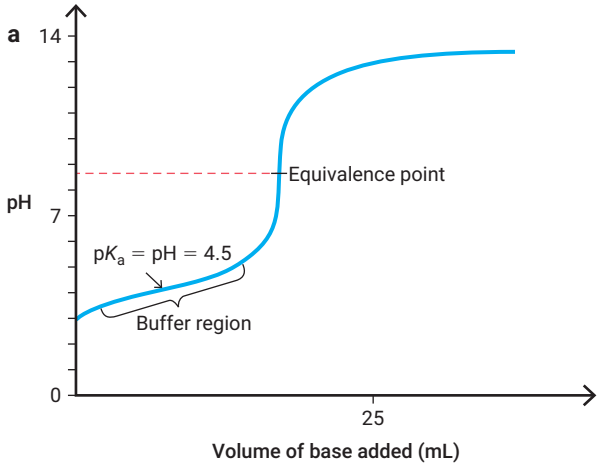
$n(NH_3) = 0.003\,96$ mol

$n(NH_3)$ in 500 mL $= 0.003\,96 \times 20 = 0.0792$ mol

$[NH_3] = \dfrac{0.0792}{0.5} = 0.158$ mol L^{-1}

CROSS-CHAPTER QUESTION

15 a



b In the buffer region, the solution consists of a weak acid (CH_3COOH) and its conjugate base (CH_3COO^-):
$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
As more NaOH is added, the forward reaction is favoured, producing more H_3O^+, which neutralises the OH^-. Although the pH rises, it does so gradually, producing the buffer region.

c From the graph, the pH of the equivalence is about 8.5. At this point, just enough NaOH has been added to neutralise the H_3O^+. The only species present are $H_2O(l)$ (pH 7), Na^+ ions (no acidic or basic properties) and ethanoate ions (CH_3COO^-). The ethanoate ion is the conjugate base of a weak acid and, as such, is a weak base:
$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
The ethanoate ion has a pH of 8–9.

d This is the initial pH of the ethanoic acid.

e $K_a = \dfrac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$

f From the graph, the pH at the midpoint of the buffer region is the pK_a of the acid.
$pK_a = 4.5$
$K_a = 3.16 \times 10^{-5}$

g The addition of sodium ethanoate increases the concentration of CH_3COO^-, which will shift the equilibrium to the left, decreasing the concentration of H_3O^+ and thus increasing the pH of the solution.

h If a strong acid is added to the solution, the H_3O^+ concentration increases. This will shift the equilibrium to the right. A strong acid will overwhelm the buffer capacity of the solution and the pH will decrease becoming more acidic.

DATA ANALYSIS

16 a Equivalence point = pH 4.5. Bromocresol green ($pK_a = 4.7$; range = 3.8 – 5.4)

b Equivalence point = pH 8.5. Phenolphthalein ($pK_a = 9.3$; range = 8.3 – 10.3)

c Equivalence point = pH 7. Phenolphthalein is used because the pH changes so rapidly. (Could also use bromothymol blue.)

CHAPTER 8 REDOX REACTIONS

LEARNING CHECK 8.1

DESCRIBING

1 a Oxidation: loss of electrons

b reduction: gain of electrons

c Half-equation: an equation that shows only the oxidation reaction or the reduction reaction

2 Oxidation and reduction are complementary processes involving the transfer of electrons. For a substance to lose electrons (oxidation), another substance must be present to gain those electrons (reduction).

APPLYING

3 a i, ii, iv and v

b i K oxidised, O reduced

ii Cu oxidised, Cl reduced

iii Zn oxidised, Fe reduced

iv C oxidised, O reduced

c i, corrosion, iv, metal displacement, v, combustion

4 a $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ oxidation
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ reduction

b $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ oxidation
$Ag^+(aq) + e^- \rightarrow Ag(s)$ reduction

5 a $4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

b Aluminium has lost electrons so has been oxidised, while oxygen has gained electrons so has been reduced.

ANALYSING

6 a Yes, Zn is higher in the reactivity series than Ag.

b No, Zn is lower in the series than Na.

c Yes, Mg is higher in the reactivity series than Cu.

d Yes, Fe is higher in the reactivity series than Cu.

7 a i Mg is a more reactive metal than Fe so the electrons would flow from the Mg metal to the Fe^{2+} ions.

ii No reaction will occur. Zn is a more reactive metal than Fe so Zn metal would donate electrons Fe^{2+} ions; however, as zinc is in ionic form it has already been oxidised so no further reaction will occur.

b i Mg is being oxidised, Fe^{2+} is being reduced.

8 a i Cu^{2+} has gained 2 electrons to become Cu; therefore, the C must have lost electrons.

ii Oxygen has gained 2 electrons to become O^{2-} in the ionic compound ZnO. Zn is the same on both sides of the equation as Zn^{2+}; therefore, S must have lost electrons to the oxygen.

b i Copper reduced, carbon oxidised

ii Oxygen reduced; sulfur oxidised

LEARNING CHECK 8.2

DESCRIBING

1 a Oxidising agent: a substance that causes another substance to be oxidised

b Reducing agent: a substance that causes another substance to be reduced

c Oxidation state: the number of electrons that an atom would have gained or lost to get to its present state; it assumes that each species is completely ionic

2 Transition metals can have several oxidation states, so it is important to specify the oxidation state of the transition metal in compounds. This is done by writing the oxidation state as roman numerals in brackets after the name of the metal in the compound name.

APPLYING

3 a O_2

b CuO

4 a Fe^{2+}

b H_2

5 a +5

b −1

c +5

d +6

e +5

6 a +6

b +4

c −1

d −1

7 a Oxidised

b Oxidised

c Reduced

d Oxidised

e Neither

f Oxidised

8 a Copper(I) oxide

b Vanadium(IV) nitrate

c Nickel(III) chloride

ANALYSING

9 The redox reactions are a, b, d, e

10 For a reaction a:

a Bromine −1 to 0

b Cl_2

For reaction b:

a Iodine −1 to +5

b Mn^{3+}

For reaction d:

a Sulfur −2 to +4

b Oxygen

For reaction e:

a Phosphorus +3 to +5

b Chlorine

LEARNING CHECK 8.3

APPLYING

1 a $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

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

$Mg(s) + Br_2(l) \rightarrow Mg^{2+}(aq) + 2Br^-(aq)$

b $Na(s) \rightarrow Na^+(aq) + e^-$

$O_2(g) + 4e^- \rightarrow 2O^{2-}(aq)$

$4Na(s) + O_2(g) \rightarrow 4Na^+(aq) + 2O^{2-}(aq)$

c $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

$N_2(g) + 6e^- \rightarrow 2N^{3-}(aq)$

$2Al(s) + N_2(g) \rightarrow 2Al^{3+}(aq) + 3N^-(aq)$

2 a $NO_2(g) + H_2O(l) \rightarrow NO_3^-(aq) + 2H^+(aq) + e^-$ oxidation

b $2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2e^-$ oxidation

c $2H^+(aq) + 2HOCl(aq) + 2e^- \rightarrow Cl_2(g) + 2H_2O(l)$ reduction

d $C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$ oxidation

e $SO_2(g) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$ oxidation

f $ClO_3^-(aq) + 2H^+(aq) + e^- \rightarrow ClO_2(g) + H_2O(l)$ reduction

3 a $14H^+(aq) + 3Sn^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 3Sn^{4+}(aq) + 7H_2O(l)$

b $5C_2O_4^{2-}(aq) + 16H^+(aq) + 2MnO_4^-(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

c $3Ca(s) + 2P(s) \rightarrow Ca_3P_2(s)$

d $2K(s) + F_2(g) \rightarrow 2K^+(aq) + 2F^-(aq)$

4 a $2H^+(aq) + Cr_2O_7^{2-}(aq) + 3SO_2(g) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_2O(l)$

b $4H^+(aq) + 2NO_3^-(aq) + Ni(s) \rightarrow Ni^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$

5 a $16H^+(aq) + 2MnO_4^-(aq) + 10Cl^-(aq) \rightarrow 2Mn^{2+}(aq) + 5Cl_2(g) + 8H_2O(l)$

b $8H^+(aq) + Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(l)$

CHAPTER EXAM

MULTIPLE CHOICE

1 A
2 B
3 D
4 C
5 A
6 A
7 B
8 D
9 A
10 C

SHORT RESPONSE

11 a False – oxidation occurs when a species loses electrons.

b True

c False – magnesium is more reactive than copper and oxidises preferentially in the presence of copper.

d False – a reducing agent loses electrons.

e True

12 a Carbon's oxidation state changes from −2.66 to +4, so it has been oxidised. Oxygen's oxidation state changes from 0 to −2, so it has been reduced. The reaction involves a species being oxidised and a species being reduced therefore it is a redox reaction.

b O_2 is the oxidising agent.

CROSS-CHAPTER QUESTION

13 a 101 mL

b $H_2O(l) + C_2H_5OH(aq) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$

c i Trial 2 produced a significantly different result from Trial 1, so additional trials were necessary to achieve at least three consistent results.

ii The mean titre is obtained by averaging trial results. Because Trial 2 was an anomalous result, it was discounted. The mean calculation is:

$$\frac{20.60 + 20.64 + 20.62}{3} = 20.62 \text{ mL}$$

iii 1.55×10^{-3} mol

iv Stoichiometric ratio $Cr_2O_7^{2-}$ to C_2H_5OH = 2:3. $n(C_2H_5OH) = 2.32 \times 10^{-3}$ mol

v 2.32×10^{-2} mol

DATA ANALYSIS

14 a Iron nail: blue at both ends, pink in the middle

Blue: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

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

Corrosion, which is oxidation of iron has occurred at both ends of the nail

Iron nail wrapped with copper wire: blue all along the nail

Blue: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

Iron is more reactive than copper; therefore it undergoes corrosion (oxidises) while the copper does not.

Iron nail wrapped with zinc strip: pink at either end; no blue areas

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

Zinc is more reactive than iron, so the zinc corrodes (oxidises) instead of the iron.

b White deposit is zinc hydroxide, $Zn(OH)_2$.

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

15 a $2X^{3+}(aq) + Y(s) \rightarrow 2X^{2+}(aq) + Y^{2+}(aq)$

$Z_2(aq) + Y(s) \rightarrow 2Z^-(aq) + Y^{2+}(aq)$

b i From the results, it can be seen that Z_2 does not oxidise $X^{2+}(aq)$. This means that the reverse reaction where Z^- reduces X^{3+} will occur.

ii X^{3+} oxidises Y so the reverse reaction where Y^{2+} oxidises X^{2+} cannot occur. No reaction.

iii Z_2 oxidises Y so the reverse reaction where Y^{2+} oxidises Z^- cannot occur. No reaction.

c $X^{3+} > Z_2 > Y^{2+}$

X^{3+} is a stronger oxidising agent than Y^{2+} because it oxidises Y.

Z_2 is a stronger oxidising agent than Y^{2+} because it oxidises Y therefore Y^{2+} is the weakest oxidising agent. Z_2 does not oxidise X^{2+} so it is a weaker oxidising agent than X^{3+}.

CHAPTER 9 GALVANIC CELLS

LEARNING CHECK 9.1

DESCRIBING

1 An electrochemical cell allows the transformation of energy between chemical potential energy and electrical energy.

2 a Galvanic cells (or voltaic cells) and electrolytic cells.

b

Galvanic cells	Electrolytic cells
Transforms chemical potential energy into electrical energy.	Transforms electrical energy into chemical potential energy.
Chemical reactions occur spontaneously.	Chemical reactions are not spontaneous.

3 A metal reactivity series ranks metals from most to least reactive. It can be used to determine whether a metal will react with the ions of another metal and so identify oxidation and reduction processes occurring.

APPLYING

4 **a** Reactions will occur in set-ups i and ii.

b **i** $Zn(s) + Pb(NO_3)_2(aq) \rightarrow Pb(s) + Zn(NO_3)_2(aq)$

ii $Sn(s) + 2AgNO_3(aq) \rightarrow Sn(NO_3)_2(aq) + 2Ag(s)$

5 During operation of the cell, the $Cu^{2+}(aq)$ ions are reduced to Cu(s) atoms. Since the $Cu^{2+}(aq)$ ions are responsible for the blue colour, this colour eventually fades.

6 **a** **i** Left to right

ii Right to left

iii Right to left

b **i** $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$ oxidation
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ reduction

ii $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ oxidation
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ reduction

iii $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$ oxidation
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ reduction

c One half-cell would need to contain a strip of aluminium metal suspended in a solution containing Al^{3+} ions, e.g. $Al(NO_3)_3$ the other half-cell would need to contain a strip of zinc metal suspended in a solution containing Zn^{2+} ions, e.g. $Zn(NO_3)_2$.

LEARNING CHECK 9.2

DESCRIBING

1 **a** Anode: the electrode where oxidation occurs

b Cathode: the electrode where reduction occurs

c Electrolyte: a substance that conducts an electric current

2 According to the metal reactivity series, magnesium is a more active metal than lead. It will be oxidised:

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

The magnesium metal will slowly react – its mass will decrease.

3 If the Al(s) and $Sn^{2+}(aq)$ were mixed, a spontaneous reaction would take place, with electrons transferring instantaneously between the reactants rather than passing through a wire where they can be utilised.

4 It must be soluble, and it must form only soluble salts when in contact with other solutions.

5 NO_3^-. In the oxidation half-cell. the metal electrode is oxidised, positively charged metal ions move into solution. These are balanced by negatively charged nitrate ions moving into the solution from the salt bridge.

APPLYING

6 During the operation of the cell, the zinc metal of the anode is oxidised to Zn^{2+} ions. Eventually all the zinc anode has reacted and no more current flows.

ANALYSING

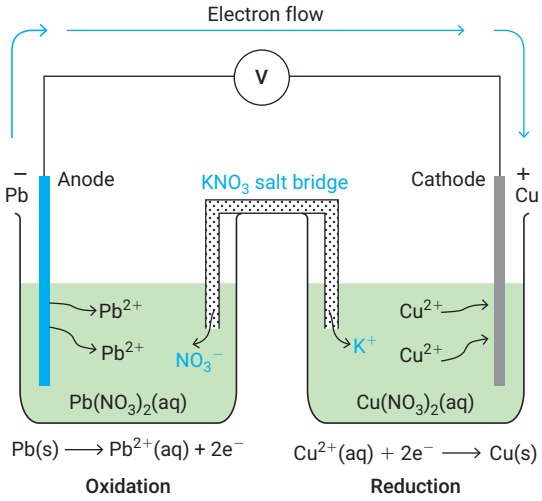
7 **a** This reaction would not produce a galvanic cell because lead is more reactive than silver, which means lead will give electrons to silver, but silver will not give electrons to lead.

b This reaction would produce a galvanic cell because zinc is more reactive than iron, so it would give up electrons to the iron ions.

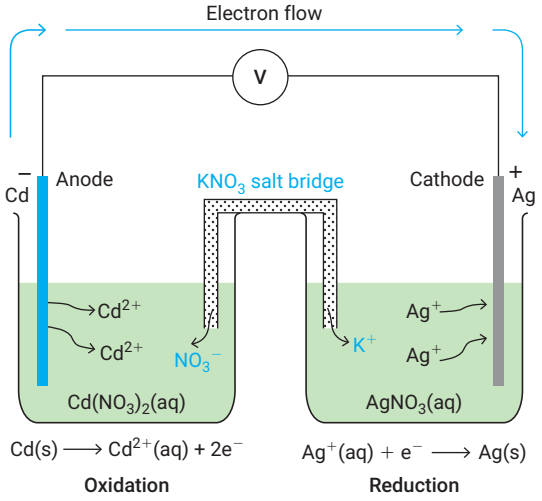
LEARNING CHECK 9.3

APPLYING

1 **a**



b

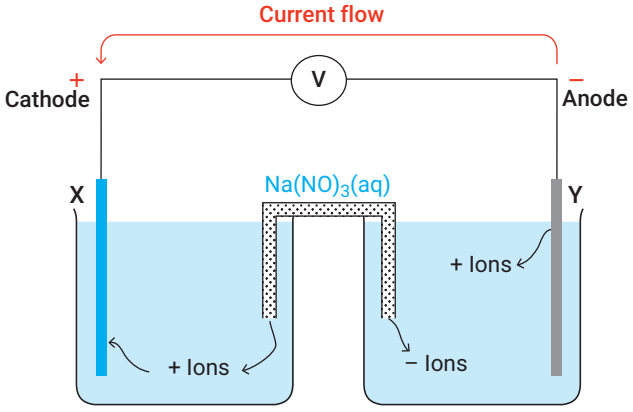


2 **a** $Pb(s)|Pb^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$

b $Cd(s)|Cd^{2+}(aq)||Ag^{+}(aq)|Ag(s)$

3 $Y(s) \rightarrow Y^{2+}(aq) + 2e^{-}$ oxidation

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



4 **a** Anode is Fe(s), cathode is Pb(s)

b $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$ oxidation

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

ANALYSING

5 **a** Cl_2, Pt electrode is the cathode, which is positive; Ni is the anode, which is negative.

b $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^{-}$ oxidation

$Cl_2(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)$ reduction

c Electrons flow from the nickel through the external circuit to the platinum. Negative ions flow from the chlorine electrode through the solution towards the nickel electrode. Positive ions flow from the nickel electrode through the solution towards the chlorine electrode.

d In this galvanic cell, chlorine gas is the oxidising agent. Since the chlorine gas is not in direct contact with the nickel metal, a reaction will not spontaneously occur, so it is not necessary to have two separate half-cells. Thus a salt bridge is not needed.

e $Cl^{-}(aq)|Cl_2(g)|Pt$

CHAPTER EXAM

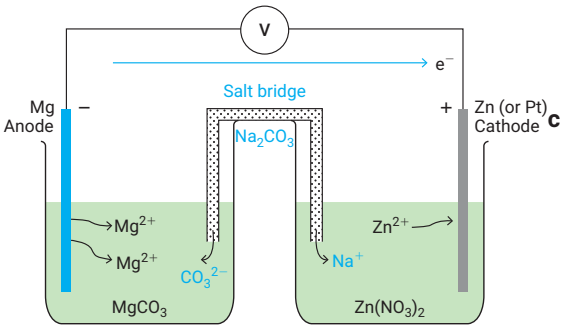
MULTIPLE CHOICE

1 D
2 D
3 A
4 B
5 D
6 C
7 D
8 B
9 B
10 C

SHORT RESPONSE

11 **a** Pieces of zinc and magnesium should be used as the two electrodes (platinum could replace the zinc); magnesium carbonate and zinc nitrate solutions should be used as the electrolyte solutions (sodium carbonate could replace the magnesium carbonate); sodium carbonate solution should be used for the salt bridge.

b



Anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^{-}$, oxidation

Cathode: $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$, reduction

c

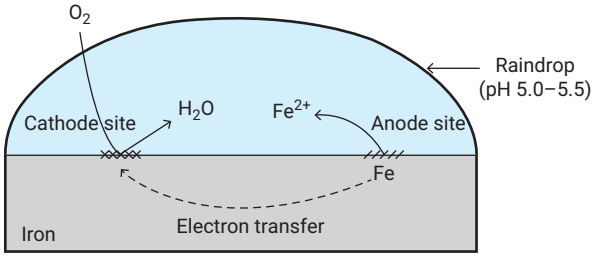
d Changes suggested will depend on substances chosen. Zn electrode could be replaced with Pt (or vice versa) because it is less reactive than Mg and will not react with the electrolyte solution. Sodium carbonate could also be used as the electrolyte solution in the Mg half-cell because neither ion will react with Mg or Mg^{2+} ions that are produced.

12 **a** **i** Oxidation half-equation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$

ii Reduction half-equation:
$O_2(g) + 4H^{+}(aq) + 4e^{-} \rightarrow 2H_2O(l)$

iii Overall equation:
$2Fe(s) + O_2(g) + 4H^{+}(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

b



c Oxidation and reduction occur at two different sites, so there is an anode and a cathode. Electrons are transferred from the anode to the cathode through a conducting metal. The water layer on the surface acts as a salt bridge where the Fe^{2+} ions migrate from the metal surface.

9780170483544

d The oxidation state of iron changes (increases) from +2 to +3, showing it is oxidised. The oxidation state of oxygen changes (decreases) from 0 to −2, showing it is reduced. This is therefore a redox reaction.

CROSS-CHAPTER QUESTION

13 a Cu(s) electrode is the anode; $Cl_2(g)|C(s)$ electrode is the cathode.

b i $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ oxidation

ii $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ reduction

iii $Cu(s) + Cl_2(g) \rightarrow Cu^{2+}(aq) + 2Cl^-(aq)$

c i $PV = nRT$, $P = 100$ kPa, $V = 283.3$ mL $= 0.2833$ L, $T = 25°C = 298$ K, $R = 8.31$

$$n = \frac{PV}{RT} = \frac{100 \times 0.2833}{8.31 \times 298} = 0.0114 \text{ mol}$$

ii $n(Cl_2) = n(Cu) = 0.0114$ mol

$m(Cu) = 0.0114 \times 63.55 = 0.724$ g

iii $$\% \text{ Cu} = \frac{0.724}{0.761} \times 100 = 95.1\%$$

iv The copper electrode only contained 95.1% Cu, so it must have 4.9% other substances so is not pure.

DATA ANALYSIS

14 a T > Q > L > G

b i, ii Cell a:

$T(s) \rightarrow T^{2+}(aq) + 2e^-$, oxidation, anode

$G^{2+}(aq) + 2e^- \rightarrow G(s)$, reduction, cathode

Cell b:

$Q(s) \rightarrow Q^{2+}(aq) + 2e^-$, oxidation, anode

$L^{2+}(aq) + 2e^- \rightarrow L(s)$, reduction, cathode

Cell c:

$T(s) \rightarrow T^{2+}(aq) + 2e^-$, oxidation, anode

$L^{2+}(aq) + 2e^- \rightarrow L(s)$, reduction, cathode

Cell d:

$L(s) \rightarrow L^{2+}(aq) + 2e^-$, oxidation, anode

$G^{2+}(aq) + 2e^- \rightarrow G(s)$, reduction, cathode

15 a There is a relationship because the graph shows as anode concentration increases so does cell voltage. This means cell voltage produced is directly proportional to the anode electrolyte concentration.

b More ions means increased likelihood of a reaction taking place.

c Equilibrium has been reached.

d It would look the same.

CHAPTER 10 STANDARD ELECTRODE POTENTIAL

LEARNING CHECK 10.1

DESCRIBING

1 a Standard electrode potential: a measure of the potential difference of an individual electrode under standard conditions, measured relative to the standard hydrogen electrode

b Hydrogen electrode: a half-cell composed of $H^+(aq)$ ions in contact with $H_2(g)$ under standard conditions

c Oxidising agent: a chemical species that causes another species to be oxidised

d Reducing agent: a chemical species that causes another species to be reduced

2 Standard conditions – 298 K, 100 kPa, solution concentrations of 1 mol L^{-1}

3 A reference cell enables the potential of all other half-cells to be measured relative to a standard. In this way, the potentials of half-cells can easily be compared.

APPLYING

4 The more positive an $E°$ value is, the stronger is its oxidising strength and the more likely it is to be reduced.

Species A = −1.4 V

Species B = +0.70 V

Species B is more likely to be reduced.

5 a $KMnO_4$ is the oxidising agent because it has the higher $E°$ value

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

b Ni is the reducing agent:

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

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

LEARNING CHECK 10.2

DESCRIBING

1 a Standard cell potential: the difference in electrode potential between the two half-cells that make up a galvanic cell

b Positive cell potential: indicates that a spontaneous reaction will occur between the electrodes of a galvanic cell

c Negative cell potential: indicates that reaction will not occur spontaneously

2 Step 1: Identify the relevant equations from a suitable table of standard electrode potentials.

Step 2: Determine which substance is being oxidised (anode) and which substance is being reduced (cathode).

Step 3: Use $E°_{cell} = E°_{reduction\ half\text{-}cell} - E°_{oxidation\ half\text{-}cell}$ to determine the cell potential.

3 When $E°_{cell}$ is calculated, a positive value indicates that a spontaneous reaction is occurring.

4 **a** This is oxidation. The value from the table is reversed; −1.18 V becomes +1.18 V.

b This is reduction. The value from the table is +1.08 V.

c This is oxidation. The value from the table is reversed; −2.36 V becomes +2.36 V.

5 $E°$ values give an indication of the difference in electrical potential energy between the two sides of the equation – this does not change when the quantities in the equation change.

APPLYING

6 Since an iron electrode has a negative $E°$ value (−0.44 V) and the overall cell potential is positive, the iron must be oxidised, so it will be the anode.

$E°_{cell} = E°_{reduction\ half\text{-}cell} - E°_{oxidation\ half\text{-}cell}$

$+1.95 = E°_{red} - (-0.44)$

$+1.51\ V = E°_{red}$

The electrode is the permanganate electrode, which is the cathode.

7 **a** $+1.36 - (+0.77) = +0.59$ V

b −0.80 V

LEARNING CHECK 10.3

DESCRIBING

1 **a** Kinetic stability: the relative stability of reagents in a reaction, dependant on the activation energy

b Non-standard conditions: conditions under which a cell operates that are not at 298 K, solutions are not 1 mol L^{-1} and gases are not at 100 kPa pressure

2 Reactions that are very close to one another in the table. Reactive metals such as aluminium that form impervious oxide coatings on exposure to air.

APPLYING

3 Using concentrated HCl ensures a greater transfer of electrons from the larger number of Cl^- ions. This ensures a smaller negative value for the oxidation of Cl^- ions leading to a positive cell potential.

LEARNING CHECK 10.4

DESCRIBING

1 An oxidising agent is more likely to gain electrons than hydrogen. Therefore, it has a positive standard electrode potential.

2 Fe, Cu, Ag, O_2, Br_2, Cl_2

APPLYING

3 $E°$ = 1.64 V; therefore, a spontaneous reaction will occur.

4 Yes

5 **a** $E° = +0.80 - (+1.36) = -0.56$ V

b This cell will not operate as constructed because the reaction will not spontaneously occur, as can be seen by the negative $E°$.

6 $Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$

CHAPTER EXAM

MULTIPLE CHOICE

1 C

2 A

3 A

4 B

5 A

6 D

7 A

8 A

9 D

10 D

SHORT RESPONSE

11 **a** $Ag(s) \rightarrow Ag^+(aq) + e^-$, oxidation, $E° = -(+0.80\ V) = -0.80$ V

$Zn^{2+} + 2e^- \rightarrow Zn(s)$, reduction, $E° = -0.76$ V

$E°_{cell} = -0.76 + (-0.80) = -1.56$ V

Negative $E°$ indicates reaction will not be spontaneous.

b $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$, oxidation, $E° = -(-0.13\ V) = +0.13$ V

$SO_4^{2-} + 4H^+(aq) + 2e^- \rightarrow SO_2(aq) + 2H_2O(l)$, reduction, $E° = +0.16$ V

$E°_{cell} = +0.13 + (+0.16) = +0.29$ V

Positive $E°$ indicates reaction will be spontaneous.

c $2I^-(aq) \rightarrow I_2(g) + 2e^-$, oxidation, $E° = -(+0.54)$ V

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$, reduction, $E° = +1.51$ V

$E°_{cell} = +1.51 + (-0.54) = +0.97$ V

Positive $E°$ indicates reaction will be spontaneous.

12 The following reduction half-reaction is required:

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$, reduction, $E° = +1.51$ V

Possible oxidation reactions:

a $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$, $E° = -(+0.77)$ V

b $Fe^{3+}(aq)$ cannot be further oxidised.

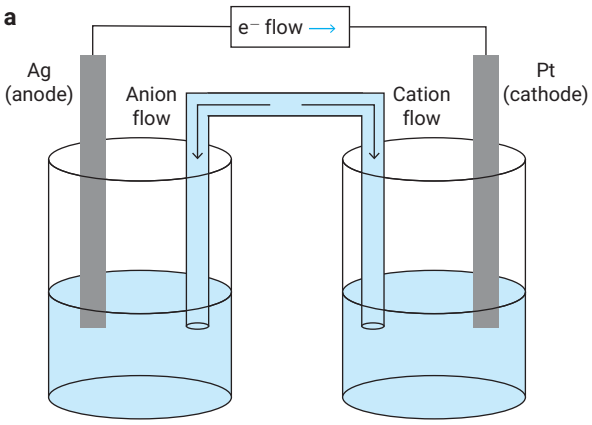
c $2I^-(aq) \rightarrow I_2(g) + 2e^-$, $E° = -(+0.54)$ V

d $Cl_2(g)$ will not be oxidised.

Therefore, solutions a and c would react spontaneously with $KMnO_4$ to decolourise the solution because both combinations have a positive $E°$ value.

CROSS-CHAPTER QUESTION

13 a



b Half-equations:

$X_2(aq) + 2e^- \rightarrow 2X^-(aq)$

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

Overall reaction:

$2Ag(s) + X_2(aq) \rightarrow 2\,Ag^+(aq) + 2X^-(aq)$

c **i** $E° = 0.28\text{ V} + 0.80\text{ V}$

$= 1.08$ V

ii Br_2

d $n(Ag) = \dfrac{1.09}{107.87}$

$= 0.0101$ mol

$n(Ag) : n(X_2)$ is 2 : 1

$n(X_2) = \dfrac{0.0101}{2}$

$= 5.05 \times 10^{-3}$ mol

$m(Br_2) = 5.05 \times 10^{-3} \times 159.8$

$= 0.807$ g

DATA ANALYSIS

14 Cell Q–T = +1.5 V

Cell G–Q = +2.0 V

Cell Q–L = +0.50 V

Cell M–Q = +1.0 V

If Q is set as the reference electrode = 0.0 V:

T = −1.5 V

L = −0.5 V

Q = 0.0 V

M = +1.0 V

G = +2.0 V

15

	$X(NO_3)_2$ (aq)	$Q(NO_3)_2$ (aq)	$T(NO_3)_2$ (aq)	$R(NO_3)_2$ (aq)	$M(NO_3)_2$ (aq)	$G(NO_3)_2$ (aq)
X		✓	✓	✓	✗	✓
Q	✗		✓	✓	✗	✗
T	✗	✗		✓	✗	✗
R	✗	✗	✗		✗	✗
M	✓	✓	✓	✓		✓
G	✗	✓	✓	✓	✗	

$X(s) + Q^{2+}(aq) \rightarrow X^{2+}(aq) + Q(s)$

(others will be similar)

CHAPTER 11 ELECTROLYTIC CELLS

LEARNING CHECK 11.1

DESCRIBING

1 In an electrolytic cell, the polarities of the anode and cathode are determined by the external power source, whereas in a galvanic cell, they are determined by the spontaneous redox reaction.

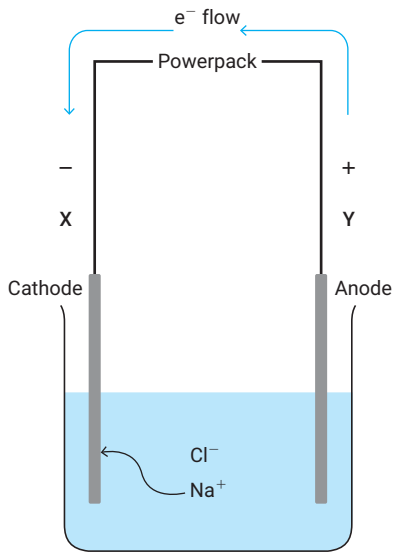
2 Because the ions in the electrolyte will not spontaneously react they do not need to be separated.

3

	Cell reaction	Anode	Cathode
Galvanic	Spontaneous	−	+
Electrolytic	Non-spontaneous	+	−

APPLYING

4 a



b Oxidation: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Reduction: $Na^+(l) + e^- \rightarrow Na(l)$

LEARNING CHECK 11.2

DESCRIBING

1 a The nature of the electrolyte, the concentration of the electrolyte and the nature of the electrode

b The electrolyte is a molten substance composed of the ions of the melted salt; therefore, the only products are the elements of the salt. Concentration does not affect the products because the electrolyte is a pure liquid. The nature of the electrode will affect the product if it is a substance that reacts directly with the ions in the electrolyte.

2 Inert electrodes do not interfere chemically in the electrolytic process.

3 In electrolysis of a molten salt, the only products (provided inert electrodes are used) are the elements of the ions of the salt, whereas in an aqueous solution, the electrolyte is dissolved in water, which also can be oxidised and reduced, so the products can be the elements of the salt and/or the products of the electrolysis of water.

4 Polyatomic ions are extremely stable and require very large voltages for them to be oxidised. Water will always be oxidised (producing oxygen at the anode) preferentially to polyatomic ions because it has a less negative $E°$.

5 The relative electrode potentials of the ions present and the oxidation and reduction of water

6 Concentrated: $E°$ values for oxidation of water to give oxygen and oxidation of Cl^- ions to give Cl_2 gas are similar but, due to the increased number of Cl^- ions present, Cl_2 gas is produced. Dilute: Oxygen gas is produced because there are too few Cl^- ions, the water is oxidised preferentially.

APPLYING

7 Anode (oxidation): $2Br^-(l) \rightarrow Br_2(g) + 2e^-$

Cathode (reduction): $Cu^{2+}(l) + 2e^- \rightarrow Cu(s)$

8 a $2I^-(aq) \rightarrow I_2(s) + 2e^-$
or $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

b $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$
or $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

c The presence of yellow colour and dark-coloured crystals indicates iodine is produced so the anode reaction is $2I^-(aq) \rightarrow I_2(s) + 2e^-$

The red-brown solid indicates the presence of iron so the cathode reaction is $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$.

d $E°_{cell} = -0.54 + (-0.44) = -0.98$ V

A voltage of 0.98 V would need to be applied.

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

b $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

c Anode: colourless, odourless gas produced

Cathode: colourless, odourless gas produced

d Gas produced at anode is O_2. This can be identified by collecting the gas in a test tube and observing if it relights a glowing splint. Gas produced at the cathode is H_2. This can be identified by collecting the gas in a test tube and observing if it goes 'pop' when a lit match is placed in the test tube.

e $E°_{cell} = -0.83 + (-1.23) = -2.06$ V

A voltage of 2.06 V would need to be applied.

10 Anode (oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$, $E° = -(+1.23$ V)

Cathode (reduction): $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$, $E° = -0.76$ V

$E°_{cell} = -0.76 + (-1.23) = -1.99$ V

11 Anode = $O_2(g)$

Cathode = $H_2(g)$

Voltage required = 2.06 V

$6H_2O(l) \rightarrow 2H_2(g) + O_2(g) + 4H^+(aq) + 4OH^-(aq)$

12 a Oxygen: relights a glowing splint

Hydrogen: pop test

b Both electrodes involve the oxidation and reduction of water.

The electrode with the red solution in it is the anode because it is acidic so involves the oxidation of water to produce oxygen gas and H^+

Anode = oxidation: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode = reduction: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

c H_2O exists in the ratio 2 atoms of hydrogen to 1 atom of oxygen. There is more hydrogen to be liberated than oxygen.

LEARNING CHECK 11.3

DESCRIBING

1 a Electrorefining: the refining (purification) of a metal by electrolysis

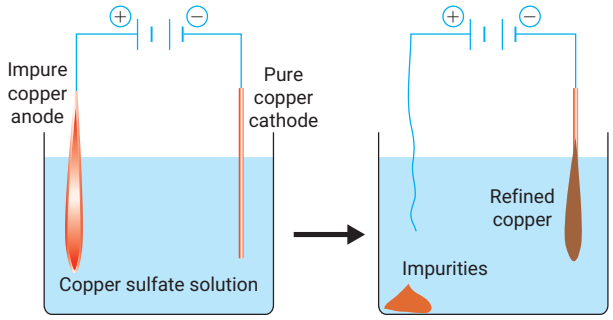
b Electroplating: the process by which a metal is deposited onto a conductor using an electric current

2 The impure metal must be the anode because it needs to be oxidised.

3 The object to be plated must be cathode because the plating metal ions need to be reduced onto the object.

APPLYING

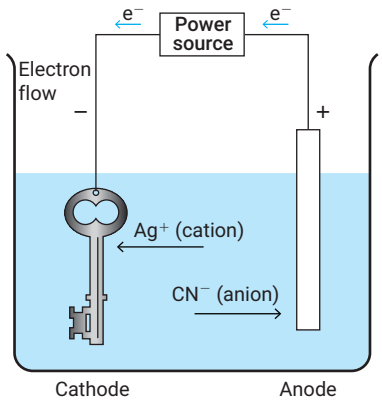
4 a



b The concentration would be 1 mol L^{-1}.

At the anode, copper is oxidised to Cu^{2+} and the ions move into the electrolyte solution. At the cathode, Cu^{2+} ions are reduced to Cu metal, which is plated onto the cathode. So, for every copper atom that is oxidised at the anode, one is produced at the cathode; therefore, the concentration of the electrolyte should not change.

5 a



b The most appropriate metal is silver because that is the metal being used for plating the key.

c Anode (oxidation): $Ag(s) \rightarrow Ag^+(aq) + e^-$

Cathode (reduction) $Ag^+(aq) + e^- \rightarrow Ag(s)$

LEARNING CHECK 11.4

DESCRIBING

1 The mass of a substance produced or consumed at an electrode during electrolysis is proportional to the quantity of electricity that passes through the electrolytic cell.

2 The quantity of electricity, in coulombs (C), carried by 1 mole of electrons. Equal to 96 485 C mol^{-1}.

3 The charge in coulombs is calculated from the formula $q = I \times t$. The number of moles of electrons passing through the system is calculated by rearranging the formula $q = n(e^-) \times F$ where F is the Faraday constant, to $n(e^-) = \frac{q}{F}$. The half-equation for the production of chlorine gas is $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$. So, the production of one mole of chlorine requires two mole of electrons which means $n(e^-)$ must be divided by 2 to obtain the number of moles of $Cl_2(g)$ produced.

APPLYING

4 $n(e^-) = \frac{q}{F} = \frac{20\,000}{96\,485} = 0.207\,29$ mol

$Na^+(l) + e^- \rightarrow Na(s)$; $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

$n(Na) = n(e^-) = 0.207\,29$ mol

$n(Cl_2) = \frac{n(e^-)}{2} = 0.103\,65$ mol

$m(Na) = 0.207\,29 \times 22.99 = 4.77$ g;
$m(Cl_2) = 0.103\,65 \times (35.45 \times 2) = 7.35$ g

5 $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

$n(Ni) = \frac{0.500}{58.69} = 0.008\,519$ mol;

$n(e^-) = 0.008519 \times 2 = 0.017\,038$ mol

$q = n(e^-) \times F = 0.017\,038 \times 96\,485 = 1644$ C

$I = \frac{q}{t} = \frac{1644}{5 \times 60} = 5.48$ A

6 $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

$n(Zn) = \frac{3.5}{65.38} = 0.0535$ mol

$n(e^-) = 0.0535 \times 2 = 0.107$ mol

$q = n(e^-) \times F = 0.107 \times 96\,485 = 10\,324$ C

$t = \frac{q}{I} = \frac{10\,324}{0.106} = 97\,396$ s $= 27.1$ h

ANALYSING

7 14.7 g

8 10.1 g

9 a $q = It = 0.200 \times 200 = 40$ C

$n(e^-) = \frac{q}{F} = \frac{40}{96485} = 0.000\,41\,46$ mol

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

$n(H_2) = \frac{n(e^-)}{2} = 0.000\,207\,3$ mol

$V = \frac{nRT}{P} = \frac{0.000\,207\,3 \times 8.31 \times 298}{100} = 0.005\,13$ L

b $n(OH^-) = n(e^-) = 0.000\,414\,6$ mol

$[OH^-] = \frac{n}{V} = \frac{0.000\,414\,6}{0.080} = 0.005\,18$ mol L^{-1}

$p(OH) = -\log 0.005\,18 = 2.29$;
$pH = 14 - 2.29 = 11.7$

10 $n(e^-) = \frac{q}{F} = \frac{3300}{96\,485} = 0.034\,20$ mol

$X^{2+}(l) + 2e^- \rightarrow X(s)$

$n(X) = \frac{n(e^-)}{2} = \frac{0.034\,20}{2} = 0.017\,10$ mol

$M(X) = \frac{m}{n} = \frac{1.950}{0.017\,10} = 114.0$ g

CHAPTER EXAM

MULTIPLE CHOICE

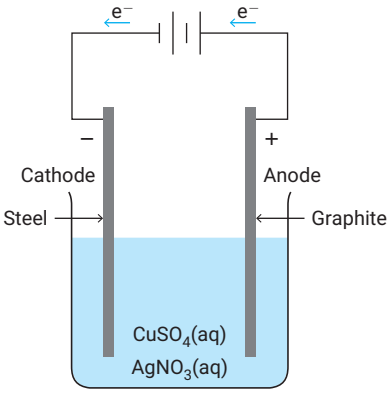
1 C
2 C
3 C
4 A
5 D
6 D
7 A
8 A
9 B
10 D

SHORT RESPONSE

11 Similarities: Oxidation at anode and reduction at cathode; anions move towards anode and cations move towards cathode; electrolyte for movement of ions; external wire for movement of electrons.

Differences: Galvanic cell reactions are spontaneous, whereas electrolytic cell reactions are non-spontaneous; galvanic cells produce electricity by chemical reactions, whereas electrolytic cells use electricity to produce a chemical reaction; in a galvanic cell, the anode is negative and the cathode is positive, whereas in an electrolytic cell, the anode is positive and the cathode is negative.

12 a



b Possible cathode reactions:

$Ag^+(aq) + e^- \rightarrow Ag(s)$, $E° = +0.80$ V

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

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$, $E° = -0.83$ V

Possible anode reactions:

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$, $E° = -1.23$ V

(NO_3^- and SO_4^{2-} are highly stable so are not oxidised)

Reactions with the largest $E°$ are the ones that will initially occur so preferred reactions are:

Cathode:

$Ag^+(aq) + e^- \rightarrow Ag(s)$, $E° = +0.80$ V

Anode:

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$, $E° = -1.23$ V

c At the cathode, there will be a deposit of silver crystals; at the anode, bubbles of O_2 gas will be observed.

d As the cell continues, once all the Ag^+ ions have been reduced, the Cu^{2+} ions will be the next to be reduced and deposited on the cathode as this half-equation has the next largest $E°$ value. Once all the copper has been extracted, hydrogen gas will be produced.

CROSS-CHAPTER QUESTION

13 a Oxidation: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Reduction: $X^{2+}(aq) + 2e^- \rightarrow X(s)$

b $c(OH^-) = 0.020$ mol L^{-1}, $V = 50$ mL $= 0.050$ L

$n(OH^-) = cV = 0.020 \times 0.050 = 0.0010$ mol

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

$n(H^+) = n(OH^-) = 0.0010$ mol

c Overall cell reaction:

$2X^{2+}(aq) + 2H_2O(l) \rightarrow 2X(s) + O_2(g) + 4H^+(aq)$

$n(X) = \frac{n(H^+)}{2} = \frac{0.0010}{2} = 0.000\,50$ mol

$m(X) = 0.0327$ g

$n = \frac{m}{M}$ so $M = \frac{m}{n} = \frac{0.0327}{0.000\,50} = 65.4$ g

14 a The galvanic cell powers the electrolytic cell.

The electrolysis of $CuSO_4$:

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

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$,
$E° = -(+1.23) = -1.23$ V

$E°_{cell} = +0.34 + (-1.23) = -0.89$ V

The galvanic cell must produce at least 0.89 V.

$E°_{cell} = E°_{red} + E°_{ox}$

$+0.89 = +0.80 + E°_{ox}$

$-(+0.09) = E°_{ox}$

The metal closest to −0.09 V in the table is Pb = Metal B

Solution A is a soluble lead compound = $Pb(NO_3)_2(aq)$

9780170483544

b Oxidation occurs at electrode B – this produces electrons. Therefore, electrode D is the negative electrode of the electrolytic cell. This is where reduction occurs:

Electrode D (reduction): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Electrode C (oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Electrode C = oxygen gas

Electrode D = copper metal

c A. Ag electrode = cathode = reduction:
$Ag^+(aq) + 2e^- \rightarrow Ag(s)$

B. Pb electrode = anode = oxidation:
$Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$

C. Inert electrode = anode = oxidation:
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

D. Cu electrode = cathode = reduction:
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

d Appropriate half-equations are shown in question 14c.

15 a $q = It = 12.50 \times (7.5 \times 60) = 5625$ C

$$n(e^-) = \frac{q}{F} = \frac{5625}{96485} = 0.0583 \text{ mol}$$

$$n(Zn) = \frac{n(e^-)}{2} = \frac{0.0583}{2} = 0.029\,15 \text{ mol}$$

$m(Zn) = n \times M = 0.029\,15 \times 65.38 = 1.91$ g

b $$n(O_2) = \frac{n(e^-)}{4} = \frac{0.0583}{4} = 0.014\,58 \text{ mol}$$

$$V(O_2) = \frac{nRT}{P} = \frac{0.014\,58 \times 8.31 \times 298}{100} = 0.361 \text{ L}$$

CHAPTER 12 STRUCTURE OF ORGANIC COMPOUNDS

LEARNING CHECK 12.1

DESCRIBING

1 A functional group is a specific group of atoms within a molecule that is responsible for the characteristic chemical reactions of that molecule. For example, the hydroxyl group (–OH) is the functional group present in alcohols.

2 Pentane: semi-structural formula: $CH_3CH_2CH_2CH_2CH_3$

Molecular formula: C_5H_{12}; empirical formula: C_5H_{12}

3 a Hydroxyl

b Alkene

c Ketone

d Halide

e Carboxylic acid

APPLYING

4 a Aldehyde

b Carboxylic acid

c Amide

d Haloalkane

5 a Hydroxyl

b Carboxyl

c Amine

d Ester

e Ketone

f Aldehyde

g Amide

LEARNING CHECK 12.2

DESCRIBING

1 a Alcohol

b Haloalkane

c Carboxylic acid

d Alkene

e Amine

2 Similarities: All three have a carbonyl group.

Differences: Ketone has a carbonyl group (C=O) bonded to two carbon atoms (e.g. acetone). Aldehyde has a carbonyl group (C=O) bonded to at least one hydrogen and one carbon (e.g. methanal). Carboxylic acid has a carbonyl group (C=O) bonded to a hydroxyl group (-OH), forming the carboxyl group (–COOH, e.g. ethanoic acid).

APPLYING

3 a $CH_3CH_2CH_2CH_2CH_3$

b CH_3OH

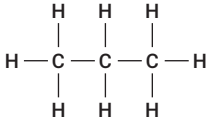
c $CH_3CH_2CH_2CH_2Br$

d $CH_3CH_2CH_2CH(OH)CH_3$

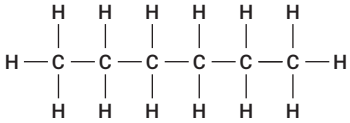
LEARNING CHECK 12.3

DESCRIBING

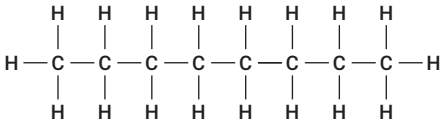
1 a Propane



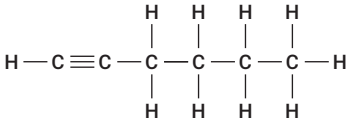
b Hexane



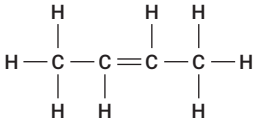
c Octane



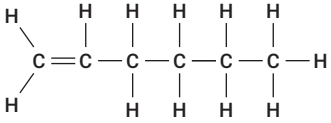
d 1-Hexyne



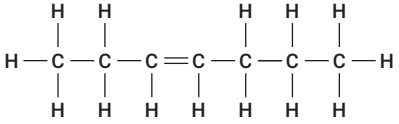
e 2-Butene



f 1-Hexene



g 3-Heptene



2 **a** 1-Hexyne: $CH{\equiv}CCH_2CH_2CH_2CH_3$

b 3-Hexyne: $CH_3CH_2C{\equiv}CCH_2CH_3$

c 3,3-Dimethyl-1-butene: $CH_2{=}CHC(CH_3)_2CH_3$

d 3-Methyl-1-butanol: $CH_2(OH)CH_2CH(CH_3)CH_3$

e Butanal: $CH_3CH_2CH_2CHO$

f 3-Methyl-2-pentanone: $CH_3CH(=O)CH(CH_3)CH_2CH_3$

g 2,3-Dimethylbutanoic acid: $CH_3CH(CH_3)CH(CH_3)COOH$

h Butyl ethanoate: $CH_3COOCH_2CH_2CH_2CH_3$

i 2-Methyl-3-octanamine: $CH_3CH(CH_3)CH(NH_2)CH_2CH_2CH_2CH_2CH_3$

j *N*-Methyl methanamide $HC(=O)NHCH_3$

APPLYING

3 **a** 2,2-Dimethylbutane

b 3-Methyl-1-butene

c 2-Butanol

d Propanal

e Pentanoic acid

f Propyl pentanoate

g 1-Hexanol

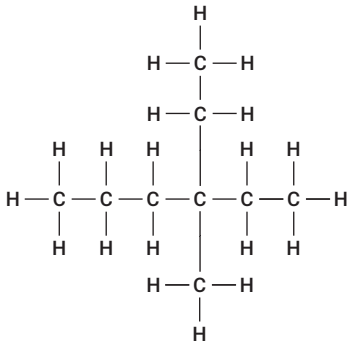
h 2-Butanamine

i Ethanamide

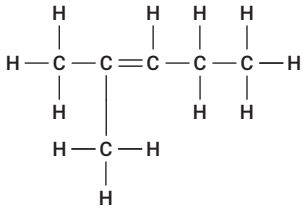
j 2-hydroxypropanoic acid

k 3-chloro-1-propanol

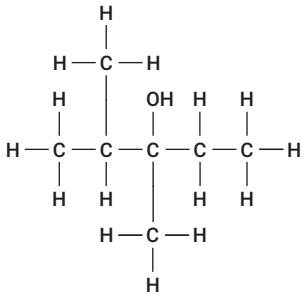
4 **a**



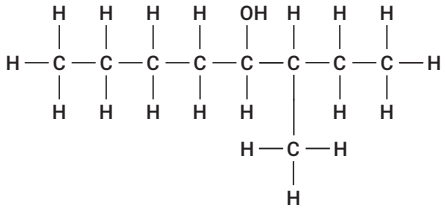
b



c



d



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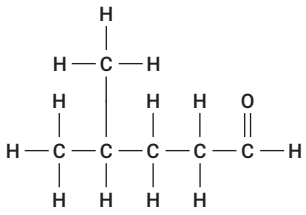

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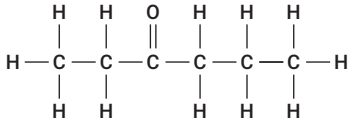

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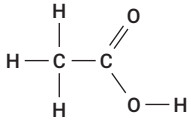

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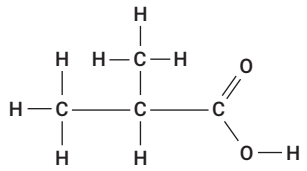

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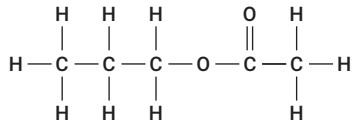


LEARNING CHECK 12.4

DESCRIBING

1 1-Butanol $CH_3CH_2CH_2CH_2OH$ and 2-butanol $CH_3CH_2CH(OH)CH_3$

2 Structural isomers are compounds that have the same molecular formula but differ in the connectivity of their atoms, meaning the arrangement of the atoms is different.
For example, butane (C_4H_{10}) ($CH_3CH_2CH_2CH_3$ (straight chain), 2-methylpropane (C_4H_{10}) $CH_3CH(CH_3)CH_3$(branched chain)

APPLYING

3 1-Pentene $CH_2{=}CHCH_2CH_2CH_3$ and 2-pentene $CH_3CH{=}CHCH_2CH_3$

4 Methyl propanoate $CH_3CH_2COOCH_3$, ethyl ethanoate $CH_3COOCH_2CH_3$, propyl methanoate $HCOOCH_2CH_2CH_3$

LEARNING CHECK 12.5

DESCRIBING

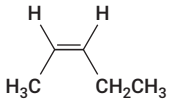
1 A structural isomer has the same molecular formula as another compound but differs in the arrangement of the atoms. These isomers can have distinct physical and chemical properties. For example, 1-butanol and 2-methylpropan-1-ol are structural isomers with the formula C_4H_9OH.

2 Geometric isomers (*cis*/*trans*) are molecules that have the same molecular formula and order of atoms but differ in the spatial arrangement around a double bond or ring structure (e.g. *cis*-2-butene and *trans*-2-butene). Optical isomers (enantiomers) are molecules that are mirror images of each other and cannot be superimposed. They usually have a chiral carbon, an atom bonded to four different groups (e.g. the two enantiomers of 2-butanol).

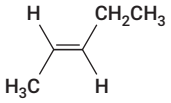
APPLYING

3 *cis*-2-Pentene: $CH_3{-}CH{=}CH{-}CH_2{-}CH_3$ (same groups on the same side of the double bond)

trans-2-Pentene: $CH_3{-}CH{=}CH{-}CH_2{-}CH_3$ (same groups on opposite sides of the double bond)



cis-2-Pentene



trans-2-Pentene

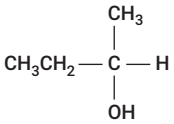
4 **a** Yes

b No

c Yes

d No

5



LEARNING CHECK 12.6

APPLYING

1 Calculate number of moles:

$$n(C) = \frac{40.0}{12.0} = 3.3 \text{ mol}$$

$$n(H) = \frac{6.7}{1.0} = 6.7 \text{ mol}$$

$$n(O) = \frac{53.3}{16.0} = 3.3 \text{ mol}$$

C	:	H	:	O
$\frac{3.3}{3.3}$	:	$\frac{6.7}{3.3}$	:	$\frac{3.3}{3.3}$
1	:	2	:	1

Empirical formula: CH_2O

$$\text{Molecular formula} = \frac{180}{30.0} = 6$$

$6 \times CH_2O = C_6H_{12}O_6$

2 $$\text{Carbon: } = \frac{3 \times 12.0}{58.0} \times 100 = 62.1\%$$

$$\text{Hydrogen: } = \frac{6.0 \times 1.0}{58.0} \times 100 = 10.3\%$$

$$\text{Oxygen: } = \frac{1 \times 16.0}{58.0} \times 100 = 27.6\%$$

3 $$n(C) = \frac{4.2}{12.0} = 0.35 \text{ mol}$$

$$n(H) = \frac{0.70}{1.00} = 0.70 \text{ mol}$$

$$n(O) = \frac{2.80}{16.0} = 0.175 \text{ mol}$$

C	:	H	:	O
$\frac{0.35}{0.175}$	:	$\frac{0.70}{0.175}$	:	$\frac{0.175}{0.175}$
2	:	4	:	1

Empirical formula: C_2H_4O

4 $n(C) = \frac{79.9}{12.0} = 6.66$

$n(H) = \frac{20.1}{1.0} = 20.1$

C	:	H
$\frac{6.66}{6.66}$	:	$\frac{20.1}{6.66}$

Empirical formula: CH_3

5 a $n(C) = \frac{54.5}{12.0} = 4.54$ mol

$n(H) = \frac{9.1}{1.0} = 9.1$ mol

$n(O) = \frac{36.4}{16.0} = 2.28$ mol

C	:	H	:	O
$\frac{4.54}{2.28}$	:	$\frac{9.1}{2.28}$	:	$\frac{2.28}{2.28}$
2	:	4	:	1

Empirical formula: C_2H_4O

b Molecular formula for A $= \frac{88.0}{44.0} = 2$

$2 \times C_2H_4O = C_4H_8O_2$

Molecular formula for B $= \frac{176.0}{44.0} = 4$

$4 \times CH_4O = C_8H_{16}O_4$

c Ethanoic acid

CHAPTER EXAM

MULTIPLE CHOICE

1 D
2 C
3 D
4 A
5 A
6 C
7 C
8 B
9 D
10 B

SHORT RESPONSE

11 a Classes of organic compounds are based on functional groups because these groups determine the chemical properties and reactivity of the molecules, making them essential in classifying and predicting behaviour in chemical reactions.

b Both aldehydes and ketones have a carbonyl group (C=O), but in aldehydes, the carbonyl group is bonded to at least one hydrogen atom (R–CHO), whereas in ketones, it is bonded to two carbon atoms (R–CO–R'). In aldehydes, the carbonyl group is at the end of a carbon chain, whereas ketones it is within the chain.

c Amines are organic compounds derived from ammonia (NH_3), where one or more hydrogen atoms have been replaced by alkyl or aryl groups (RNH_2). Amides are compounds that have a carbonyl group (C=O) directly attached to a nitrogen atom ($RCONH_2$). The key difference is the presence of the carbonyl group in amides.

d **i** 1-Pentyne

ii Butane

iii 2-Pentanone

iv 3-Methylpentane

12 a The name '3-ethylbutane' suggests a four-carbon chain (butane) with an ethyl group attached at the third position. However, the chain should be named for the longest continuous carbon chain. IUPAC name: 3-methylpentane; structural formula: $CH_3CH_2CH(CH_3)CH_2CH_3$.

b The longest carbon chain here is eight carbons long, not six as indicated by 'hexane'. Also, the substituents must be arranged to follow the IUPAC rules. IUPAC name: 4-ethyloctane; structural formula: $CH_3CH_2CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$.

c The double bond should be numbered to give it the lowest possible number, so the correct parent name needs to be used. IUPAC name: 2-methyl-1-butene; structural formula: $CH_2{=}C(CH_3)CH_2CH_3$.

d The numbering of the main chain is incorrect, leading to a non-systematic name. IUPAC name: 3,3-dimethyl-1-pentyne; structural formula: $CH{\equiv}CCH_2C(CH_3)_2CH_3$.

13 a $n(C) = \frac{72.0}{12.0} = 6$ mol

$n(H) = \frac{12.0}{1.0} = 12$ mol

$n(O) = \frac{16.0}{16.0} = 1$ mol

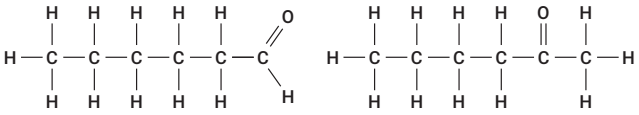
C	:	H	:	O
$\frac{6.0}{1.0}$	:	$\frac{12.0}{1.0}$	:	$\frac{1.0}{1.0}$
6	:	12	:	1

Empirical formula: $C_6H_{12}O$

b Molecular formula: $= \frac{72.0}{72.0} = 1$

Molecular formula: $C_6H_{12}O$

c



Hexanal

Hexan-2-one

CROSS-CHAPTER QUESTION

14 a Propene

b Unsaturated. Propene has a double bond between carbon atoms, which makes it an unsaturated hydrocarbon.

c No, it cannot form an optical isomer. Optical isomers (enantiomers) are possible only when a molecule has a chiral carbon (a carbon atom bonded to four different groups). Propene does not have a chiral centre, so it cannot exhibit optical isomerism.

d Molecular formula of propene: C_3H_6

Carbon (C): $12.01 \text{ g mol}^{-1} \times 3 = 36.03 \text{ g mol}^{-1}$

Hydrogen (H): $1.01 \text{ g mol}^{-1} \times 6 = 6.06 \text{ g mol}^{-1}$

Total molecular mass $= 36.03 + 6.06 = 42.09 \text{ g mol}^{-1}$

e $n(\text{propene}) = \frac{m}{M_r} = \frac{5}{42.09} = 0.119 \text{ mol}$

Assuming complete reaction, 1 mol of propene forms 1 mol of 2-propanol.

f Number of moles of propene (from part e): 0.119 mol

According to the mol ratio, 0.119 mol of water would react with propene to form 2-propanol.

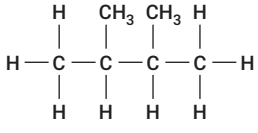
$m(H_2O) = 0.119 \times 18.01 = 2.14 \text{ g}$

Total mass of product formed = m(water) + m(propene) = 2.14 + 5.00 = 7.14 g

DATA ANALYSIS

15 a 2,2-Dimethylbutane

b



2,3-Dimethylbutane

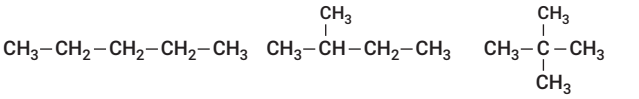
c 2,2-Dimethylbutane is a branched alkane with a four-carbon chain (butane) with two methyl groups attached to the second carbon. The branching reduces the surface area and makes the molecule more compact. In comparison, hexane is a straight-chain alkane with six carbons. The straight chain has more dispersion forces, which leads to higher boiling point.

d According to the data in the graph, as branching increases, the boiling point decreases.

16 a As the number of carbon atoms in an alkane chain increases, the number of possible isomers also increases. This trend occurs because more carbon atoms allows for more varied arrangements, including different branching patterns.

b The significant increase from two isomers for butane to 75 isomers for decane demonstrates how the number of possible isomers rises rapidly with the increase in the carbon chain length due to more opportunities for different branching.

c



Pentane | 2-Methylbutane | 2,2-Dimethylpropane

d C_5H_{11}

e Optical isomers require the presence of a chiral carbon – a carbon atom bonded to four different groups. For straight or branched alkanes, there is no chiral centre because each carbon atom is typically bonded to identical or similar groups (hydrogen atoms and other carbon atoms). Therefore, none of the alkane isomers will exhibit optical isomerism.

CHAPTER 13 PHYSICAL PROPERTIES AND TRENDS OF ORGANIC MOLECULES

LEARNING CHECK 13.1

DESCRIBING

1 Alkanes have non-polar C–H bonds, so experience dispersion intermolecular forces, which are relatively weak.

2 Dispersion forces, dipole–dipole forces, hydrogen bonding

3 C

4 B is an alkene; the others are all alkanes.

5 Dispersion forces are the only force present.

APPLYING

6 Carboxylic acids and alcohols both have –OH (hydroxyl) groups, which allow for hydrogen bonding between molecules. Alkanes and alkenes only have C–H non-polar bonds, so they can only have dispersion forces between molecules.

LEARNING CHECK 13.2

DESCRIBING

1 The larger the molecule, the higher the boiling point because of increased number of dispersion forces as the carbon chain increases in length.

2 Straight-chain molecules have higher boiling points than branched-chain molecules. Straight chains have a larger surface area in contact, which increases the number and overall strength of dispersion forces. Branched chains are more compact in structure, leading to fewer dispersion forces and lower boiling points.

3 A

APPLYING

4 Alcohols have higher boiling points than alkanes, because they have –OH groups that allow hydrogen bonding, a stronger intermolecular force than dispersion forces. The carboxylic acids have even higher boiling points than alcohols because their –COOH group forms hydrogen bonds, including the possibility of dimer formation making intermolecular attractions even stronger.

5 Volatility decreases with carbon chain length because of increased dispersion forces holding molecules together. Greater intermolecular attraction requires more energy to break, reducing volatility.

6 Ethane is more volatile than ethanoic acid because it experiences weak dispersion forces only. Ethanoic acid has a –COOH group, enabling hydrogen bonding and even dimer formation, resulting in stronger intermolecular forces. Therefore, it is less volatile because it requires more energy to overcome the intermolecular forces.

7 Pentene is the least volatile because it is the longest carbon chain and therefore experiences more dispersion forces between molecules.

8 As the number of carbons increases, vapour pressure decreases, and therefore volatility decreases. This is due to increased dispersion forces between longer molecules.

LEARNING CHECK 13.3

DESCRIBING

1 Solubility decreases with molecular size across all homologous series because C–H bonds are non-polar. The longer the carbon chain, the more non-polar regions there are in the molecule, overcoming the effect of any polar functional groups present. Longer carbon chains do not interact favourably with polar solvents such as water, so solubility decreases as the molecules become larger.

2 The hydroxyl (–OH) functional group is polar and forms hydrogen bonds with water molecules. This strong force of attraction allows short-chain alcohols to dissolve, as the intermolecular hydrogen bonding can overcome the non-polar nature of the short carbon chains.

3 All alcohols are generally soluble because the –OH group forms hydrogen bonds with water, which is a large force of attraction that allows the molecule to dissolve to some degree.

4 Solubility decreases as the alkane chain of the alcohol gets longer because the carbon chain is non-polar and is not attracted to water. This decreases the effect of the hydroxyl group in proportion to the increased chain size.

APPLYING

5 Propanoic acid → 1-propanol → propane

6 Water is polar and hexane is non-polar. The longer carbon chain of octanol is non-polar, which would be soluble in non-polar solvent. The –OH functional group is polar, which forms hydrogen bonds with water but not with hexane. Therefore, the solubility of 1-octanol is different in each solvent.

ANALYSING

7 Octane is not soluble in water (polar) but is highly soluble in hexane (non-polar).

8 Octanoic acid has limited solubility in water because although the non-polar chain is not attracted to polar water, there is some hydrogen bonding with the polar –COOH group. It is soluble in hexane because the longer non-polar carbon chain is attracted through dispersion forces to hexane. In contrast, octane is readily soluble in hexane because of the attraction of the non-polar molecules to each other, but is not attracted to polar water molecules.

9 Polar functional groups allow a substance to dissolve in water, because they will form intermolecular attraction (dipole–dipole or hydrogen bonding) to water molecules.

10 Short-chain carboxylic acids would have limited solubility in hexane because the non-polar carbon chain forms dispersion forces with hexane. But the polar –COOH group does not form hydrogen bonds with the non-polar hexane solvent. Therefore, the short-chain carboxylic acids may be partially soluble in hexane, but not as soluble as a similar-sized alkane or alkene.

LEARNING CHECK 13.4

DESCRIBING

1 Alkanes, alkenes, alcohols and carboxylic acids all have intermolecular bonds of different strengths. Alkanes and alkenes are non-polar compounds, held together by weak dispersion forces. In comparison, alcohols and carboxylic acids are polar, allowing for hydrogen bonding. As such, alkanes and alkenes generally have lower boiling and melting points and are highly volatile compared to the corresponding alcohols and carboxylic acids. Since carboxylic acids can form dimers, they have the strongest intermolecular bonds, the highest melting and boiling points, and the lowest volatility of the different types of organic compounds of a similar size.

APPLYING

2 Hydrocarbon chains are non-polar and therefore exhibit only dispersion forces. Introducing functional groups allow compounds to have dipole–dipole interactions as well as hydrogen bonding. This depends on the functional group. The increase in strength of bonds can increase the boiling point. An increase in chain length increases intermolecular bonding strength, which can also contribute to an increase in boiling point.

3 **a** $CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_2OH$, CH_3CH_2COOH

b Butane ($CH_3CH_2CH_2CH_3$) has the weakest intermolecular forces of all three molecules, being held together by only dispersion forces. Therefore, it has the lowest boiling point. Propanoic acid has a carboxyl group, allowing for hydrogen bonding and dipole–dipole interactions. This has the strongest intermolecular attraction of all three molecules and would have the highest boiling point.

4 Pentane would be the most soluble. Hexane is non-polar, so the most non-polar molecules would be most soluble in hexane. Pentane is non-polar and has no functional groups and is least polar of the two molecules, so it would be most soluble in hexane.

ANALYSING

5

Formula	Molar mass (g mol^{-1})	Boiling point (°C)
CH_4	16	–161
CH_3OH	32	65
C_4H_{10}	58	–0.5
HCOOH	46	101

CHAPTER EXAM

MULTIPLE CHOICE

1 B
2 B
3 A
4 B
5 D
6 B
7 B
8 C
9 C
10 D

SHORT RESPONSE

11 **a** Carboxylic acids

b Solubility in water decreases as the carbon chain length increases because the hydrophobic alkane portion increases, reducing the molecule's overall polarity.

c Volatility decreases with increasing carbon chain length because longer chains have stronger dispersion forces.

d $C_5H_{11}COOH$ would be the most soluble in hexane because it has the longest non-polar chain, which interacts well with hexane.

12 Pentan-1-ol would have the highest boiling point because the position of the –OH group affects the ability for hydrogen bonding to occur. The –OH group in pentan-1-ol is most accessible, which allows the –OH to form hydrogen bonds, resulting in the highest boiling point of the three isomers.

CROSS-CHAPTER QUESTION

13 **a** Unsaturated

b Alkene

c 2-Methylpropene

d This molecule is insoluble in water because it is non-polar and will not form intermolecular forces with water molecules.

e Dispersion forces are the only type of intermolecular forces for this non-polar molecule.

f This molecule will be more volatile than 1-butene because branched alkenes have lower boiling points than linear counterparts.

DATA ANALYSIS

14 a A, because it has the highest vapour pressure

b C, because it forms the least vapour

c A alkane, B alcohol and C carboxylic acid

d Vapour pressure decreases as intermolecular forces strengthen.

15 a 2.23 g per 100 mL

b As chain length increases, solubility increases.

c As chain length increases, solubility decreases.

d The alkanes would be highly soluble in hexane because of the non-polar nature of both the alkane and the hexane solvent.

e Octanoic acid, because it has a –COOH group that can form dipole–dipole interactions as well as hydrogen bonding. As a result, octanoic acid has the strongest intermolecular bonds compared to octane (dispersion) and 1-octanol (dispersion and hydrogen) and so has the highest boiling point.

CHAPTER 14 ORGANIC REACTIONS AND REACTION PATHWAYS

LEARNING CHECK 14.1

DESCRIBING

1 a A substitution reaction with a halogen is when one or more hydrogen atoms in an alkane are replaced by halogen atoms (e.g. Cl or Br), usually under UV light.

b A combustion reaction involves an alkane reacting with oxygen to produce CO_2 and H_2O (complete) or $CO/C + H_2O$ (incomplete), releasing heat.

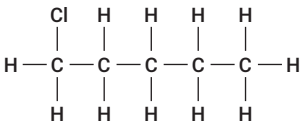
2 Complete combustion produces only carbon dioxide and water. Incomplete combustion produces carbon monoxide or carbon (soot) along with water.

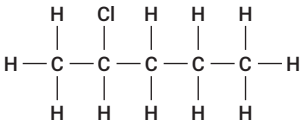
3 $C_5H_{12}(g) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$

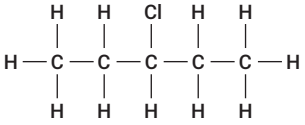
4 $C_5H_{12}(g) + 3O_2(g) \rightarrow 5C(s) + 6H_2O(l)$

5 a $C_5H_{12} + Cl_2 \rightarrow C_5H_{11}Cl + HCl$ (requires UV light)

b







Possible products: 1-chloropentane, 2-chloropentane, 3-chloropentane

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

b Octane is a larger hydrocarbon molecule, making complete combustion harder and more likely to produce soot in atmospheric oxygen conditions.

7 Reagents: I_2, UV light. Process: Free radical substitution to form 2-iodohexane.

APPLYING

8 Free radical substitution is difficult to control selectively, and it can be difficult to manage risks with these organic reactions.

9 Alkanes undergo only substitution reactions because they are saturated and lack reactive double bonds.

LEARNING CHECK 14.2

DESCRIBING

1 Nucleophilic substitution is when a nucleophile replaces a leaving group (e.g. halogen) in an organic molecule.

2 Elimination reactions involve removal of atoms or groups to form a double bond (alkene).

3 A polar covalent bond is a covalent bond in which electrons are unequally shared, resulting in partial positive and negative charges on different atoms.

4 Substitution: low temperature dilute OH^-, aqueous. Elimination: high temperature concentrated OH^-, ethanolic.

APPLYING

5 a $CH_3CH_2CH_2Br(l) + NaOH(aq) \rightarrow CH_3CH_2CH_2OH(l) + NaBr(aq)$

b $CH_3CHClCH_2CH_3(l) + NH_3(aq) \rightarrow CH_3CH(NH_2)CH_2CH_3(l) + HCl(aq)$

c $CH_3CH_2I(l) + KCN(aq) \rightarrow CH_3CH_2CN(l) + KI(aq)$

d $(CH_3)_3Cl(l) + NaOH(alc) \rightarrow (CH_3)_2C{=}CH_2(g) + NaI(aq) + H_2O(l)$

6 Substitution → 2-propanol; elimination → propene. Secondary alcohols can undergo both substitution and elimination. Adjust temperature, concentration of NaOH and solvent to favour either reaction. High concentrations of hydroxide solution favour elimination, whereas low concentrations favour substitution. A higher temperature favours elimination; a lower temperature favours substitution. A higher proportion of water than ethanol favours substitution, whereas a greater proportion of ethanol favours elimination.

7 3-Hexanol + NaCl

LEARNING CHECK 14.3

DESCRIBING

1 a Addition reactions add atoms across a double bond to form a saturated molecule.

b Addition polymerisation joins alkene monomers into long-chain polymers.

2 Alkenes are unsaturated and reactive; alkanes are saturated and unreactive.

3 a $CH_3CH{=}CH_2(g) + Br_2(l) \rightarrow CH_3CHBrCH_2Br(l)$

b $(CH_3)_2C{=}CH_2(g) + H_2O(l) \rightarrow (CH_3)_2C(OH)CH_3(l)$; phosphoric acid catalyst and heat

c $CH_3CH{=}CHCH_3(g) + H_2(g) \rightarrow CH_3CH_2CH_2CH_3(g)$

d $CH_3CH{=}CHCH_3(g) + HBr(g) \rightarrow CH_3CHBrCH_2CH_3(l)$ (only one product 2-bromobutane can form)

APPLYING

4 The reaction in question 3d can give multiple products. Markovnikov's rule predicts the major product (H to the C with the most H atoms already bonded). Theoretically, the reaction in question 3b can form a minor product but the amount is negligible because it is not a stable product.

LEARNING CHECK 14.4

DESCRIBING

1 An alkyne is an unsaturated hydrocarbon that has at least one triple bond (C≡C) between two carbon atoms.

2 Alkenes and alkynes are regarded as unsaturated because they have double or triple bonds, which can undergo addition reactions. By contrast, alkanes are saturated and only have single bonds.

APPLYING

3 a $CH{\equiv}CCH_3(g) + Br_2(l) \rightarrow CHBr{=}CHBr{-}CH_3(l)$

b $CH{\equiv}CCH_2CH_3(g) + 2H_2(g) \rightarrow CH_3CH_2CH_2CH_3(g)$

c $2CH_3C{\equiv}CCH_3(g) + 11O_2(g) \rightarrow 8CO_2(g) + 6H_2O(l)$

4 Ethyne (acetylene) is used in high-temperature torches because it combusts with a very hot flame (above 3000°C) when mixed with oxygen, making it suitable for cutting and welding metals.

5 a Step 1: $C_5H_8(g) + H_2(g) \rightarrow C_5H_{10}(g)$
Step 2: $C_5H_{10}(g) + H_2(g) \rightarrow C_5H_{12}(g)$

b Alkene: butene. Alkane: butane

c These are hydrogenation (addition) reactions. Hydrogen acts as a reducing agent that saturates the multiple bonds.

d 1-Hexyne + $2H_2$ → hexane (C_6H_{12})

LEARNING CHECK 14.5

DESCRIBING

1 Primary alcohol: –OH attached to a carbon bonded to one other carbon (e.g. 1-butanol). Secondary alcohol: –OH attached to a carbon bonded to two other carbons (e.g. 2-butanol). Tertiary alcohol: –OH attached to a carbon bonded to three other carbons (e.g. 2-methyl-2-propanol).

2 Common oxidising agents: acidified potassium dichromate(VI) ($K_2Cr_2O_7$) and acidified potassium manganate(VII) ($KMnO_4$).

3 a Hydroxyl group: –OH

b Aldehyde group:

c Ketone group

4 a $CH_3CHOHCH_3(l) + HBr(aq) \rightarrow CH_3CHBrCH_3(l) + H_2O(l)$

b 2-Bromopropane

c Nucleophilic substitution. Hydrogen halide provides the halide ion that replaces the hydroxyl group.

APPLYING

5 Oxidation of 1-propanol to propanal:
$CH_3CH_2CH_2OH(l) \rightarrow CH_3CH_2CHO(l) + 2H^+(aq) + 2e^-$
Oxidation of propanal to propanoic acid:
$CH_3CH_2CHO(l) + H_2O(l) \rightarrow CH_3CH_2COOH(l) + 2H^+(aq) + 2e^-$
Reduction (acidified $KMnO_4$):
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
Overall: $5CH_3CH_2CH_2OH(l) + 4MnO_4(aq) + 12H^+(aq) \rightarrow 5CH_3CH_2COOH(l) + 4Mn^{2+}(aq) + 11H_2O(l)$

6 a $3CH_3(CH_2)_3CH_2OH\ (l) + 2Cr_2O_7^{2-}\ (aq) + 16H^+\ (aq) \rightarrow 3CH_3(CH_2)_3COOH\ (l) + 4Cr^{3+}\ (aq) + 11H_2O\ (l)$

b $3CH_3CH(OH)CH_2CH_3(l) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 3CH_3COCH_2CH_3(l) + 2Mn^{2+}(aq) + 6H_2O(l)$

c $CH_3(CH_2)_2C(CH_3)(OH)CH_3(l) + Cr_2O_7^{2-}(aq) \rightarrow$ no reaction (tertiary alcohol)

d $3CH_3CH_2CHO(l) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 3CH_3CH_2COOH(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$

7 Aldehyde-containing sugars are reducing because they can be oxidised easily; ketones cannot be oxidised under mild conditions.

8 Ethanol in wine is oxidised to ethanoic acid (acetic acid) when exposed to air, producing a vinegary taste.

LEARNING CHECK 14.6

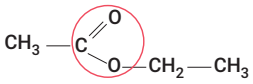
DESCRIBING

1 Carboxylic acids are called monoprotic because each molecule can donate only one proton (H^+). The only ionisable hydrogen is the one bonded to the –COOH group:

$R–COOH(aq) + H_2O(l) \rightleftharpoons R–COO^-(aq) + H_3O^+(aq)$

2 Condensation reaction – a reaction in which two molecules combine to form a larger molecule and a small molecule, usually water, is produced.

3



APPLYING

4 **a** $2HCOOH(aq) + 2Na(s) \rightarrow 2HCOONa(aq) + H_2(g)$

b $CH_3CH_2CH_2CH_2OH(l) + CH_3COOH(aq) \rightleftharpoons CH_3COOCH_2CH_2CH_2CH_3(l) + H_2O(l)$

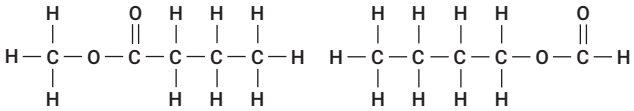
c $CH_3CH(OH)CH_2CH_3(l) + CH_3CH_2COOH(aq) \rightarrow CH_3CH_2COOCH(CH_3)CH_2CH_3(l) + H_2O(l)$

d $CH_3COOCH_2CH_2CH_3(l) + H_2O(l) \rightarrow CH_3COOH(aq) + CH_3CH_2CH_2OH(l)$

e $CH_3CH_2CH_2COOCH_3(l) + NaOH(aq) \rightarrow CH_3CH_2CH_2COONa(aq) + CH_3OH(aq)$

f $CH_3CH_2CH_2CH_2CH_2OH(l) + CH_3CH_2CH_2COOH(aq) \rightarrow CH_3CH_2CH_2COOCH_2CH_2CH_2CH_2CH_3(l) + H_2O(l)$

5



Methyl butanoate

Butyl methanoate

Methyl butanoate is formed from the reaction between methanol and butanoic acid, whereas butyl methanoate is formed from the reaction between butanol and methanoate.

6 $CH_3CH_2COOH(aq) + NaOH(aq) \rightarrow CH_3CH_2COONa(aq) + H_2O(l)$

In this reaction, propanoic acid donates its H^+, which interacts with the OH^- from the NaOH to form water and a salt.

7 $2CH_3COOH(aq) + CaCO_3(s) \rightarrow (CH_3COO)_2Ca(aq) + CO_2(g) + H_2O(l)$

8 Esterification is a condensation reaction, which forms an ester and water from a carboxylic acid and an alcohol. Hydrolysis of esters involves the reaction between an ester and water, resulting in the reformation of the carboxylic acid and alcohol from which it was formed. Although both reactions involve water, esterification reactions release water, whereas hydrolysis requires water.

9 The ability to be amphoteric means that carboxylic acids can both donate and accept protons, acting as both an acid and a base. In the first example, ethanoic acid can accept a proton and act as a base. In the second example, ethanoic acid donates a proton and acts as an acid.

LEARNING CHECK 14.7

DESCRIBING

1 Amines contain a nitrogen atom bonded to one or more carbon atoms and are derived from ammonia (NH_3). They have the general structure $R–NH_2$. Amides contain a nitrogen atom bonded to a carbonyl group (C=O), with the general structure $R–CO–NH_2$, formed from the reaction of a carboxylic acid and an amine.

2 **a** $CH_3CH_2NH_2(aq) + HNO_3(aq) \rightarrow CH_3CH_2NH_3^+NO_3^-(aq)$

b $CH_3CH(NH_2)CH_2CH_3(l) + CH_3COOH(l) \rightarrow CH_3CONHCH(CH_3)CH_2CH_3(l) + H_2O(l)$

c $CH_3CH_2CH_2COOH(l) + CH_3NH_2(aq) \rightarrow CH_3CH_2CH_2CONHCH_3(l) + H_2O(l)$

d $CH_3COOH(l) + CH_3CH_2CH_2CH_2NH_2(l) \rightarrow CH_3CONHCH_2CH_2CH_2CH_3(l) + H_2O(l)$

3 $CH_3COOH(l) + C_3H_7NH_2(l) \rightarrow CH_3CONHC_3H_7(l) + H_2O(l)$

4 Amide formation is a condensation reaction because a carboxylic acid and an amine combine to form a larger molecule (an amide), while releasing a smaller molecule (water) as a by-product.

APPLYING

5 Amines are amphoteric because they can act as weak bases by accepting protons (due to the lone pair on nitrogen), but under certain conditions they can also show weak acidic behaviour and accept protons.

6 **a** Ethanamine

b Water (forward reaction), ethylammonium ion (reverse reaction)

c Removing OH^- ions will cause equilibrium to shift to the right to allow the system to partially oppose the change. This decreases the concentration of Compound A (ethanamine).

LEARNING CHECK 14.8

DESCRIBING

1 Reaction type: substitution reaction (specifically, a free radical substitution)

Reaction conditions: The reaction requires UV light to initiate the process. The UV light breaks the halogen molecule (e.g. Cl_2 or Br_2) into reactive free radicals, allowing one or more hydrogen atoms in the alkane to be substituted with halogen atoms.

2 You can distinguish between 2-pentanol and 2,2-dimethylpropan-1-ol by adding an acidified oxidising agent such as potassium dichromate ($K_2Cr_2O_7$). 2-Pentanol (a secondary alcohol) will cause the orange solution to turn green, whereas 2,2-dimethylpropan-1-ol (a tertiary alcohol) will not react, and the colour will remain orange.

3 You would need to oxidise butan-1-ol (a primary alcohol). The oxidation of butan-1-ol first produces butanal (an aldehyde), which can be further oxidised to butanoic acid, using an oxidising agent such as acidified potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$).

LEARNING CHECK 14.9

DESCRIBING

1 Step 1: Chloromethane (CH_3Cl) reacts with aqueous sodium hydroxide to produce methanol: $CH_3Cl + NaOH \rightarrow CH_3OH + NaCl$

Step 2: Oxidise methanol using an acidified oxidising agent (e.g. $K_2Cr_2O_7/H^+$) to form methanoic acid (HCOOH): $CH_3OH + [O] \rightarrow HCOOH$

Step 3: React 2-butanol with methanoic acid under acidic conditions (concentrated H_2SO_4) in a condensation (esterification) reaction:

$CH_3CH(OH)CH_2CH_3(l) + HCOOH(l) \rightarrow HCOOCH(CH_3)CH_2CH_3(l) + H_2O(l)$

Product: 2-butyl methanoate

2 Step 1: Chloropropane ($CH_3CH_2CH_2Cl$) undergoes substitution with ammonia (NH_3) to form propylamine: $CH_3CH_2CH_2Cl(l) + NH_3(aq) \rightarrow CH_3CH_2CH_2NH_2(aq) + HCl(aq)$

Step 2: Butanoic acid ($CH_3CH_2CH_2COOH$) reacts with propylamine in a condensation reaction to form *N*-propyl butanamide and water:

$CH_3CH_2CH_2COOH(l) + CH_3CH_2CH_2NH_2(l) \rightarrow CH_3CH_2CH_2CONHCH_2CH_2CH_3(l) + H_2(g)$

APPLYING

3 **a** 2-Butene ($CH_3CH{=}CHCH_3$). It is the precursor for the formation of 2-butanol via addition of water.

b Reagents: acidified potassium dichromate ($K_2Cr_2O_7/H^+$) or acidified (potassium manganate $KMnO_4/H^+$)

Conditions: Heating under reflux

c Step 1: addition reaction (hydration of an alkene to form an alcohol)

Step 2: oxidation reaction (secondary alcohol to ketone)

d Overall equation (using the half-equation method and acidified $K_2Cr_2O_7$ as the oxidant):

$3CH_3CH(OH)CH_2CH_3(l) + Cr_2O_7^{2-}(aq) + 18H^+(aq) \rightarrow 3CH_3COCH_2CH_3(l) + Cr^{3+}(aq) + 7H_2O(l)$ (2-butanol to 2-butanone)

4 **a** Compound P: pent-2-ene ($CH_3CH{=}CHCH_2CH_3$)

Compound R: pentan-3-ol (formed by hydration of the alkene)

b Compound S: 2-pentanol.
Structure: $CH_3CH_2CH_2CH(OH)CH_3$

Compound T: pentanoic acid.
Structure: $CH_3CH_2CH_2CH_2COOH$

5 **a** To oxidise 1-propanol (a primary alcohol) to propanoic acid, use a strong oxidising agent such as acidified potassium dichromate ($K_2Cr_2O_7/H^+$) or acidified potassium permanganate ($KMnO_4/H^+$). The reaction should be carried out under reflux conditions to ensure complete oxidation to the carboxylic acid.

b This is a condensation reaction between a carboxylic acid and a primary amine, forming an amide. C_2H_5COOH is propanoic acid; $CH_3CH_2NH_2$ is ethanamine. The product formed is ethyl propanamide.

LEARNING CHECK 14.10

DESCRIBING

1 Add acidified potassium dichromate and heat; a primary alcohol turns the solution green (oxidation), while a tertiary alcohol shows no change. Or add acidified potassium manganate and heat; if it is a primary alcohol the solution will go from purple to colourless.

2 Add bromine water; an alkene decolourises the bromine water because of an addition reaction, while an alkane does not react and the solution remains brown.

APPLYING

3 Add bromine water. If it decolourises: 1-butene. If no reaction: others.

Add acidified potassium dichromate and heat. If it turns green: 1-butanol. If no change: butane.

Add Tollens reagent to a sample that turned green with acidified potassium. If a silvery mirror colour occurs, sample is butanal.

Add a sample of calcium carbonate. If bubbles form, sample is butanoic acid.

4 a Bubbling or effervescence due to carbon dioxide gas being released

b $2CH_3CH_2COOH(aq) + Na_2CO_3(s) \rightarrow 2CH_3CH_2COONa(aq) + CO_2(g) + H_2O(l)$

5 a Reagent A is acidified potassium dichromate ($K_2Cr_2O_7/H^+$) or acidified potassium manganate ($KMnO_4/H^+$).

b Because colour change occured twice, it would be a primary alcohol.

ANALYSING

6 The hydrocarbon is an alkane because it did not decolourise bromine water. This indicates it is saturated and lacks a carbon–carbon double bond.

CHAPTER EXAM

MULTIPLE CHOICE

1 A
2 B
3 C
4 D
5 D
6 B
7 B
8 D
9 B
10 A

SHORT RESPONSE

11 a $CH_3COOCH_2CH_2CH_3$

b Compound K (ethanol): CH_3CH_2OH.
Compound L (1-propanol): CH_3CH_2OH

c NaOH

12 a $CH_3CHClCH_3(l) + NH_3(g) \rightarrow CH_3CH(NH_2)CH_3(l) + HCl(g)$

b 2-Aminopropane

c Nucleophilic substitution

CROSS-CHAPTER QUESTION

13 a Ionisation of ethanoic acid: $CH_3COOH\ (aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

b Carboxylic acids only partially ionise in water, meaning only a small proportion of carboxylic acid molecules ionise at any one time.

c Carboxylic acid and carboxylate ion are a conjugate acid–base pair.

d Calculate $[H^+]$ from $K_a = 1.8 \times 10^{-5}$ and $[CH_3COOH] = 0.10$ M:

$$[H^+] = \sqrt{K_a \times [HA]}$$
$$= \sqrt{1.8 \times 10^{-5} \times 0.10}$$
$$\approx 1.34 \times 10^{-3} \text{ mol L}^{-1}$$

e $pH = -\log[H^+] = -\log(1.34 \times 10^{-3}) \approx 2.87$

DATA ANALYSIS

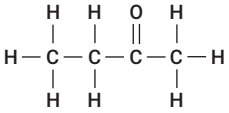
14 a 1-Butene because it decolourised bromine

b $CH_2{=}CHCH_2CH_3 + Br_2 \rightarrow CH_2BrCHBrCH_2CH_3$

1-Butene (an alkene) reacts with bromine (Br_2) in an addition reaction across the double bond. This reaction breaks the C=C double bond and adds one bromine atom to each of the formerly double-bonded carbon atoms. The orange-brown colour of bromine water disappears, indicating the reaction has occurred. Product is 1,2-dibromobutane

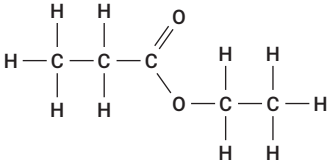
c Butane. Only alcohols will decolourise in acidifed potassium permanganate solution.

d Butanone



e 2-Butanol

f $CH_3CH_2COOCH_2CH_3$



g Ethyl propanoate

15 a Bottle A: Water (H_2O). Water is soluble, non-flammable, and does not react with bromine.

Bottle B: 1-hexene (C_6H_{12}). Alkenes are insoluble in water and decolourise bromine because of the presence of a C=C double bond.

Bottle C: Pentane (C_5H_{12}). Pentane is a non-polar alkane, insoluble in water, flammable, and does not react with bromine.

Bottle D: Ethanol (C_2H_5OH). Ethanol is polar and soluble in water, flammable, and does not decolourise bromine because it lacks a double bond.

b Combustion of ethanol (C_2H_5OH):
$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
Combustion of pentane (C_5H_{12}):
$C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$

CHAPTER 15 ORGANIC MATERIALS: STRUCTURE AND FUNCTION

LEARNING CHECK 15.1

DESCRIBING

1 a Polymer: a large molecule made from many thousands of repeating monomer units joined by covalent bonds

b Monomer: a small individual molecule that links with others to form a polymer

c Copolymer: a polymer made from more than one type of monomer

2 Addition polymerisation involves monomers joining without producing by-products. The polymers formed (e.g. polyethene) are generally not biodegradable because they have strong, stable carbon–carbon backbones. Condensation polymerisation produces polymers (e.g. proteins, polyesters) with the elimination of a small molecule such as water. These polymers tend to be more biodegradable because the ester or amide linkages can be hydrolysed.

3 The primary structure is the sequence of monomers in a polymer chain. The secondary structure is the regular folding patterns (e.g. α-helices or β-sheets) from hydrogen bonding. The tertiary structure is the overall 3D shape formed by interactions between side chains. The quaternary structure is the arrangement of multiple polymer chains interacting together.

4 a Biodegradability is the ability of a substance to be broken down naturally by enzymes or micro-organisms.

b Tensile strength is a material's resistance to being pulled or stretched.

c Density is the mass of the material per unit volume and is influenced by how tightly packed the polymer chains are.

5 Cross-links increase rigidity and hardness by bonding chains together. Branching reduces how closely chains can pack, decreasing density and increasing flexibility. Side groups can increase stiffness (e.g. large side groups such as benzene rings reduce flexibility).

6 a As the chains in crystalline regions are closely packed, this increases the density, strength and rigidity of the polymer.

b Longer chains result in an increase in properties such as strength, higher melting points and hardness of polymers.

APPLYING

7 Synthetic polymers are less likely to biodegrade because they have stable carbon–carbon backbones formed by addition polymerisation, which do not break down easily in nature. Natural polymers, with ester or amide linkages from condensation reactions, are more easily hydrolysed.

8 Cross-linked polymers have high tensile strength because covalent bonds form a rigid network (e.g. epoxy). Branched polymers have weaker intermolecular forces because of their irregular structure, resulting in lower tensile strength (e.g. LDPE).

9 LDPE has branched chains, which prevent tight packing, resulting in weak dispersion forces and low intermolecular attractions. In contrast, HDPE has linear chains that pack closely, leading to strong dispersion forces and higher intermolecular attractions, giving it greater strength and density.

10 a 1.35 g cm^{-3}

b 1.00 g cm^{-3}

c The density of polypropene is 0.85 g cm^{-3}, which is lower than the density of HDPE at 0.90 g cm^{-3}.

d LDPE is less dense than water, so it is likely to float in water.

e Polytetrafluoroethylene is likely to not have a branching structure because it is much denser than polypropylene, which is not very dense, and has a branched structure.

LEARNING CHECK 15.2

DESCRIBING

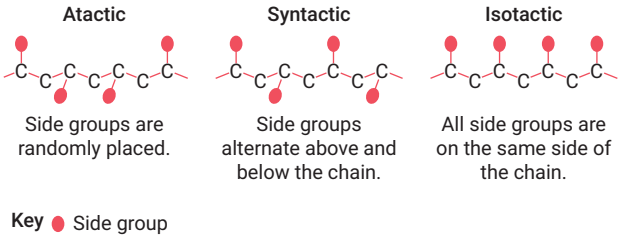
1 a An amorphous polymer has tangled, disordered chains with no regular arrangement. A crystalline polymer has regions where polymer chains are packed closely in a regular, ordered structure.

b Crystalline polymers tend to have higher density, rigidity, melting points and strength due to stronger intermolecular forces. Amorphous polymers are more flexible, transparent, less dense, and have lower melting points due to weaker forces between disordered chains.

2 A copolymer is a polymer made from two or more different types of monomers arranged in the polymer chain.

APPLYING

3 a Three possible variations of polypropene (polypropylene) are: isotactic (CH_3 groups all on the same side), syntactic (CH_3 groups alternate sides) and atactic (CH_3 groups randomly positioned).



b Isotactic – high crystallinity, strong intermolecular forces: high melting point, strong and rigid

Syntactic – some crystallinity: moderately strong and tough

Atactic – amorphous: soft, flexible, low melting point

4 HDPE has a higher density than LDPE because it has linear chains that pack closely together, leading to strong dispersion forces and crystalline regions. LDPE has branched chains, which prevent tight packing, creating amorphous regions with lower density.

ANALYSING

5 Melamine, being a thermosetting polymer, has strong cross-linking between chains, making it hard and brittle, not flexible. PVC is more flexible, as it has linear or slightly branched chains.

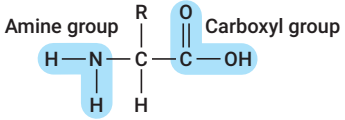
6 Polylactic acid (PLA) contains ester linkages, which can be hydrolysed. So, it is biodegradable. Polyamides (e.g. nylon) contain amide linkages, so they are also biodegradable, but more resistant than esters. Polyesters also contain ester linkages,. so can be biodegradable, depending on their structure.

Prediction: All three are more biodegradable than addition polymers such as polyethene, with PLA being the most biodegradable due to weaker and more hydrolysable ester links.

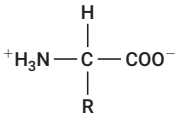
LEARNING CHECK 15.3

DESCRIBING

1 a An amino acid has a central alpha carbon bonded to an amine group ($-NH_2$), a carboxyl group ($-COOH$), a hydrogen atom and an R group (side chain).



b Zwitterion formation: The carboxyl group donates a proton to the amine group, resulting in a molecule with both a positive and negative charge. The amine g



Amine group gains $H^+ \rightarrow NH_3^+$ Carboxyl group loses $H^+ \rightarrow COO^-$

The molecule has no net charge but contains both positive and negative ions.

2 The isoelectric point (pI) is the pH at which a zwitterion has no overall net charge; below the pI, the molecule carries a positive charge, and above the pI, it carries a negative charge.

3 Categories of amino acids (based on side chains):

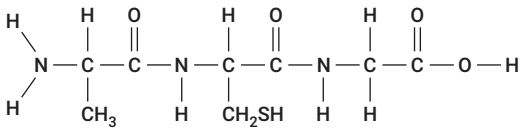
- Non-polar R groups: hydrophobic side chains (e.g. glycine, alanine, valine)
- Polar R groups (ionisable): side chains with groups like $-COOH$ or $-NH_2$ that can ionise (e.g. aspartic acid)
- Polar R groups (non-ionisable): contain $-OH$ or $-SH$ groups but do not ionise (e.g. serine, cysteine).

APPLYING

4 An amide link is formed when a carboxylic acid reacts with an amine, resulting in the formation of a $-CONH-$ group. This reaction produces a condensation polymer, such as nylon, and releases water (H_2O) as a by-product. Amide links are typically found in synthetic polymers.

A peptide link is a specific type of amide link that occurs between amino acids. It forms when the carboxyl group ($-COOH$) of one amino acid reacts with the amine group ($-NH_2$) of another. This also creates a $-CONH-$ group, producing a polypeptide or protein, along with water as a by-product. Peptide links are found in biological molecules and are essential to the structure of proteins.

5 a



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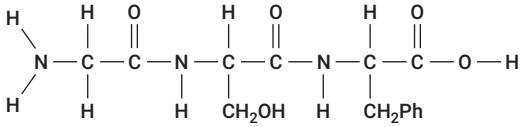
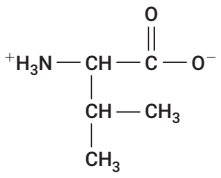
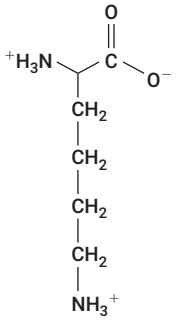


6 a



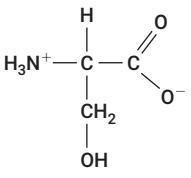
Valine

b



Lysine

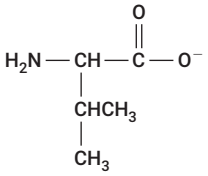
c



Serine

ANALYSING

7 At high pH (basic conditions), the $-NH_3^+$ group loses a proton, becoming neutral ($-NH_2$), while the carboxyl group remains deprotonated ($-COO^-$). It would have an overall negative charge (anion) due to $-COO^-$.



LEARNING CHECK 15.4

DESCRIBING

1 Monosaccharides are the simplest form of carbohydrates, consisting of a single sugar unit such as glucose or fructose. In contrast, disaccharides are formed when two monosaccharide units are joined together through a condensation reaction. Examples of disaccharides are sucrose, lactose and maltose.

2 Saccharide monomer units are joined together by a glycosidic bond (–C–O–C–), which is formed through a condensation reaction between two hydroxyl (–OH) groups, one from each sugar unit.

3 When two saccharide units are joined together, a disaccharide is formed. This molecule contains a glycosidic bond, and one molecule of water is released during its formation.

APPLYING

4 Monosaccharides and disaccharides are soluble in water because they contain multiple hydroxyl (–OH) groups that can form hydrogen bonds with water molecules. These interactions allow the sugar molecules to dissolve easily in aqueous environments, making them highly water-soluble.

CHAPTER EXAM

MULTIPLE CHOICE

1 D
2 C
3 B
4 B
5 C
6 A
7 C
8 C
9 D
10 D

SHORT RESPONSE

11 a Carboxylic acid group (–COOH) and the hydroxyl group (–OH)

b Water (H_2O)

c Ester link (–COO–)

d During polymerisation, the –OH group from the carboxylic acid reacts with the H from the hydroxyl group of the alcohol. This forms an ester bond (–COO–) and releases water in a condensation reaction.

e PET is strong and impermeable, making it suitable for food and beverage containers. These properties are due to its rigid benzene rings and strong intermolecular forces such as dipole–dipole interactions in its partially crystalline structure.

12 Aspartic acid has a negatively charged carboxyl side chain and a low isoelectric point (~2.8), resulting in a net negative charge at pH 7, while lysine has a positively charged amine side chain and a high isoelectric point (~9.7), giving it a net positive charge at pH 7.

13 a Polymer 3: isotactic – methyl groups all on the same side

Polymer 2: syntactic – alternating methyl groups

Polymer 1: atactic – random methyl group placement

b Polymer 1 (atactic) would have the lowest melting point because its irregular structure leads to low crystallinity and weaker dispersion forces.

c Polypropene should be recycled to reduce plastic waste, conserve resources, and minimise environmental impact, as it is non-biodegradable.

CROSS-CHAPTER QUESTION

14 a Glucose is highly soluble in water due to its many hydroxyl groups which form hydrogen bonds with water.

b Molecular mass of glucose ($C_6H_{12}O_6$) = $(6 \times 12.01) + (12 \times 1.008) + (6 \times 16.00) = 180.16$ g mol^{-1}

c $\%C = \frac{72.06}{180.16} \times 100 = 40.0\%$

$\%O = \frac{96.00}{180 \cdot 16} \times 100 = 53.3\%$

d Balanced equation for disaccharide formation:
$C_6H_{12}O_6 + C_6H_{12}O_6 \rightarrow C_{12}H_{22}O_{11} + H_2O$

e Empirical formula of glucose: CH_2O

DATA ANALYSIS

15 a 45–80 MPa

b 8–12 MPa

c Atactic PP: 2–4 MPa (branched, weak)

PLA: 50–70 MPa (linear, strong)

Hence, PLA is much stronger due to linear chains, strong ester bonds and dipole–diople interactions between chains.

d Linear polymers generally have higher tensile strength due to closer packing and stronger intermolecular forces, whereas branched polymers have lower strength.

CHAPTER 16 ANALYTICAL TECHNIQUES

LEARNING CHECK 16.1

DESCRIBING

1 a Adsorb: attach to the stationary phase

b Desorb: detach from the stationary phase and move into the mobile phase

c Component: one of the substances in a mixture being separated by chromatography

d Retention factor: the ratio of the distance moved by the amino acid to the distance moved by the solvent

2 The sample is spotted on to a base line 2–3 cm from the bottom of the paper. The paper is placed in a liquid mobile phase, which moves up the paper. The mobile phase carries the sample with it. Different components of the sample adsorb to the stationary phase to different extents and therefore travel at different speeds along the paper. Therefore, the different components can be differentiated according to their retention factor.

3 The greater the polarity of an amino acid, the smaller its R_F. The more polar the amino acid, the stronger the attachment to the stationary phase so the less distance it will travel along the plate. Non-polar amino acids have the largest R_F values.

APPLYING

4 X contains alanine, serine and aspartic acid; Y contains leucine, alanine and lysine.

5 Examine the structure of the two amino acids and compare their polarities. Then choose a different solvent, either more or less polar, that will provide better separation.

6 a $R_F = \frac{16}{20} = 0.8$

b Of the three, valine is the most likely. Based on the structures, glutamic acid is the most polar followed by cysteine, which has some polarity due to the –SH group, and valine is non-polar. As the stationary phase is polar and the mobile phase is non-polar, it is likely that the non-polar valine would travel furthest in the non-polar solvent and thus have a larger R_F.

ANALYSING

7 a The R_F value of the unknown amino acid could be compared to the R_F values of the known amino acids. A larger value would mean it is less polar than the ones below it, whereas a smaller value would mean it is more polar than the ones above it. This means more polar and less polar amino acids could be eliminated, thus reducing the possibilities.

b Once possible amino acids have been identified, a new analysis could be conducted. This would involve using known samples of the possible amino acids. The new analysis should be conducted under the same conditions as the first and R_F values of the possibilities compared to the R_F of the unknown in the first analysis. The mixture may also be included in the new analysis if the same conditions cannot be met.

LEARNING CHECK 16.2

DESCRIBING

1 **a** Electrophoresis: the process of separating large, charged molecules by placing them in an electric field and observing their subsequent migration through a medium such as a gel

b Migration: the movement of charged molecules through a gel

c Electric field: a region of influence around a charged particle where a force is exerted on other charged objects

d Isoelectric point: the pH at which an amino acid has an overall neutral charge and therefore is insoluble

e Buffer solution: a solution that maintains a constant pH when small amounts of acid and base are added

2 The electric field exerts a force on charged particles within it and, hence, is required to cause the molecules to migrate through the gel.

3 Different amino acid molecules have different sizes and different charges, so migrate at different speeds through the gel.

4 The buffer solutions provide a pH gradient across the gel, so that as the amino acids reach their isoelectric point, they become neutral molecules and therefore insoluble and visible.

APPLYING

5 **a** Glycine, valine and phenylalanine will all move towards the negative electrode because the pH of the buffer solution is less than their isoelectric points, so all these have a positive charge due to the H_3N^+– species.

b All three amino acids will have a net charge of +1 so the migration rate will be determined by their size. Glycine will migrate the furthest because it is the smallest and phenylalanine will migrate the least distance because it has a bulky benzene ring.

6 **a** **i** Negative electrode **ii** Neither as it is neutral **iii** Positive electrode **iv** Positive electrode

b It would have moved further at pH 11.0 than at pH 8 because at pH 11 it has two negative charges, whereas at pH 8 it has only one negative charge.

7

	Chromatography	Electrophoresis
Property used for separation	Affinity to stationary phase and mobile phase	Charge and size
Seeing amino acid	Ninhydrin solution	Ninhydrin solution
Conditions	Change solvent to improve separation	Change pH of solution to vary charge on amino acid
Equipment	Simple	More complicated and expensive

ANALYSING

8 **a** Cysteine because the experiment shows the isoelectric point is 5.0

b Lysine because the isoelectric point must be greater than 6.0 but less than 11.0

9 **a** P is lysine. Its pI must be greater than 6.0 because it moved towards the negative electrode, so must have formed a positive ion.

b R is cysteine. It has an isoelectric point of 5.0. S is aspartic acid because it has an isoelectric point of 3.0 so is negative at pH 5.0. Q is either glycine, alanine or valine because they all have an isoelectric point of 6.0.

LEARNING CHECK 16.3

DESCRIBING

1 **a** Radical: an atom or molecule with an unpaired high energy electron

b Ionisation: the removal of an electron from a molecule to produce a positive ion

c Parent molecular ion: a complete molecule with one electron removed

d Mass-to-charge ratio: the relative mass of a fragment divided by its charge

e Base peak: the highest peak in a mass spectrum that represents the most abundant fragment. The intensities of other peaks are calculated relative to this one

2 The parent molecular ion – the entire molecule with one electron removed. It is the peak with the largest *m*/*z* ratio.

3 If the molecule contains an atom that has more than one abundant isotope.

4 The different fragments produced and revealed on the mass spectrum can be analysed and can provide information about the structure of the molecule that they have originated from.

APPLYING

5 $m/z = 15$, CH_3^+; $m/z = 29$, $CH_2CH_3^+$; $m/z = 41$, $CH_2CHCH_2^+$; $m/z = 43$, $CH_3CH_2CH_2^+$; $m/z = 57$, $CH_3CH_2CH_2CH_2^+$

6 $m/z = 43$, $C_3H_7^+$; $m/z = 57$, $C_4H_9^+$; $m/z = 71$, $C_5H_{11}^+$

7 Spectrum A is propanal and spectrum B is propanone. Both have a parent molecular peak at 58, which is molecular ion $C_3H_6O^+$.

In spectrum A, the other main peaks are $m/z = 26$, $C_2H_2^+$; $m/z = 27$, $C_2H_3^+$; $m/z = 28$, $C_2H_4^+$ and/or CO^+; $m/z = 29$; $C_2H_5^+$ and/or HCO^+; $m/z = 57$, $C_3H_6O^+$.

In spectrum B, the other main peaks are $m/z = 15$, CH_3^+; $m/z = 43$, CH_3CO^+.

ANALYSING

8 a Both isomers have the same mass, so would both have a parent ion with an $m/z = 86$.

b Both base peaks represent fragments generated by breaking the C–C bond adjacent to the C=O group. Hence, in molecule A, this fragment is $C_4H_7O^+$ and in molecule B it is $C_3H_5O^+$.

c A fragment of $m/z = 29$ indicates a $C_2H_5^+$ ion can be formed. If this does not exist, the molecule must be A.

9 a Comparing the mass spectrum with that of the contaminated sample shows a major peak at $m/z = 32$, which is not in the ethanol spectrum.

b It is likely the contaminant is methanol because it has a parent molecular peak CH_3OH^+ at $m/z = 32$.

LEARNNG CHECK 16.4

DESCRIBING

1 Infrared light is of the correct energy to cause the atoms in molecules to vibrate about their covalent bonds.

2 Because different bonds absorb specific frequencies of infrared energy as they vibrate.

3 The fingerprint region is the area of a spectrum with a wavenumber less than 1500 cm^{-1}, where there is a range of absorptions that cannot be attributed to any specific bond, but which provides a pattern unique to that specific molecule, a 'fingerprint' that can be matched to previous images stored in a library.

4 a The compounds that would show a broad peak at 3300 cm^{-1} are alcohols and amines: 1-propanol, 2-propanol, ethanol, 1-methylamine.

b A peak at 2500–3000 cm^{-1} along with a peak at 1700–1750 cm^{-1} could be used to identify the carboxylic acids – ethanoic acid, methanoic (formic) acid and butanoic acid. A peak at 1700–1750 cm^{-1} and the absence of a peak at 2500–3000 cm^{-1} could identify the ester – ethyl ethanoate. Ethane could be identified with specific peaks in the fingerprint region.

APPLYING

5 a X and Y would be methanol and ethanoic acid. Hence, ethanoic acid would have a strong absorption at approximately 1700 cm^{-1}, but methanol would not.

b Methyl ethanoate would have no O–H absorption at approximately 3300 cm^{-1}, but would have a C=O absorption at 1700 cm^{-1}.

c It is difficult to use infrared spectroscopy to determine purity; however, the best way is to compare the spectrum produced to a library spectrum of pure methyl ethanoate. The presence of any additional absorptions would suggest that the sample is not pure.

6 a Ethene would have a short but sharp absorption at 1620–1680 cm^{-1}, due to the presence of the C=C bond. This would not be present in ethane.

b The infrared spectra of these molecules would be very similar and could only be distinguished by comparing the spectra to library samples of pure compounds.

c The infrared spectra of these molecules would be very similar and could only be distinguished by comparing the spectra to library samples of pure compounds. However, the iodomethane should have an absorption due to the C–I bond at 490–620 cm^{-1}, which would not be present in the spectrum of 2-chloropropane. However, this falls within the fingerprint region where it is difficult to observe specific absorptions.

d Propanoic acid will show an absorption at about 1750 cm^{-1}, due to the presence of the carboxylic acid C=O bond, which propanol will not show. In addition, the –OH absorption in propanoic acid will be at approximately 3000 cm^{-1}, whereas that in propanol will be at approximately 3500 cm^{-1}.

ANALYSING

7 Looking at the non-fingerprint region (wavenumbers greater than 1500 cm^{-1}), both spectra have absorptions at 3000 cm^{-1} and 1500 cm^{-1}, due to the presence of C–H and C–C bonds. However, the first spectrum has an additional absorption at approximately 1620 cm^{-1}, which indicates the presence of a C=C bond, and, hence, must be the spectrum of 1-hexene.

8 a 3000 cm^{-1} –OH acid; 1700 cm^{-1} –C=O; 1650 cm^{-1} C=C

b Structure should contain a double bond and a COOH group, e.g. $CH_3CH_2CH{=}CHCOOH$.

9 The spectrum is Y. Hydration of 2-butene produces an alcohol and only Y shows an O–H absorption (3200–3600 cm^{-1}).

Y has absorption peaks for the O–H (alcohol) bond (3200–3600 cm^{-1}) and the C–H bonds (2850–3090 cm^{-1}).

ACTIVITY 16.5.1

Spectrum 1 Molecule f – methyl ethanoate

Spectrum 2 Molecule c – ethyl ethanoate

Spectrum 3 Molecule a – propanoic acid

Spectrum 4 Molecule b – 2-chloropropane

Spectrum 5 Molecule d – 3-propanol

Spectrum 6 Molecule b – 1-chloropropane

CHAPTER EXAM

MULTIPLE CHOICE

1 A

2 B

3 C

4 A

5 C

6 B

7 D

8 B

9 A

10 D

SHORT RESPONSE

11 a Infrared spectroscopy

b Paper and thin-layer chromatography as well as electrophoresis

c Mass spectrometry

d Electrophoresis

12 a Alanine has a non-polar R group so will not absorb on the highly polar chromatography paper so it will continue to move with the solvent. The other two amino acids have polar R groups due to –COOH and $–NH_2$ so will form strong hydrogen bonds with the stationary phase and only move slowly along the paper.

b Aspartic acid has pI 3.0, so in a buffer of pH 6, it will form a negative ion and migrate towards the positive electrode; whereas lysine has pI 9.7, so in a buffer of pH 6, it will form positive ion and move towards the negative electrode.

c The pI of alanine is equal to the pH of the buffer so it will be present as neutral molecule and not be attracted to either electrode.

CROSS-CHAPTER QUESTION

13 a C_3H_7Cl

b Parent ion has $m/z = 78$, so molecular formula is also C_3H_7Cl.

c Due to the presence of the additional chlorine-37 isotope, there is an additional parent ion at $m/z = 80$.

d Students should draw 1-chloropropane and 2-chloropropane.

e 43, $CH_3CHCH_3^+$; 63, $CH_3CH^{35}Cl^+$; 65, $CH_3CH^{37}Cl^+$

f 2-Chloropropane is the most likely isomer because of the presence of the CH_3CHCl fragment.

DATA ANALYSIS

14 a $C_6H_{13}NO_2$

b Amides

c Clear differences in the wavenumber values of the peaks in the two infrared spectra, indicating that the bonds present in the molecules are different.

15 a Ethanol: CH_3CH_2OH, broad OH band at 3300 cm^{-1}; no C=O band

b Ethyl ethanoate: $CH_3COOCH_2CH_3$, no OH band; C=O and C–O bands

c Ethanoic acid CH_3COOH, broad OH band at 3300 cm^{-1}, C=O band 1700 cm^{-1}

d Ethyl ethanoate: $CH_3COOCH_2CH_3$, molecular mass 88

e Ethanol: CH_3CH_2OH, molecular mass 46

f Ethanoic acid: CH_3COOH, molecular mass 60

CHAPTER 17 CHEMICAL SYNTHESIS

LEARNING CHECK 17.1

DESCRIBING

1 Rate of reaction determines how quickly the product is produced, whereas the yield relates to the position of equilibrium and the percentage of reactant molecules that are converted to products.

2 To the right

3 100%

4 Removing the product prevents the system from reaching equilibrium and encourages the reactant molecules to continue reacting.

APPLYING

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

$n(N_2) = \frac{3.0}{22.7} = 0.132\,\text{mol}$

$n(H_2) = \frac{5.0}{22.7} = 0.220\,\text{mol}$

$SR = \frac{3}{1} = 3$

$AR = \frac{0.220}{0.132} = 1.67$

SR > AR; therefore, H_2 is the limiting reactant.

$n(NH_3) = \frac{2}{3} \times 0.220 = 0.147\,\text{mol}$

$m(NH_3) = 0.147 \times 17 = 2.50\,\text{g}$

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

$n(SO_2) = \frac{1000}{64.06} = 15.6\,\text{mol}$

$n(O_2) = \frac{1000}{32.00} = 31.3\,\text{mol}$

$SR = \frac{1}{2} = 0.5$

$AR = \frac{31.3}{15.6} = 2$

Since AR > SR, SO_2 is the limiting reactant.

$n(SO_3) = 15.6\,\text{mol}$

$m(SO_3) = 15.6 \times 80.06 = 1.25\,\text{kg}$

6 Theoretical yield of acetylsalicylic acid:

$n(C_7H_6O_3) = \frac{30.0}{138.12} = 0.217\ \text{mol}$

The mole ratio of acetylsalicylic acid and salicylic acid is 1:1, then:

$n(C_9H_8O_4) = 0.217\ \text{mol}$

$m(C_9H_8O_4) = 0.217 \times 180.17 = 39.1\ \text{g}$

$\text{Percentage yield} = \frac{25.0}{39.1} \times 100 = 63.9\%$

7 If the temperature is decreased, the forward reaction will be favoured and, hence, the yield of $Ca(OH)_2$ will be increased.

8 Assuming that density of water is 1 g mL^{-1},
100 mL = 100 g

$n(H_2O) = \frac{100}{18.02} = 5.55\ \text{mol}$

Since the molar ratio between H_2O and O_2 is 2:1:

$n(O_2) = \frac{5.55}{2} = 2.78\ \text{mol}$

$m(O_2) = 2.78 \times 32.0 = 89.0\ \text{g}$

$\text{Percentage yield} = \frac{65.9}{89.0} = 74.0\%$

9 Theoretical yield of aluminium chloride:

$n(Al(OH)_3) = \frac{25.0}{78.01} = 0.320\ \text{mol}$

Since the molar ratio between $Al(OH)_3$ and $AlCl_3$ is 1:1:

$n(AlCl_3) = 0.320\ \text{mol}$

$m(AlCl_3) = 0.320 \times 133.33 = 42.7\ \text{g}$

$\text{Percentage yield} = \frac{20.0}{42.7} \times 100 = 46.8\%$

10 Theoretical yield of chlorobenzene:

$n(C_6H_6) = \frac{90.0}{78.12} = 1.152\ \text{mol}$

Since the molar ratio between C_6H_6 and C_6H_5Cl is 1:1:

$n(C_6H_5Cl) = 1.152\ \text{mol}$

$m(C_6H_5Cl) = 1.152 \times 112.56 = 129.7\ \text{g}$

$\text{Percentage yield} = \frac{125.0}{129.7} \times 100 = 96.4\%$

11 a $Cl_2(g) + H_2(g) \rightarrow 2HCl(g)$

b High temperature and high pressure

c Lower temperature

d $n(Cl_2) = \frac{3000}{70.90} = 42.3\,\text{mol}$

$n(H_2) = \frac{150}{2.00} = 75\,\text{mol}$

$SR = \frac{1}{1} = 1$

$AR = \frac{75}{42.3} = 1.78$

Since AR > SR, Cl_2 is the limiting reactant.

LEARNING CHECK 17.2

DESCRIBING

1 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ – catalyst of iron/iron oxide; temperature 450°C; pressure 200 atm

2 $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ – temperature 400–450°C; pressure 1–2 atm; catalyst vanadium(V) oxide

3 Reaction is exothermic, so as the temperature increases, the system acts to oppose the change and reduce the temperature by favouring the endothermic reverse reaction.

4 Reaction involves a reduction in volume. As the pressure is increased, the concentration of all particles increases. Hence, the system acts to oppose this change by favouring the forward reaction and reducing the number of particles.

5 It is important that the reactants are introduced to the reactant vessel in the correct molar ratio to ensure that neither is in excess and so avoid wastage.

6 Catalysts enable the reactions to occur at a higher rate at lower temperatures, which saves costs and also prevents the issues of reducing yield.

7 Temperature, pressure, catalyst, recycling of unreacted products, reacting ratio of products, recycling of heat evolved, safety and economic considerations

LEARNING CHECK 17.3

DESCRIBING

1 A biofuel is a material that can be combusted to release energy but can be produced from living matter.

2 Because they are renewable and, hence, there is an infinite supply

3 A fuel cell is a galvanic cell that converts the energy from a chemical reaction into electricity, but with a continuous supply of reactants.

4 Chemical energy into electrical energy

5 To lower the activation energy of a reaction without itself being used up in the reaction

6 Platinum, rhodium and nickel

7 Fermentation of glucose and hydration of ethene

8 No. Ethene comes from crude oil, which is a fossil fuel, and so ethanol produced by this method cannot be regarded as a biofuel.

9 Oxidation: $C_6H_{12}O_6(aq) + 6H_2O(l) \rightarrow 6CO_2(g) + 24e^- + 24H^+$

Reduction: $6O_2(g) + 24e^- + 24H^+ \rightarrow 12H_2O(l)$

10 By connecting a number of fuel cells in series.

APPLYING

11 a Anode: $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$

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

b Water

c Electrons and hydrogen ions move from the anode towards the cathode. Electrons move through the wire, producing a potential difference. Hydrogen ions move through the proton exchange membrane.

CHAPTER EXAM

MULTIPLE CHOICE

1 A

2 A

3 B

4 D

5 D

6 D

7 C

8 B

9 D

10 D

SHORT RESPONSE

11 a Raw materials: methane, carbon monoxide, water, oxygen. Waste products: carbon dioxide

b To provide a high concentration of oxygen.

c After Reactor 1: CO, H_2, CH_4, CO_2 and H_2O

After Reactor 2: CO, H_2, CO_2

After methanol reactor: CH_3OH, H_2O, H_2

Water is recycled in the steam generator, unreacted H_2 is reacted after the methanol reactor.

d Reactors 1 and 2 require high energy to sustain high temperatures. The methanol reactor requires energy to sustain high pressure.

e Energy can be recycled from the methanol reactor and Reactor 2, where the heat generated from the exothermic reactors can be used to heat the other reactors.

f Catalysts are used to maintain a higher rate at a lower temperature to save costs and also enable a higher yield.

g The number of moles of gas decreases as the reaction occurs; hence, a high yield is favoured by high pressure.

12 a Since the molar ratio between H_2 and NH_3 is 3:2:

$$n(NH_3) = \frac{2}{3} \times 825 = 550 \text{ mol}$$

b $$n(N_2) = \frac{2.00}{28.02} = 0.0714 \text{ mol}$$

Since the molar ratio of N_2 and NH_3 is 1:2:

$n(NH_3) = 0.0714 \times 2 = 0.143$ mol

$m(NH_3) = 0.1428 \times 17.04 = 2.43$ g

c Percentage yield $= \frac{12}{80} \times 100 = 15\%$

CROSS-CHAPTER QUESTION

13 a Given the balanced equation for the reaction is:

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

	N_2	H_2	NH_3
Initial	0.002	0.01	0
Change	0.000 935	0.002 81	$+1.87 \times 10^{-3}$
Equilibrium	0.001 07	0.007 19	1.87×10^{-3}

$$K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]}$$

$$= \frac{(1.87 \times 10^{-3})^2}{(0.00719)^3(0.001\,07)}$$

$K_c = 8790$

b Q_c is larger than K_c, the reaction will proceed in the reverse (to the left) to form more N_2 and H_2 until equilibrium is reached.

c $SR = \frac{3}{1} = 3$

$$AR = \frac{1.500}{0.500} = 3$$

Since SR = AR, there is no limiting reactant.

Theoretical yield of ammonia:

$n(N_2):n(NH_3)$

1 : 2

$n(NH_3) = 0.500 \times 2 = 1.000$ mol

Therefore the theoretical yield of ammonia is 1.000 mol

d If the concentrations of the reactants are increased, according to Le Châtelier's principle, the system will change to reduce the increased concentration of reactants. The equilibrium will shift to the right, increasing the production of ammonia to return to equilibrium.

DATA ANALYSIS

14 a As the pressure increases, the percentage yield of ethanol increases.

b As the temperature increases, the percentage yield of ethanol decreases.

c The highest percentage yield of ethanol occurs at 160 atm and 300°C, where the yield is 50%.

d A pressure of 70 atm is probably used for a balance between yield and practicality. Although higher pressures such as 160 atm increase the yield, they also increase the cost and energy required to maintain such high pressures. It offers a reasonable yield while also being more cost effective and manageable in terms of equipment safety and energy consumption.

e At 400°C and 100 atm, the percentage yield can be predicted to be 26–28%.

f The equilibrium constant decreases as temperature increases, which indicates that the forward reaction is exothermic. According to Le Châtelier's principle, if the reaction is exothermic, increasing the temperature will shift the equilibrium to the left, decreasing the value of K_c. Therefore, the reaction is exothermic.

CHAPTER 18 MACROMOLECULES: POLYMERS, PROTEINS AND CARBOHYDRATES

LEARNING CHECK 18.1

DESCRIBING

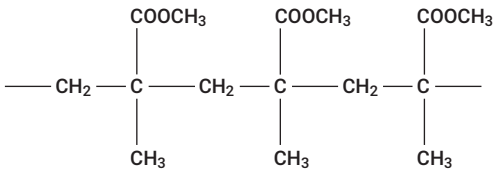
1 a The monomer must have a double bond.

b One of the bonds in each of the –C=C– double bonds is broken under the influence of a catalyst at high temperature and pressure. This leads to the formation of covalent bonds between adjacent monomers, eventually forming long chains of monomers bonded together, an addition polymer.

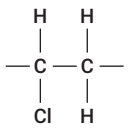
2 Ethene, polyethene

APPLYING

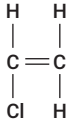
3



4 a



b



9780170483544

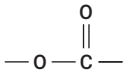
LEARNING CHECK 18.2

DESCRIBING

1 Polyesters and polyamides

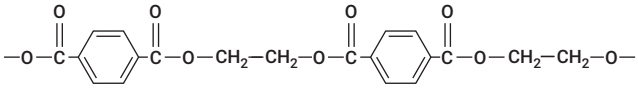
2 Similarity: Both processes result in the formation of long-chain polymers made from smaller monomers.
Difference: Condensation polymerisation requires monomers with two or more reactive functional groups (e.g. –OH, –COOH, $–NH_2$), whereas addition polymerisation requires unsaturated monomers with double or triple bonds (e.g. alkenes or alkynes). Condensation polymerisation produces a small molecule by-product, usually water, whereas addition polymerisation does not form by-products.

3



APPLYING

4

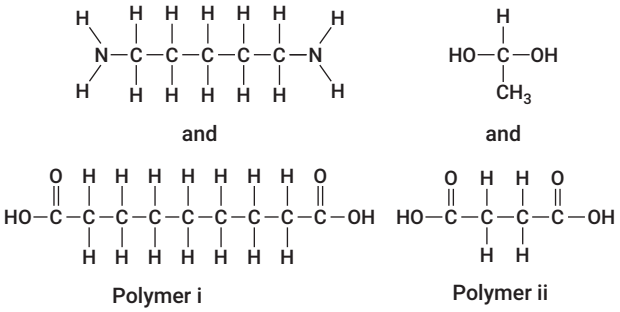


5 a Polyester

b Carboxyl group and hydroxyl group

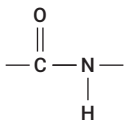
6 a i Polyamide **ii** Polyester

b



LEARNING CHECK 18.3

1 a



b –C–O–C–

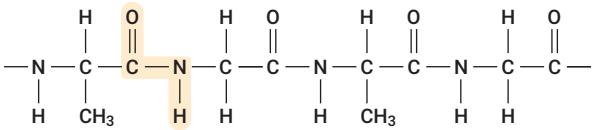
2 Similarity: Both linkages join monomer units together.

Difference: An ester link is a when a hydroxyl group (–OH) of one molecule and a carboxyl group (–COOH) of an adjoining molecule react. A peptide bond is a formed from the reaction between an amino group ($–NH_2$) of an amino acid and a carboxyl group (–COOH) of another amino acid. It is the bond between the carbon atom of one α-amino acid and a nitrogen atom on an adjacent α-amino acid along a peptide or protein chain.

3 Monosaccharides are one monomer unit, whereas disaccharides are two monomer units joined together.

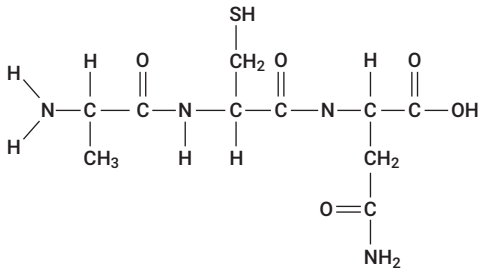
APPLYING

4

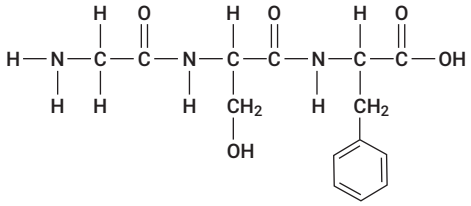


Peptide bond

5 a i



ii

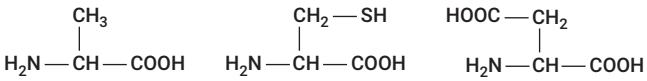


b i Ala–Cys–Asp; alanylcysteinylasparagine

ii Gly–Ser–Phe; glycylserylphenylalanine

6 a Three

b



7 a When a disaccharide undergoes hydrolysis, a water molecule is added. This is incorporated into the resulting monosaccharides.

b $C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$

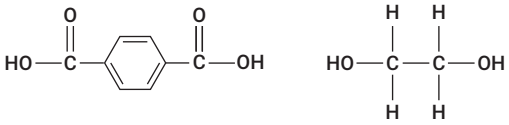
CHAPTER EXAM

MULTIPLE CHOICE

1 B
2 C
3 A
4 B
5 C
6 A
7 D
8 B
9 D
10 D

SHORT RESPONSE

11



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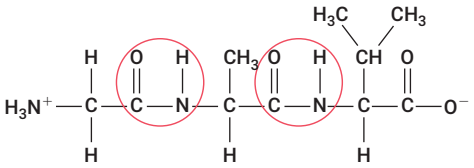
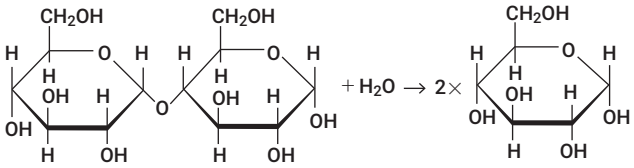


Peptide bonds join the three amino acids together.

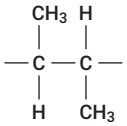
13



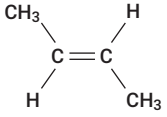
CROSS-CHAPTER QUESTION

14 a 2-Butene

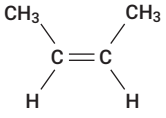
b Addition polymerisation



c

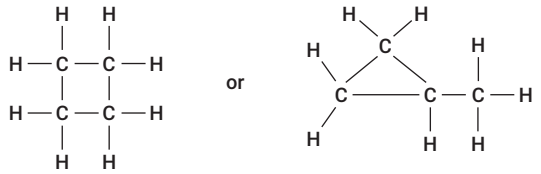


trans-2-Butene

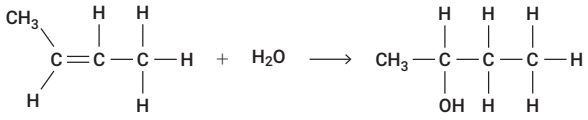


cis-2-Butene

d



e



$CH_3CHCHCH_3(g) + H_2O(l) \rightarrow CH_3CH(OH)CH_2CH_3(l)$

2-Butanol

Class: alcohol

f Hydroxyl group

DATA ANALYSIS

15 a So that the amount of plasticiser in the PVC is the independent variable that affects the bending of the samples. Size is a controlled variable.

b To help determine the reliability of the investigation or check for anomalous data

c 21

d The PVC sample has been used in the first three trials, so it is becoming weaker.

e It does not bend easily, making it suitable for the rigid window and door frames.

GLOSSARY

2-amino acid (or alpha-amino acid) an amino acid with one carbon atom separating the amino and carboxyl groups

A

absolute uncertainty the magnitude of the difference between the observed/measured value and the true value

accepted value the value of a substance or quantity that is universally agreed as being a best estimate due to multiple and highly accurate measurements

accuracy the degree to which a measurement conforms to the correct value; depends on the measuring instrument being used

acid dissociation equilibrium constant (K_a) the equilibrium expression of a weak acid

activated complex the intermediate state of a chemical reaction in which bonds are breaking and forming

activation energy, E_a the minimum amount of energy required for a chemical reaction to occur

addition polymer a polymer that forms by monomers joining together without the loss of any atoms

addition polymerisation the formation of polymer chains by the addition reaction of unsaturated monomers

addition reaction a reaction in which atoms are added to unsaturated molecules through the breaking of multiple bonds; a reaction in which two or more molecules combine to form a single product, without producing any by-products

adsorb to be attracted to the surface of the material; the opposite of desorb

alcohol an organic molecule containing one or more hydroxyl functional groups

aldehyde an organic molecule containing an aldehyde functional group at the end of the carbon chain

aldose a sugar containing an aldehyde group

aliquot a sample of specific volume of a larger volume of solution

alkane a class of hydrocarbons containing carbon chains with only single bonds between carbons

alkene a class of hydrocarbon with at least one double bond present between two carbons

alkyl chain a carbon group branch attached to a main carbon chain; commonly found as side groups in organic molecules and are often represented by the symbol R in chemical structures

alkyl group a group consisting of carbon and hydrogen atoms formed by the replacement of a hydrogen from an alkane

alkyne a class of hydrocarbon with at least one triple bond present between two carbons

alpha-carbon (or α-carbon) the first carbon atom bonded to a functional group; in an amino acid, the carbon that separates the amino and carboxyl groups

amidation a reaction between a carboxyl (–COOH) and an amine ($–NH_2$) group that forms an amide functional group

amide an organic molecule containing an amide ($–CONH_2$) functional group

amide link the –CONH– group formed when an amine reacts with a carboxylic acid

amine an organic molecule containing an amine ($–NH_2$) functional group

amino acid an organic compound containing a carboxyl (–COOH) and an amino group ($–NH_2$)

amorphous shapeless; not having an extended ordered arrangement of atoms, ions or molecules

amphiprotic a substance or species that can gain or lose a hydrogen ion to act as an acid or a base

amphoteric a substance that can act as an acid or act as a base depending on the reaction conditions

analyte a solution of an unknown concentration that will be analysed

anode the electrode where oxidation occurs

atactic a polymer in which the side-chain functional groups are randomly arranged on the polymer chain

B

base dissociation equilibrium constant (K_b) the equilibrium expression of a weak base

base peak the largest peak in a mass spectrum; assigned a value of 100% with other peaks relative to it

biodegradable able to decay naturally due to the action of enzymes produced by bacteria

biofuel a fuel produced from plants, algae or animal waste

branched hydrocarbon a hydrocarbon that has one or more carbon side chains attached

branching the presence of side chains on a polymer chain

buffer a solution that maintains a constant pH when small amounts of acid and base are added

buffer region the part of a titration curve during which the pH changes little as titrant is added; occurs when one of the reagents is a weak acid or a weak base and is the result of a buffer solution being set up

C

C-terminus the amino acid on the end of a peptide chain that has the free carboxyl group

carbon skeleton the arrangement of carbon atoms that other atoms join to in an organic molecule

carboxylic acid an organic molecule containing a carboxyl functional group

catalyst a substance that affects the rate of certain reactions by providing an alternative pathway

catalytic cracking the process of heating large organic molecules and converting them into smaller, more useful molecules

cathode the electrode where reduction occurs

chain structure the way in which the polymer chains are organised

chemical change a change in which a new substance is produced

chemical equilibrium a situation in which forward and reverse reactions occur at equal rates, leading to constant concentrations of reactants and products

chemical synthesis the process of making a product through a series of reactions

chemical system the chemicals involved in a reaction

chiral carbon atom a carbon atom that is bonded to four different groups or atoms, resulting in two possible arrangements (optical isomers) of the molecule

chromatography a group of techniques that separate substances based on differential distribution between a stationary phase and a mobile phase

class a broad category of molecules that share the same functional group

closed system a system in which the chemicals involved in a reaction are all contained in a fixed space

collision theory for a reaction to occur, the particles must collide with sufficient energy and in the required orientation

complete combustion burning of an organic compound in sufficient oxygen to produce only carbon dioxide and water

concentration a measure of the amount of solute in a given volume of solvent

concordant titres titres that differ by 0.1 mL from the highest to the lowest value

condensation polymer a polymer that forms by the elimination of a small molecule (often water) when monomers join

condensation reaction a reaction in which two molecules combine to produce a larger molecule and a small molecule, usually water

confounding variable a variable that is related to the independent and dependent variables

conjugate acid the acid that is formed when a base accepts one or more protons from an acid

conjugate base the base that is formed when an acid donates one or more protons to a base

contact process the industrial production of sulfuric acid

copolymer a polymer made from more than one type of monomer

cross-link a covalent or ionic bond between polymer chains, holding them together firmly

crystalline having an ordered arrangement of atoms, ions or molecules in the solid form

crystallinity the degree of order to the polymer structure

D

density the mass per unit volume

dependent variable the variable that changes due to changes to the independent variable

desorb the action of a substance moving from the stationary phase to the mobile phase; the opposite of adsorb

diamine a molecule that has two amino ($-NH_2$) functional groups

dicarboxylic acid a molecule that has two carboxyl ($-COOH$) functional groups

dimer a molecular complex consisting of two identical molecules linked together

diol an alcohol molecule that has two hydroxyl ($-OH$) functional groups

dipeptide two amino acids joined together with a peptide bond

dipole–dipole interaction the attraction between molecules with permanent dipoles

diprotic a substance that can donate two protons

disaccharide a sugar made from two monosaccharide units

dispersion force a weak intermolecular force that arises from electrostatic attractions between instantaneous dipoles in neighbouring molecules

disproportionation reaction typically a redox reaction, where a molecule is transformed into two or more dissimilar products

dissociation reaction a reaction in which an ionic substance separates in a solution

distillation a separation technique of a liquid mixture based on boiling point; the mixture is heated and the vapour produced condensed

dynamic equilibrium a closed system in balance in which the forward and reverse reactions occur at the same rate

E

electric field a region of influence around a charged particle where a force is exerted on other charged objects

electrochemical cell a device that transforms energy between electrical energy and chemical potential energy

electrode the conductor of a cell connected to the external circuit; also the combination of conductor and associated ions in solution

electrolyte a substance that dissociates into ions when dissolved in a solvent

electrolytic cell an electrochemical cell that transforms electrical energy into chemical potential energy

electrorefining a process used to produce a pure sample of a metal from an impure sample using electrolysis

elimination reaction a reaction in which a molecule is lost from a larger molecule, producing an unsaturated product

empirical formula the simplest whole-number ratio of atoms or ions in a substance

enantiomers the mirror image forms of optical isomers

end point the physical sign that indicates that the equivalence point has been reached; achieving the correct end point depends on using an appropriate indicator that will undergo a physical change at the appropriate point

endothermic reaction a reaction in which energy is absorbed from the surroundings, causing temperature to decrease

enthalpy total energy content of a chemical substance

equilibrium constant the value of the ratio between the concentrations of the reactants and products, represented as K_c

equilibrium expression the ratio of the concentrations of products to reactants used to calculate the equilibrium constant

equivalence point the point at which the reactants are present in the ratio shown by the mole ratio in the balanced chemical equation for the reaction

error the difference between a measured value and true value

ester an organic molecule containing the ester functional group, –COO–

ester link the –COO– group that links two alkyl chains in an ester molecule

esterification the condensation reaction in which an ester is formed from an alcohol and a carboxylic acid

excess reactant the reactant that is not completely consumed when a reaction is complete

exothermic reaction a reaction in which energy is released to the surroundings, causing temperature to increase

external circuit the circuit of an electrochemical cell consisting of the connecting wires and voltmeter or electrical appliance

extraneous variable any variable that is not directly related to the experiment but could affect the results of the experiment

F

Faraday constant the quantity of electricity, in coulombs, C, carried by 1 mole of electrons; equal to 96 485 coulombs per mole ($C\ mol^{-1}$)

Faraday's first law of electrolysis the mass of a substance produced or consumed at an electrode during electrolysis is proportional to the quantity of electricity that passes through the electrolytic cell

fingerprint region a region in an infrared spectrum of absorption of 1400 cm^{-1} or less, where it is difficult to assign peaks to specific bonds; the region is used to identify a molecule by comparing it to a library standard

fractional distillation the separation of a mixture of organic compounds according to their different boiling points

free radical substitution reaction a UV-light-initiated reaction, where a hydrogen atom is replaced with a halogen atom

fuel cell a galvanic cell that generates electricity from a chemical reaction, but where there is a continuous supply of fuel and also removal of products

functional group a group of atoms in a molecule that causes the molecule to chemically react in a distinctive way

G

galvanic cell (or voltaic cell) an electrochemical cell that transforms chemical potential energy to electrical energy in a spontaneous chemical reaction

gel electrophoresis the process of separating large charged molecules by placing them in an electric field and observing their migration through a medium such as a gel

geometric isomers molecules with the same structural formula but different arrangements of atoms in space, typically around a rigid central double bond

glycosidic link the ether bond (–C–O–C–) that connects two monosaccharide units in a carbohydrate

H

Haber process the industrial production of ammonia

half equivalence point the point at which exactly half of the acid in the buffer solution has reacted with the titrant

half-cell the part of a galvanic cell where oxidation or reduction occurs

half-equation the oxidation reaction or the reduction reaction of a redox reaction

haloalkane an alkane with a halogen (I, Cl, F or Br) attached to a carbon

halogen any of the reactive non-metallic elements from group 17 of the periodic table (fluorine, chlorine, bromine, iodine)

halogenation an addition reaction involving a halogen molecule

heterogeneous system a system in which there is a mixture of phases of reactants and products

homogeneous system a system in which all the reactants and products are in the same phase

homologous series a series of organic molecules within the same class, with different-length carbon chains

homopolymer a polymer made from one type of monomer

hydrogen bond the attraction of a H atom that is bonded to an O, N or F atom to the lone pair of electrons of N, O or F of an adjacent molecule

hydrogenation an addition reaction in which hydrogen is the molecule added

hydrolysis a reaction in which a larger molecule is split into two smaller molecules by reacting with water in the presence of an acid or base catalyst

hydronium ion the ion that forms when a proton is donated to a water molecule (H_3O^+)

hydrophilic having a tendency to attract water

hydrophobic having a tendency to repel water

incomplete combustion burning of an organic compound in limited oxygen to produce carbon monoxide or carbon and water

I

independent variable the variable that is purposely changed or manipulated in an experiment

instrumental uncertainty the inherent limitations and potential errors associated with the measuring instruments or tools used in scientific experiments or observations

intermediate a short-lived chemical species formed during a reaction

intermediate species species formed during a reaction pathway as precursors to the desired product

intermolecular force an attractive force that causes molecules to aggregate to form liquids and solids

internal circuit the circuit of an electrochemical cell consisting of the strips of metal, solutions and salt bridge

ionisation reaction the process in which a molecular substance, often an acid, dissolves in water and separates into ions by the gain or loss of an electron

isoelectric point the pH value at which there is no net charge on an amino acid

isotactic a polymer in which the side-chain functional groups are regularly arranged on the same side of the chain

K

ketone an organic molecule containing a carbonyl functional group within the carbon chain

ketose a sugar containing a ketone group

kinetically stable where the cell potential indicates that a reaction will occur but, in practice, there is no perceptible reaction because of the high activation energy

L

Le Châtelier's principle the principle that states that if a change is imposed on a system at equilibrium, then the system will act to partially counteract the change

limiting reactant the reactant that is completely consumed when a chemical reaction is complete

line of best fit a straight line through data points in a graph that best expresses the relationship shown in a scatterplot

logbook a complete, permanent record of how an experiment or research project was conducted; it shows what was done at every step along the way

M

macroscopic property a property that is observable, e.g. pressure, temperature, colour, mass

Markovnikov's law in reactions involving the addition of a hydrogen atom and another group (e.g. halide, hydroxide), the hydrogen adds to the carbon with the most hydrogen atoms

maximum trendline a trendline with the greatest gradient that fits within the data within the uncertainty values

mean the average value of a set of values

minimum trendline a trendline with the smallest gradient that fits within the data within the uncertainty values

mobile phase the fluid used to carry the components of a mixture up the stationary phase so they can separate

molecular formula a representation of the actual number of atoms of each element present in one molecule of a substance

molecular ion (M^+) the ion formed when a molecule is ionised without being fragmented in a mass spectrometer

monomer an individual unit of a polymer

monomer arrangement organisation of repeating units in the monomer

monoprotic a substance that can donate one proton

monosaccharide the simplest form of sugar that cannot be broken down into smaller units

N

N-terminus the amino acid on the end of a peptide chain that has the free amine group

neutral neither acidic nor basic; has a pH of 7

nucleophile an electron-rich species that donates a pair of electrons to form a covalent bond

nucleophilic substitution a reaction of organic molecules in which a nucleophile replaces a functional group (the leaving group)

O

open system a system in which one or more reactants or products in a reaction can be added or lost

optical isomers molecules that are non-superimposable mirror images of one another

oxidation (of an organic compound) a reaction in which an organic compound gains oxygen or loses hydrogen (e.g. primary alcohols are converted to aldehydes and carboxylic acids, and secondary alcohols are converted to ketones)

oxidation the loss of electrons from an atom, which is said to be oxidised

oxidising agent or oxidant a substance that causes another substance to be oxidised

P

parallax error an error in measurement due to the observer's position relative to the meaningful scales; if the reading is taken at an angle to the scale, then an error is introduced

parent molecular ion the molecular ion that gives the molecular mass of the original compound in mass spectrometry

partial pressure the pressure exerted by an individual gas in a gaseous mixture

Pearson correlation coefficient (R) a statistical measure that quantifies the direction and strength of a relationship between two variables

peptide bond an amide-type bond form by joining the carboxyl group of one amino acid to the amino group of another

percentage error the difference between a measurement result and an accepted value, expressed as a percentage of the accepted value

percentage ionisation the percentage of acid that has ionised in water

percentage uncertainty a measure of the uncertainty of a measurement compared with the size of the measurement, given as a percentage

percentage yield the percentage of the maximum possible amount of product from a reaction that has experimentally been produced

physical change a change in which no new substance is produced

physical equilibrium a situation in which rates of opposing processes, such as phase changes (e.g. evaporation/condensation), are equal, resulting in no net change to the system

planar in the same plane

plastic a synthetic polymer that is malleable, pliable and capable of being moulded by heat and pressure

polarity a measure of the unequal sharing of electrons in a covalent bond; the result of the difference in electronegativity of the bonded atoms

polyalkane a long repeating chain of alkane molecules joined together

polyamide a polymer formed by a condensation polymerisation reaction between an amine group and a carboxylic acid group

polyester a polymer formed by a condensation polymerisation reaction between a hydroxyl group and a carboxylic acid group

polylactic acid (PLA) a biodegradable polymer produced from lactic acid molecules joined by ester links

polymer a large molecule made from many thousands of repeating units

polymerisation the process by which monomers link together to form a polymer

polypeptide long chains of amino acids joined together with peptide bonds

polysaccharide a carbohydrate molecule made from many monosaccharide units

polytetrafluoroethene (PTFE) addition polymer formed from repeating units of tetrafluoroethene

position of equilibrium the relative concentrations of the products and reactants are at equilibrium

precision a measure of how close a number of independent measurements of the same quantity are to each other

prefix a part of the name of an organic molecule that denotes a functional group and its position on the carbon chain; it comes at the start of the name

primary alcohol an alcohol in which the –C–OH group is joined to one other carbon atom

primary data data collected directly by a person or group

primary standard a solution of accurately known concentration that remains stable under common laboratory conditions for extended periods of time

primary structure the sequence of monomers in a biopolymer chain

protein an organic compound made from long chains of amino acids; an essential food group

Q

qualitative data information that is not numerical in nature

quantitative data numerical information

quaternary structure the shape of two or more polymer chains aggregated together, held by intermolecular interactions

R

radical a molecule with an unpaired electron; generally highly reactive

random error a variation that affects a measurement in a random way so that successive measured values may reflect small changes from each other

range the difference between the maximum and minimum values of a measured confidence interval

reaction mechanism the steps involved in a reaction

reaction pathway a series of reactions leading to a specific outcome or product

reaction quotient (Q) the value of the equilibrium expression when calculated, Q

reactivity series of metals a list of metals in order of decreasing ease of reactivity (i.e. most easily oxidised to least easily oxidised)

redox reaction a reaction that involves the oxidation of one atom and the reduction of another atom

reducing agent or reductant a substance that causes another substance to be reduced

reducing sugar another name for an aldose sugar

reduction (hydrogenation) a hydrogenation reaction of alkene, alkynes or amines

reduction the gain of electrons by an atom, which is said to be reduced

reference cell an electrode used for reference on half-cell potential reactions

reflux a process of heating a reaction mixture to its boiling point and then condensing the vapour back into the reaction vessel

reliability the extent to which the results of assessments are consistent, replicable and free from error

research question a question that directs the scientific inquiry activity; it focuses the research investigation or student experiment, informing the direction of the research, and guiding all stages of inquiry, analysis, interpretation and evaluation

retention factor (R_F) the distance travelled by the components of a sample from its origin divided by the distance moved by the solvent from the origin (also called retardation factor)

reversible a reaction in which the products can be converted back to the reactants

S

salt bridge a link containing an electrolyte between the oxidation and reduction half-cells of a galvanic cell

saturated compound an organic compound containing only single bonds between carbon atoms

secondary alcohol an alcohol in which the –C–OH group is joined to two other carbon atoms

secondary data data that is collected by someone else

secondary structure the regular folding patterns in a biopolymer chain caused by (mainly) hydrogen bonds

self-ionisation constant (K_w) the equilibrium expression that shows water ionising into two ions

semi-structural formula a condensed version of the structural formula showing the sequence of atoms listed by carbon atom but not the bonds

side group a functional or hydrocarbon group on a polymer chain that is not part of the main chain

solubility product a type of equilibrium constant used to indicate the relative solubility of a precipitate in a solvent to form a saturated solution at a particular temperature

standard cell potential the difference in electrode potential between the two half-cells that make up a galvanic cell

standard electrode potential ($E°$) the potential of an electrode (measured in volts) in its standard state relative to the standard hydrogen electrode

standard laboratory conditions (SLC) a set of conditions commonly used when performing calculations on gases, such as gas density; standard laboratory temperature is 298 K (25°C), standard laboratory pressure is 1 atm (100 kPa)

standard temperature and pressure (STP) a set of conditions commonly used when performing calculations on gases, such as gas density; standard temperature is 273 K (0°C), standard pressure is 1 atm (100 kPa)

stationary phase the immobile surface that different components of a mixture can adhere to when carried along by the mobile phase

steady state an open system in balance in which the inflow of materials from the surroundings equals the outflow of materials to the surroundings

stem the part of the name of an organic molecule that denotes the length of the longest carbon chain

stereoisomers molecules with the same molecular formula but different spatial arrangements of atoms

stereoregular polymer a polymers with small, regularly ordered units in a single chain

strong acid an acid that readily donates a proton to water

structural formula a displayed arrangement of the atoms in a molecule, showing all bonds

structural isomers molecules with the same molecular formula but different arrangements of atoms

suffix a part of the name of an organic molecule that denotes a functional group and its position on the carbon chain; it comes at the end of the name

surroundings everything except the chemicals involved in a reaction

syntactic a polymer in which the side-chain functional groups alternate above and below the chain

systematic error an error that acts to give a consistent offset in data; e.g. consistently above or consistently below

T

tensile strength the resistance of a substance to being pulled or stretched

tertiary alcohol an alcohol in which the –C–OH group is joined to three other carbon atoms

tertiary structure the 3D shape of a single polymer chain held together by interactions from different parts of the molecule

theoretical yield the amount (mass) of a product that is produced from a complete reaction of the limiting reactant

thermoplastic a plastic polymer that can be melted and re-formed

thermosetting a plastic polymer that cannot be melted and re-formed

titrant a solution of known concentration that is added to another solution from a burette

titration a type of volumetric analysis for determining an end point

titration curve a graphical representation of a titration; the x-axis shows the volume of titrant added, and the y-axis shows the pH of the solution

tripeptide a short chain of three amino acids linked by peptide bonds

triprotic a substance that can donate three protons

U

uncertainty the range of values for a measurement result, taking account of the likely values that could be attributed to the measurement result given the measurement equipment, procedure and environment

unsaturated compound organic compound that has at least one double bond or triple bond between carbon atoms

V

validity the extent to which the experiment measures what it is intended to measure

volatility how readily a substance vaporises to form a gas at regular temperatures and pressures

W

weak acid an acid in which only a small proportion of the molecules donate a proton to water

Z

zwitterion the form of an amino acid in which the amino group is protonated at the same time as the carboxyl group is deprotonated, so that there is no net charge

INDEX

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