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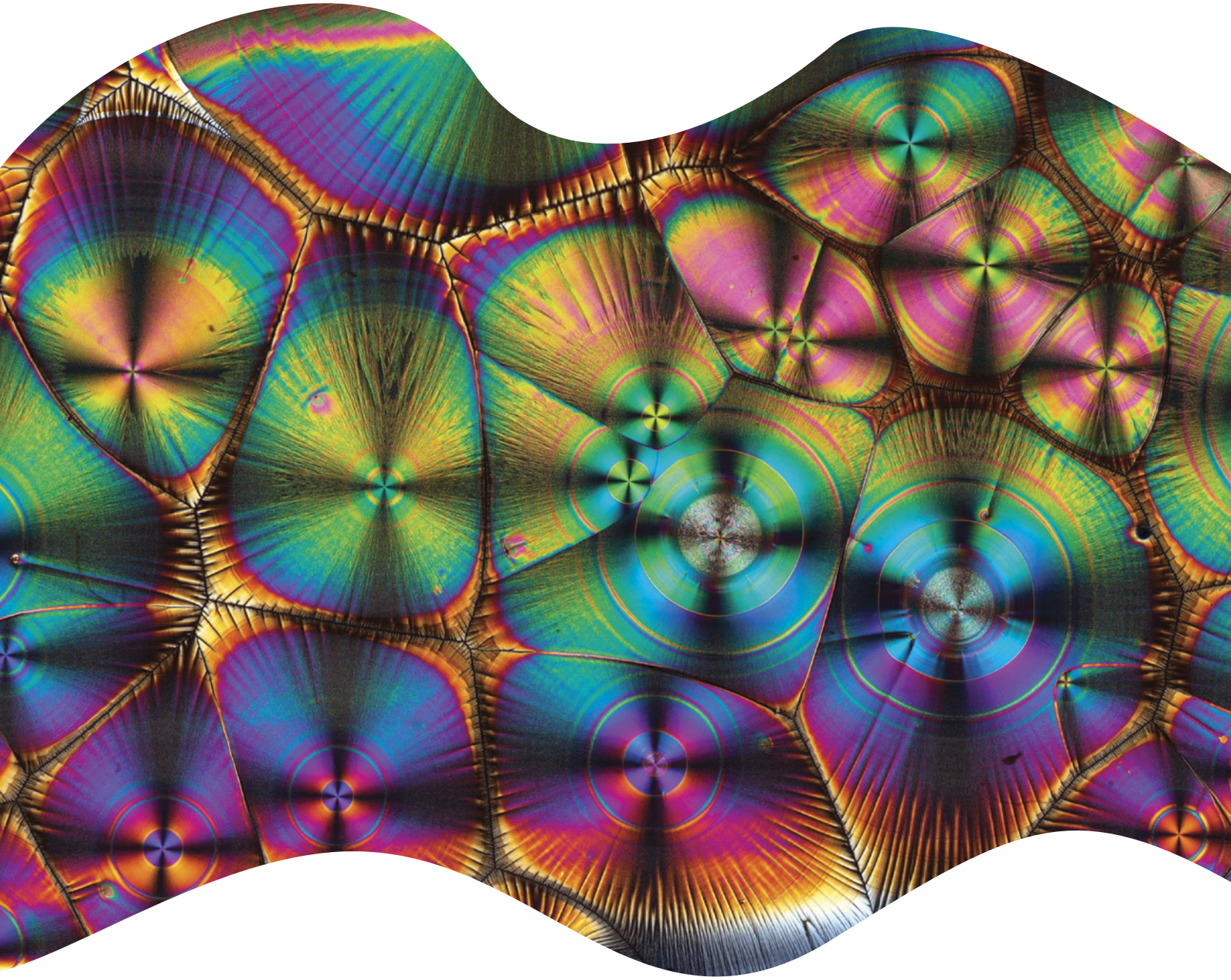
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QCE 2019 SYLLABUS

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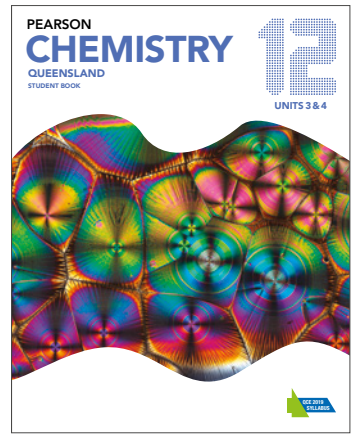
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The CEA has established a tradition of providing up-to-date text, electronic material and support resources for both students and teachers, and professional development opportunities for teachers.

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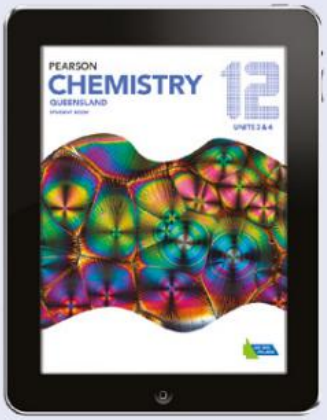
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How to use this book

PEARSON CHEMISTRY 12 QUEENSLAND STUDENT BOOK

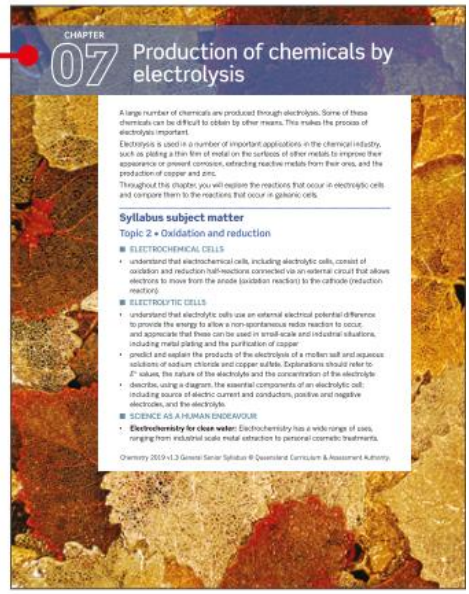
Pearson Chemistry 12 Queensland Student Book has been written to the new QCAA Chemistry 2019 General Senior Syllabus. The book is an easy-to-use resource that covers Units 3 and 4, and comprehensively addresses the skills and assessment requirements. Explore how to use this book below.

Design

Featuring best-practice literacy and instructional design, this series supports all learners with careful scaffolding of concepts and defined learning objectives. A simple to navigate, predictable design enables ease of use. The high-quality, relevant photos and illustrations assist student understanding of concepts.

Chapter opener

The syllabus subject matter addressed in each chapter is clearly listed, along with any Science as a human endeavour features and mandatory practicals.


CHAPTER 07
Production of chemicals by electrolysis

A large number of chemicals are produced through electrolysis. Some of these chemicals can be difficult to obtain by other means. This makes the process of electrolysis important.

Electrolysis is used in a number of important applications in the chemical industry, such as plating a thin film of metal on the surfaces of other metals to improve their appearance or prevent corrosion, extracting reactive metals from their ores, and the production of copper and zinc.

Throughout this chapter, you will explore the reactions that occur in electrolytic cells and compare them to the reactions that occur in galvanic cells.

Syllabus subject matter

Topic 2 • Oxidation and reduction

■ ELECTROCHEMICAL CELLS

- understand that electrochemical cells, including 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)

■ ELECTROLYTIC CELLS

- understand that electrolytic cells use an external electrical potential difference to provide the energy to allow a non-spontaneous redox reaction to occur, and appreciate that these can be used in small-scale and industrial situations, including metal plating and the purification of copper
- predict and explain the products of the electrolysis of a molten salt and aqueous solutions of sodium chloride and copper sulfate. Explanations should refer to E° values, the nature of the electrolyte and the concentration of the electrolyte
- describe, using a diagram, the essential components of an electrolytic cell; including source of electric current and conductors, positive and negative electrodes, and the electrolyte.

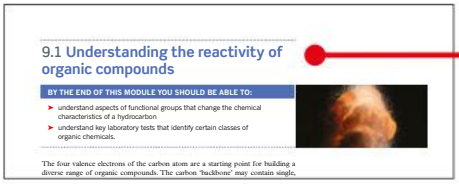
■ SCIENCE AS A HUMAN ENDEAVOUR

- **Electrochemistry for clean water:** Electrochemistry has a wide range of uses, ranging from industrial-scale metal extraction to personal cosmetic treatments.

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Module opener

Module openers outline the key concepts and skills developed and link to syllabus subject matter listed in the chapter opener.


9.1 Understanding the reactivity of organic compounds

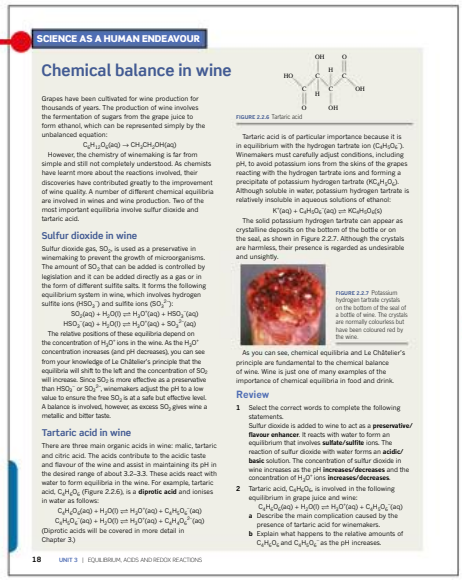
BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand aspects of functional groups that change the chemical characteristics of a hydrocarbon
- understand key laboratory tests that identify certain classes of organic chemicals.

The four valence electrons of the carbon atom are a starting point for building a diverse range of organic compounds. The carbon 'backbone' may contain single,

Science as a human endeavour

The Science as a human endeavour features provide an opportunity to appreciate the development of science and its use in and influence on society. They provide a segue into the development of claims and research questions for the research investigation. Questions are included to help students formulate ideas and delve more deeply into the concepts.


SCIENCE AS A HUMAN ENDEAVOUR

Chemical balance in wine

Grapes have been cultivated for wine production for thousands of years. The production of wine involves the fermentation of sugars from the grape juice to form ethanol, which can be represented simply by the unbalanced equation:

$C_6H_{12}O_6(aq) \rightarrow CH_3CH_2OH(aq)$

However, the chemistry of winemaking is far from simple and still not completely understood. As chemists have learnt more about the reactions involved, their discoveries have contributed greatly to the improvement of wine quality. A number of different chemical equilibria are involved in wines and wine production. Two of the most important equilibria involve sulfur dioxide and tartaric acid.

FIGURE 2.2.6 Tartaric acid

Sulfur dioxide in wine

Sulfur dioxide gas, SO_2, is used as a preservative in winemaking to prevent the growth of microorganisms. The amount of SO_2 that can be added is controlled by legislation and it can be added directly as a gas or in the form of different sulfite salts. It forms the following equilibrium system in wine, which involves hydrogen sulfite ions (HSO_3^-) and sulfite ions (SO_3^{2-}):

$SO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq)$

$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_3^{2-}(aq)$

The relative positions of these equilibria depend on the concentration of H_3O^+ ions in the wine. As the H_3O^+ concentration increases (and pH decreases), you can see from your knowledge of Le Châtelier's principle that the equilibria will shift to the left and the concentration of SO_2 will increase. Since SO_2 is more effective as a preservative than HSO_3^- or SO_3^{2-}, winemakers adjust the pH to a low value to ensure the free SO_2 is at a safe but effective level. A balance is involved, however, as excess SO_2 gives wine a metallic and bitter taste.

Tartaric acid in wine

There are three main organic acids in wine: malic, tartaric and citric acid. The acids contribute to the acidic taste and flavour of the wine and assist in maintaining its pH in the desired range of about 3.2–3.3. These acids react with water to form equilibria in the wine. For example, tartaric acid, $C_4H_6O_6$, (Figure 2.2.6), is a **diprotic acid** and ionises in water as follows:

$C_4H_6O_6(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_4H_5O_6^-(aq)$

$C_4H_5O_6^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_4H_4O_6^{2-}(aq)$

(Diprotic acids will be covered in more detail in Chapter 3.)

FIGURE 2.2.7 Potassium hydrogen tartrate crystals on the bottom of the seal of a bottle of wine. The crystals are normally colourless but have been coloured red by the wine.

As you can see, chemical equilibria and Le Châtelier's principle are fundamental to the chemical balance of wine. Wine is just one of many examples of the importance of chemical equilibria in food and drink.

Review

1 Select the correct words to complete the following statements.
Sulfur dioxide is added to wine to act as a **preservative/flavour enhancer**. It reacts with water to form an equilibrium that involves **sulfate/sulfite** ions. The reaction of sulfur dioxide with water forms an **acidic/basic** solution. The concentration of sulfur dioxide in wine increases as the pH **increases/decreases** and the concentration of H_3O^+ ions **increases/decreases**.

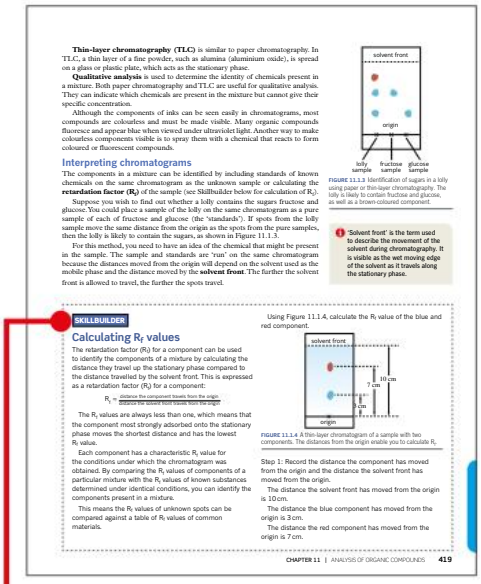
2 Tartaric acid, $C_4H_6O_6$, is involved in the following equilibrium in grape juice and wine:

$C_4H_6O_6(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_4H_5O_6^-(aq)$

a Describe the main complication caused by the presence of tartaric acid for winemakers.

b Explain what happens to the relative amounts of $C_4H_6O_6$ and $C_4H_5O_6^-$ as the pH increases.

18 UNIT 3 | EQUILIBRIUM, ACIDS AND REDOX REACTIONS


Thin-layer chromatography (TLC) is similar to paper chromatography. In TLC, a thin layer of a fine powder, such as alumina (aluminium oxide), is spread on a glass or plastic plate, which acts as the stationary phase.

Qualitative analysis is used to determine the identity of chemicals present in a mixture. Both paper chromatography and TLC are useful for qualitative analysis. They can indicate which chemicals are present in the mixture but cannot give their specific concentration.

Although the components of inks can be seen easily in chromatograms, most compounds are colourless and must be made visible. Many organic compounds fluoresce and appear blue when viewed under ultraviolet light. Another way to make colourless components visible is to spray them with a chemical that reacts to form coloured or fluorescent compounds.

Interpreting chromatograms

The components in a mixture can be identified by including standards of known chemicals on the same chromatogram as the unknown sample or calculating the **retardation factor (R_f)** of the sample (see Skillbuilder below for calculation of R_f).

Suppose you wish to find out whether a lolly contains the sugars fructose and glucose. You could place a sample of the lolly on the same chromatogram as a pure sample of each of fructose and glucose (the 'standards'). If spots from the lolly sample move the same distance from the origin as the spots from the pure samples, then the lolly is likely to contain the sugars, as shown in Figure 11.1.3.

For this method, you need to have an idea of the chemical that might be present in the sample. The sample and standards are 'run' on the same chromatogram because the distances moved from the origin will depend on the solvent used as the mobile phase and the distance moved by the **solvent front**. The further the solvent front is allowed to travel, the further the spots travel.

'Solvent front' is the term used to describe the movement of the solvent during chromatography. It is visible as the wet moving edge of the solvent as it travels along the stationary phase.

FIGURE 11.1.3 Identification of sugars in a lolly using paper or thin-layer chromatography. The lolly is likely to contain fructose and glucose, as well as a brown-coloured component.

SKILLBUILDER

Calculating R_f values

The retardation factor (R_f) for a component can be used to identify the components of a mixture by calculating the distance they travel up the stationary phase compared to the distance travelled by the solvent front. This is expressed as a retardation factor (R_f) for a component:

$R_f = \frac{\text{distance the component travels from the origin}}{\text{distance the solvent front travels from the origin}}$

The R_f values are always less than one, which means that the component most strongly adsorbed onto the stationary phase moves the shortest distance and has the lowest R_f value.

Each component has a characteristic R_f value for the conditions under which the chromatogram was obtained. By comparing the R_f values of components of a particular mixture with the R_f values of known substances determined under identical conditions, you can identify the components present in a mixture.

This means the R_f values of unknown spots can be compared against a table of R_f values of common materials.

Using Figure 11.1.4, calculate the R_f value of the blue and red component.

FIGURE 11.1.4 A thin-layer chromatogram of a sample with two components. The distances from the origin enable you to calculate R_f.

Step 1: Record the distance the component has moved from the origin and the distance the solvent front has moved from the origin.

The distance the solvent front has moved from the origin is 10 cm.

The distance the blue component has moved from the origin is 3 cm.

The distance the red component has moved from the origin is 7 cm.

CHAPTER 11 | ANALYSIS OF ORGANIC COMPOUNDS 419

Dynamic equilibrium is reached by reversible physical or chemical reactions taking place in a closed system.

Highlight box

Highlight features focus students' attention on important information such as key definitions, formulas and salient points.

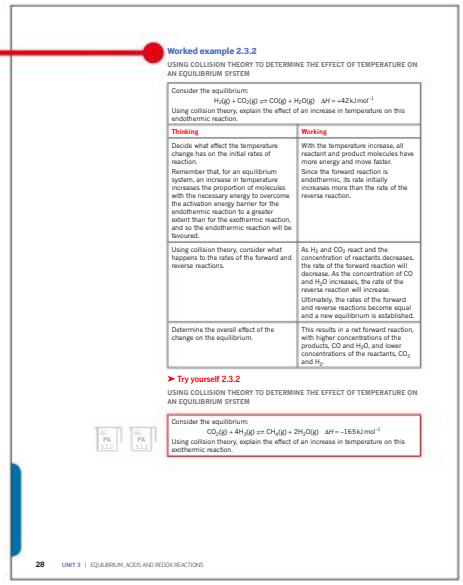
Skillbuilder

A Skillbuilder outlines a method or technique. Each one is instructive and self-contained. Skillbuilders step students through the skills required when analysing or utilising knowledge.

Worked examples

Worked examples use sequential steps of thinking and working. This research-based approach greatly enhances student understanding and application of formulas to subject matter. Each worked example is followed by a Try yourself task where students apply their learning to a mirrored problem to practise the skill.

Fully worked solutions to all Try yourself tasks are available on *Pearson Chemistry 12 Queensland Teacher Support*.



Worked example 2.3.2

USING COLLISION THEORY TO DETERMINE THE EFFECT OF TEMPERATURE ON AN EQUILIBRIUM SYSTEM

Consider the equilibrium:

$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g) \quad \Delta H = +42 kJ.mol^{-1}$

Using collision theory, explain the effect of an increase in temperature on this endothermic reaction.

Thinking	Working
Decide what effect the temperature change has on the initial rates of reaction. Remember that, for an equilibrium system, an increase in temperature increases the proportion of molecules with the necessary energy to overcome the activation energy barrier for the endothermic reaction to a greater extent than for the exothermic reaction, and so the endothermic reaction will be favoured.	With the temperature increase, all reactant and product molecules have more energy and move faster. Since the forward reaction is endothermic, its rate initially increases more than the rate of the reverse reaction.
Using collision theory, consider what happens to the rates of the forward and reverse reactions.	As H_2 and CO_2 react and the concentration of reactants decreases, the rate of the forward reaction will decrease. As the concentration of CO and H_2O increases, the rate of the reverse reaction will increase. Ultimately, the rates of the forward and reverse reactions become equal and a new equilibrium is established.
Determine the overall effect of the change on the equilibrium.	This results in a net forward reaction, with higher concentrations of the products, CO and H_2O, and lower concentrations of the reactants, CO_2 and H_2.

Try yourself 2.3.2

USING COLLISION THEORY TO DETERMINE THE EFFECT OF TEMPERATURE ON AN EQUILIBRIUM SYSTEM

Consider the equilibrium:

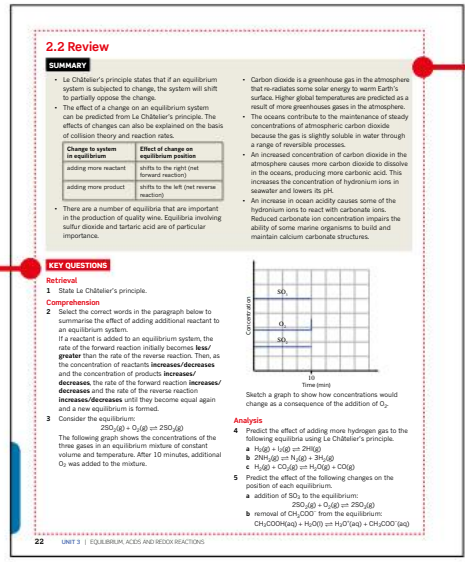
$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g) \quad \Delta H = -165 kJ.mol^{-1}$

Using collision theory, explain the effect of an increase in temperature on this exothermic reaction.

28 UNIT 3 | EQUILIBRIUM, ACIDS AND REDOX REACTIONS

Module review

Each module finishes with key questions to test students' understanding and ability to recall the key concepts of the module. Questions are carefully categorised under the relevant cognitive level—retrieval, comprehension or analysis—and are developed to assess the syllabus requirements.



2.2 Review

SUMMARY

- Le Châtelier's principle states that if an equilibrium system is subjected to change, the system will shift to partially oppose the change.
- The effect of a change on an equilibrium system can be predicted from Le Châtelier's principle. The effects of changes can also be explained on the basis of collision theory and reaction rates.

Change to system in equilibrium	Effect of change on equilibrium position
adding more reactant	shifts to the right (net forward reaction)
adding more product	shifts to the left (net reverse reaction)

- There are a number of equilibria that are important in the production of quality wine. Equilibria involving sulfur dioxide and tartaric acid are of particular importance.
- Carbon dioxide is a greenhouse gas in the atmosphere that re-radiates some solar energy to warm Earth's surface. Higher global temperatures are predicted as a result of more greenhouses gases in the atmosphere.
- The oceans contribute to the maintenance of steady concentrations of atmospheric carbon dioxide because the gas is slightly soluble in water through a range of reversible processes.
- An increased concentration of carbon dioxide in the atmosphere causes more carbon dioxide to dissolve in the oceans, producing more carbonic acid. This increases the concentration of hydronium ions in seawater and lowers its pH.
- An increase in ocean acidity causes some of the hydronium ions to react with carbonate ions. Reduced carbonate ion concentration impairs the ability of some marine organisms to build and maintain calcium carbonate structures.

KEY QUESTIONS

Retrieval

1 State Le Châtelier's principle.

Comprehension

2 Select the correct words in the paragraph below to summarise the effect of adding additional reactant to an equilibrium system.
If a reactant is added to an equilibrium system, the rate of the forward reaction initially becomes **less/greater** than the rate of the reverse reaction. Then, as the concentration of reactants **increases/decreases** and the concentration of products **increases/decreases**, the rate of the forward reaction **increases/decreases** and the rate of the reverse reaction **increases/decreases** until they become equal again and a new equilibrium is formed.

3 Consider the equilibrium:
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
The following graph shows the concentrations of the three gases in an equilibrium mixture of constant volume and temperature. After 10 minutes, additional O_2 was added to the mixture.

Sketch a graph to show how concentrations would change as a consequence of the addition of O_2.

Analysis

4 Predict the effect of adding more hydrogen gas to the following equilibria using Le Châtelier's principle.
a $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
b $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$
c $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

5 Predict the effect of the following changes on the position of each equilibrium.
a addition of SO_2 to the equilibrium:
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
b removal of CH_3COO^- from the equilibrium:
$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

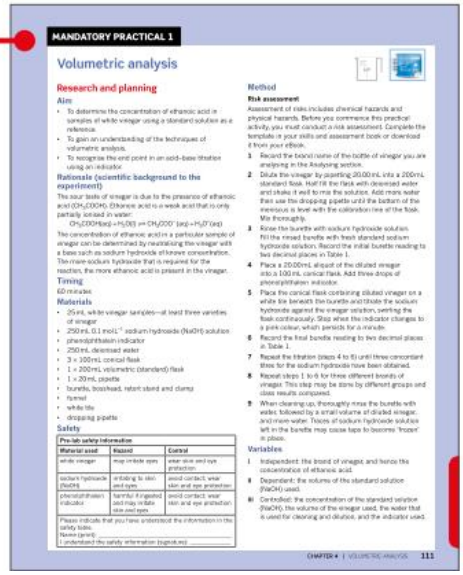
22 UNIT 3 | EQUILIBRIUM, ACIDS AND REDOX REACTIONS

Module summary

Each module concludes with a summary to help students consolidate the key points and concepts.

Mandatory practicals

All mandatory practicals are included in the student book and have been comprehensively developed to ensure they fully address the syllabus requirements. Each practical has been trialled and tested to ensure it can be safely performed and yields effective results, and includes a depth of questions and applications that enable students to develop and demonstrate required manipulative skills.



MANDATORY PRACTICAL 1

Volumetric analysis

Research and planning

Aim

- To determine the concentration of ethanoic acid in samples of white vinegar using a standard solution as a reference.
- To gain an understanding of the techniques of volumetric analysis.
- To recognise the end point in an acid–base titration using an indicator.

Rationale (scientific background to the experiment)

The sour taste of vinegar is due to the presence of ethanoic acid (CH_3COOH). Ethanoic acid is a weak acid that is only partially ionised in water:

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

The concentration of ethanoic acid in a particular sample of vinegar can be determined by neutralising the vinegar with a base such as sodium hydroxide of known concentration. The more sodium hydroxide that is required for the reaction, the more ethanoic acid is present in the vinegar.

Timing

60 minutes

Materials

- 25 mL white vinegar samples—at least three varieties of vinegar
- 250 mL 0.1 $mol.L^{-1}$ sodium hydroxide ($NaOH$) solution
- phenolphthalein indicator
- 250 mL deionised water
- 3 × 100 mL conical flask
- 1 × 200 mL volumetric (standard) flask
- 1 × 20 mL pipette
- burette, boss head, retort stand and clamp
- funnel
- white tile
- dropping pipette

Safety

Pre-lab safety information

Material used	Hazard	Control
white vinegar	may irritate eyes	wear skin and eye protection
sodium hydroxide ($NaOH$)	irritating to skin and eyes	avoid contact; wear skin and eye protection
phenolphthalein indicator	harmful if ingested; acid may irritate skin and eyes	avoid contact; wear skin and eye protection

Please indicate that you have understood the information in the safety table.
Name (print):
I understand the safety information (signature):

Method

Risk assessment

Assessment of risks includes chemical hazards and physical hazards. Before you commence this practical activity, you must conduct a risk assessment. Complete the template in your skills and assessment book or download it from your eBook.

1 Record the brand name of the bottle of vinegar you are analysing in the Analysing section.
2 Dilute the vinegar by pipetting 20.00 mL into a 200 mL standard flask. Half fill the flask with deionised water and shake it well to mix the solution. Add more water then use the dropping pipette until the bottom of the meniscus is level with the calibration line at the flask. Mix thoroughly.
3 Rinse the burette with sodium hydroxide solution. Fill the rinsed burette with fresh standard sodium hydroxide solution. Record the initial burette reading to two decimal places in Table 1.
4 Place a 20.00 mL aliquot of the diluted vinegar into a 100 mL conical flask. Add three drops of phenolphthalein indicator.
5 Place the conical flask containing diluted vinegar on a white tile beneath the burette and titrate the sodium hydroxide against the vinegar solution, swirling the flask continuously. Stop when the indicator changes to a pink colour, which persists for a minute.
6 Record the final burette reading to two decimal places in Table 1.
7 Repeat the titration (steps 4 to 6) until three concordant titres for the sodium hydroxide have been obtained.
8 Repeat steps 1 to 6 for three different brands of vinegar. This step may be done by different groups and class results compared.
9 When cleaning up, thoroughly rinse the burette with water, followed by a small volume of diluted vinegar, and more water. Traces of sodium hydroxide solution left in the burette may cause taps to become 'frozen' in place.

Variables

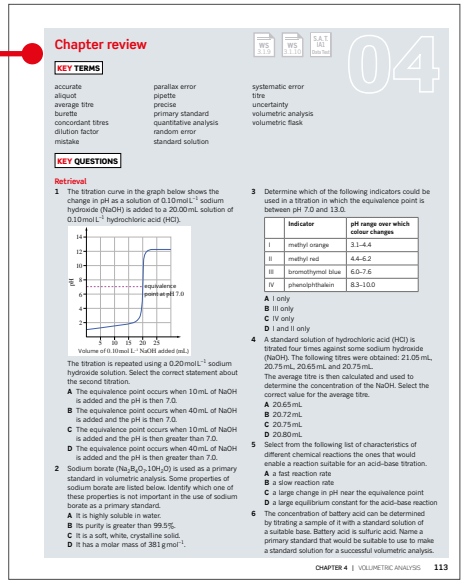
I Independent: the brand of vinegar, and hence the concentration of ethanoic acid.
D Dependent: the volume of the standard solution ($NaOH$) used.
C Controlled: the concentration of the standard solution ($NaOH$), the volume of the vinegar used, the water that is used for cleaning and dilution, and the indicator used.

CHAPTER 4 | VOLUMETRIC ANALYSIS 111

How to use this book *continued*

Chapter review

Each chapter finishes with a list of key terms covered in the chapter and a set of questions to test students' abilities to apply the knowledge gained from the chapter.


Chapter review

04

KEY TERMS

accurate
aliquot
average titre
burette
concordant titres
dilution factor
mistake
parallax error
pipette
precise
primary standard
quantitative analysis
random error
standard solution
systematic error
titre
uncertainty
volumetric analysis
volumetric flask

KEY QUESTIONS

Retrieval

1 The titration curve in the graph below shows the change in pH as a solution of 0.10 mol L^{-1} sodium hydroxide (NaOH) is added to a 20.00 mL solution of 0.10 mol L^{-1} hydrochloric acid (HCl).

The titration is repeated using a 0.20 mol L^{-1} sodium hydroxide solution. Select the correct statement about the second titration.

A The equivalence point occurs when 10 mL of NaOH is added and the pH is then 7.0.
B The equivalence point occurs when 40 mL of NaOH is added and the pH is then 7.0.
C The equivalence point occurs when 10 mL of NaOH is added and the pH is then greater than 7.0.
D The equivalence point occurs when 40 mL of NaOH is added and the pH is then greater than 7.0.

2 Sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) is used as a primary standard in volumetric analysis. Some properties of sodium borate are listed below. Identify which one of these properties is not important in the use of sodium borate as a primary standard.

A It is highly soluble in water.
B Its purity is greater than 99.5%.
C It is a soft, white, crystalline solid.
D It has a molar mass of 381 g mol^{-1}.

3 Determine which of the following indicators could be used in a titration in which the equivalence point is between pH 7.0 and 13.0.

	Indicator	pH range over which colour changes
I	methyl orange	3.1–4.4
II	methyl red	4.4–6.2
III	bromothymol blue	6.0–7.6
IV	phenolphthalein	8.3–10.0

A I only
B III only
C IV only
D I and II only

4 A standard solution of hydrochloric acid (HCl) is titrated four times against some sodium hydroxide (NaOH). The following titres were obtained: 21.05 mL, 20.75 mL, 20.65 mL and 20.75 mL.
The average titre is then calculated and used to determine the concentration of the NaOH. Select the correct value for the average titre.

A 20.65 mL
B 20.72 mL
C 20.75 mL
D 20.80 mL

5 Select from the following list of characteristics of different chemical reactions the ones that would enable a reaction suitable for an acid–base titration.

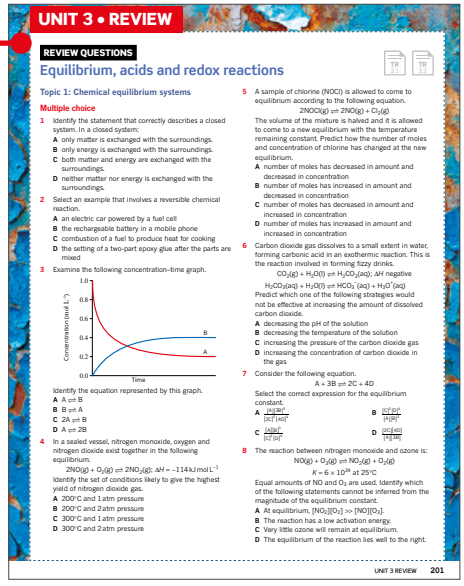
A a fast reaction rate
B a slow reaction rate
C a large change in pH near the equivalence point
D a large equilibrium constant for the acid–base reaction

6 The concentration of battery acid can be determined by titrating a sample of it with a standard solution of a suitable base. Battery acid is sulfuric acid. Name a primary standard that would be suitable to use to make a standard solution for a successful volumetric analysis.

CHAPTER 4 | VOLUMETRIC ANALYSIS 113

Unit review

Each unit concludes with a comprehensive set of exam-style questions, including multiple choice and short answer, that assist students to draw together their knowledge and understanding of the whole unit.


UNIT 3 • REVIEW

REVIEW QUESTIONS

Equilibrium, acids and redox reactions

Topic 1: Chemical equilibrium systems

Multiple choice

1 Identify the statement that correctly describes a closed system. In a closed system:

A only matter is exchanged with the surroundings.
B only energy is exchanged with the surroundings.
C both matter and energy are exchanged with the surroundings.
D neither matter nor energy is exchanged with the surroundings.

2 Select an example that involves a reversible chemical reaction.

A an electric car powered by a fuel cell
B the rechargeable battery in a mobile phone
C combustion of a fuel to produce heat for cooking
D the setting of a two-part epoxy glue after the parts are mixed

3 Examine the following concentration–time graph.

Identify the equation represented by this graph.

A A ⇌ B
B B ⇌ A
C 2A ⇌ B
D A ⇌ 2B

4 In a sealed vessel, nitrogen monoxide, oxygen and nitrogen dioxide exist together in the following equilibrium.

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$; $\Delta H = -114$ kJ mol L^{-1}

Identify the set of conditions likely to give the highest yield of nitrogen dioxide gas.

A 200°C and 1 atm pressure
B 200°C and 2 atm pressure
C 300°C and 1 atm pressure
D 300°C and 2 atm pressure

5 A sample of chlorine (NOCl) is allowed to come to equilibrium according to the following equation.

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

The volume of the mixture is halved and it is allowed to come to a new equilibrium with the temperature remaining constant. Predict how the number of moles and concentration of chlorine has changed at the new equilibrium.

A number of moles has decreased in amount and decreased in concentration
B number of moles has increased in amount and decreased in concentration
C number of moles has decreased in amount and increased in concentration
D number of moles has increased in amount and increased in concentration

6 Carbon dioxide gas dissolves to a small extent in water, forming carbonic acid in an exothermic reaction. This is the reaction involved in forming fizzy drinks.

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$; ΔH negative

$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$

Predict which one of the following strategies would not be effective at increasing the amount of dissolved carbon dioxide.

A decreasing the pH of the solution
B decreasing the temperature of the solution
C increasing the pressure of the carbon dioxide gas
D increasing the concentration of carbon dioxide in the gas

7 Consider the following equation.

$A + 3B \rightleftharpoons 2C + 4D$

Select the correct expression for the equilibrium constant.

A $\frac{[A][B]^3}{[2C]^2[4D]^4}$
B $\frac{[C]^2[D]^4}{[A][B]^3}$
C $\frac{[A][B]^3}{[C]^2[D]^4}$
D $\frac{[2C][4D]}{[A][3B]}$

8 The reaction between nitrogen monoxide and ozone is:

$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$

$K = 6 \times 10^{34}$ at 25°C

Equal amounts of NO and O_3 are used. Identify which of the following statements cannot be inferred from the magnitude of the equilibrium constant.

A At equilibrium, $[NO_2][O_2] >> [NO][O_3]$.
B The reaction has a low activation energy.
C Very little ozone will remain at equilibrium.
D The equilibrium of the reaction lies well to the right.

UNIT 3 REVIEW 201

Glossary

Key terms are shown in **bold** throughout the student book and are listed at the end of each chapter. A comprehensive glossary at the end of the book defines all the key terms. The glossary aligns with the syllabus context and includes the QCAA defined terminology.

Answers

The Teacher Reader+ eBook provides comprehensive answers and fully worked solutions for each module review, chapter review, unit review, Try yourself and Science as a human endeavour question sets.

Icons

Go To icons make important links to relevant content within the student books in the course. The Go To icons indicate where to engage with Chapter 1 in your eBook.

GO TO ➤

Every mandatory practical is supported by a complementary **SPARKlab** alternative practical.

The ***Pearson Chemistry 12 Queensland Skills and Assessment Book*** icons indicate the best time to engage with an activity for practice, application and revision. The type of activity is indicated as follows:

Worksheet (WS)

WS 3.1

Practical Activity (PA)

PA 3.2

Mandatory Practical (MP)

MP 3.2

Sample Assessment Task (SAT).

SAT 3.3

The **Reader+** icon indicates when to engage with an asset via your Reader+ eBook. Assets may include videos and interactive activities.

Pearson Chemistry 12 Queensland



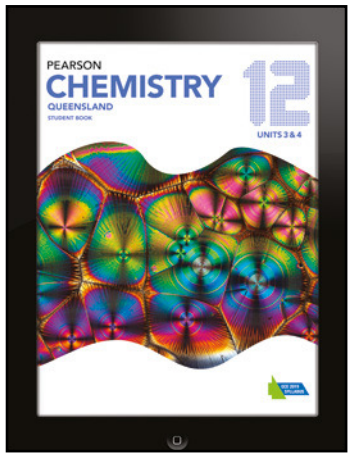
Student book

Pearson Chemistry 12 Queensland Student Book has been developed by experienced Queensland teachers to address all the requirements of the QCAA Chemistry 2019 General Senior Syllabus. The series features the very latest developments and applications of chemistry, literacy and instructional design to ensure the content and concepts are fully accessible to all students.



Skills and assessment book

The *Pearson Chemistry 12 Queensland Skills and Assessment* book gives students the edge in preparing for all forms of assessment. Specifically prepared to provide opportunities to consolidate, develop and apply subject matter and science inquiry skills, this resource features a toolkit, key knowledge summaries, worksheets, practical activities and guidance, assessment practice and topic review question sets.



Reader+ the next generation eBook

Reader+ is our next generation eBook. Students can read, take notes, save bookmarks and more in the one seamless experience. Integrated multimedia (audio/video) and interactive activities enhance and extend the learning experience.

Teacher support



Pearson Chemistry 12 Queensland Teacher Support provides:

- complete answers, fully worked solutions or suggested answers to all tasks in the student book and skills and assessment book
- expected results, common mistakes, suggested answers and full safety notes and risk assessments for all practical activities
- teaching, learning and assessment programs.

Pearson

Access your digital resources at **pearsonplaces.com.au**
Browse and buy at **pearson.com.au**

Understanding the course

Begin your study of the Chemistry Units 3 and 4 course by clearly establishing what you are required to do and where you can go to for help. Your teacher will guide you through the course. Your Pearson Chemistry 12 Queensland resources are a one-stop shop for support in every aspect of the course. This support is delivered via two resources:

- *Pearson Chemistry 12 Queensland Student Book*
- *Pearson Chemistry 12 Queensland Skills and Assessment Book*

The syllabus details all the requirements of the course. This syllabus document is long and challenging to interpret. The Pearson resources comprehensively unpack and address all aspects of the syllabus, presenting all of the subject matter, practical experiences and application opportunities (questions and activities) in a user-friendly way. Refer to the table below for a summary of where to look for different types of support.

Guide to syllabus support in Pearson resources

Where do I go for help with .... ?	*Pearson Chemistry 12 Queensland Student Book*	*Pearson Chemistry 12 Queensland Skills and Assessment* book
ensuring coverage of the syllabus	The student book is organised by units and the **unit opener** outlines the unit objectives. The student book is further organised into chapters. **Chapter openers** address specific subject matter and mandatory practicals, quoted from the syllabus. **Module openers** within each chapter restate subject matter learning outcomes in student-friendly language.	The skills and assessment book is organised by units and the **unit opener** outlines the unit objectives. The skills and assessment book is further organised into topics. Each **topic** addresses all of the subject matter and mandatory practicals, quoted from the syllabus.
subject matter and applications	All subject matter is thoroughly covered. **Skillbuilders** and **worked examples** scaffold and model applications. Further opportunities to practise are provided through mirrored **Try yourself** problems.	The subject matter is summarised for each topic in **key knowledge** summaries, which provide handy notes for revision and study. Extensive opportunities to apply learning from the student book are provided through **worksheets**, **practical activities**, end of **topic review** question sets and **sample assessment tasks**.
calculations using algorithms	**Chapter 1 Chemistry skills and assessment toolkit** (eBook) is a reference tool for refreshing your skills with calculations and other key chemistry skills. There are many **worked examples** in chapters that model use of calculations using algorithms.	Opportunities to apply and practise performing calculations and using algorithms are integrated throughout the **worksheets**, **practical activities** and **topic review** question sets.
mandatory practicals	All **mandatory practicals** are included and have been structured to reflect the structure and assessment objectives of the student experiment to provide consistency and experience.	**Mandatory practicals** are included and have been structured to reflect the structure and assessment objectives of the student experiment to provide consistency and experience. These are more scaffolded in the skills and assessment book but provide the same learning outcomes. **Additional practicals** are also included to provide further practice and opportunities for drawing out your student experiment.
general skills in science	**Chapter 1 Chemistry skills and assessment toolkit** (eBook) is a reference tool covering a wide range of basic skills and understandings, such as use of significant figures, units of measurement, tables and graphs, errors and uncertainties. **Skillbuilders** are included throughout the student book to provide just-in-time teaching moments to step you through developing and applying new skills.	
definitions of key terms	The detailed **glossary** explains all key terms that are in bold throughout the student book. Where the term is defined in the QCAA syllabus, you will find that the term's definition is reproduced in the glossary.	

practice questions and answers	At the beginning of your student book you will find a **Marzano and Kendall taxonomy guide** which unpacks each of the cognitive verbs and helps you interpret the requirements of the question. This helps ensure that the answer you provide meets the syllabus expectations and maximises the mark you will receive. A large number and variety of questions are available to check for understanding and provide practice. Questions are provided in each: • **module review** • **chapter review** • **unit review**. Questions are organised by complexity of thinking and are presented in instruction form, as per the data test and examination. You will also find questions in each **mandatory practical** and the **Science as a human endeavour** features.	**Worksheets** and **practical activities** provide contextualised opportunities to practice and answer questions.
practice exams	**Chapter 1 Chemistry skills and assessment toolkit** (eBook) Part D. **Unit review** questions are presented in a style similar to what you will experience in the exam.	**Topic review** questions are presented in a style similar to what you will experience in the exam.

Guide to summative assessment support in Pearson resources

Where do I go for help with the… ?	***Pearson Chemistry 12 Queensland Student Book***	***Pearson Chemistry 12 Queensland Skills and Assessment* book**
Data test	**Chapter 1 Chemistry skills and assessment toolkit** (eBook) Part A provides examples and steps through the processes of performing calculations, analysing and presenting data.	**Sample assessment task**
Student experiment	**Chapter 1 Chemistry skills and assessment toolkit** (eBook) Part B unpacks the requirements and provides a detailed guide for completing this assessment.	**Sample assessment task**
Research investigation	**Chapter 1 Chemistry skills and assessment toolkit** (eBook) Part C unpacks the requirements and provides a detailed guide for completing this assessment.	**Sample assessment task**
Examination	**Chapter 1 Chemistry skills and assessment toolkit** (eBook) Part D provides helpful tips and guidance in preparing for and showcasing your knowledge in an examination.	**Topic review**

Understanding assessment instructions

The QCAA Chemistry 2019 General Senior Syllabus uses an inquiry approach, guiding students in a systematic way to a better understanding of the world.

You will notice as you read through the syllabus for Units 1 to 4 that many terms are underlined. The following examples are provided:

- the General Senior Syllabus objectives
- a sample of topic subject matter.

The General Senior Syllabus objectives showing the underlining of terms

Syllabus objective		Unit 1	Unit 2	Unit 3	Unit 4
1.	describe and explain scientific concepts, theories, models and systems and their limitations	●	●	●	●
2.	apply understanding of scientific concepts, theories, models and systems within their limitations	●	●	●	●
3.	analyse evidence	●	●	●	●
4.	interpret evidence	●	●	●	●
5.	investigate phenomena	●	●	●	●
6.	evaluate processes, claims and conclusions	●	●	●	●
7.	communicate understandings, findings, arguments and conclusions	●	●	●	●

The QCAA syllabus states that students 'are required to use a range of cognitive processes to demonstrate they meet the syllabus'. Many of the underlined words in the syllabus are action verbs. These verbs are often placed at the start of dot points, to identify the level of thinking (cognitive process) you are expected to demonstrate. Note the action verbs from the two syllabus extracts.

Remember, the cognitive verbs used in the syllabus subject matter dot points indicate the highest level of thinking and subject engagement to be covered. You will not be assessed at a higher cognitive level.

A subject matter description from Chemistry Unit 3, Topic 1 showing the underlining of terms

Subject matter

Factors that affect equilibrium

- explain and predict the effect of temperature change on chemical systems at equilibrium by considering the enthalpy change for the forward and reverse reactions
- explain the effect of changes of concentration and pressure on chemical systems at equilibrium by applying collision theory to the forward and reverse reactions
- apply Le Châtelier's principle to predict the effect changes of temperature, concentration of chemicals, pressure and the addition of a catalyst have on the position of equilibrium and on the value of the equilibrium constant.

UNDERSTANDING COGNITIVE PROCESSES AND VERBS

It is important to understand that the verbs driving the syllabus objectives and topic subject matter are not randomly chosen. By gaining a better understanding of cognitive verbs, you will be able to respond more satisfactorily to questions and instructions in assessment tasks.

Cognitive verbs signal to the learner the type of thinking to be demonstrated. For example:

- the verb 'evaluate' indicates that an assessment or judgement must be made
- the verb 'describe' requires that an account or outline be provided.

There is a difference between the thinking needed by each of these verbs. To evaluate something requires a higher order level of thinking than to simply describe it. Generally, the higher the thinking level required in a task, the more challenging it is.

Cognitive verbs can be arranged or classified into different levels of thinking (also known as cognitive processes) ranging from remembering to complex thinking. The QCAA syllabus uses an arrangement (taxonomy) of cognitive processes devised by educational researchers Robert Marzano and John Kendall.

In this arrangement, four levels of cognitive process are identified: retrieval, comprehension, analysis and knowledge utilisation. An outline of these levels is provided in Chart A. A large number of different cognitive verbs are used in the syllabus. These verbs can be aligned with different levels of thinking, as shown in Chart B.

Pearson Chemistry 12 Queensland Student Book provides a comprehensive number of questions and instructions. The topic review question sets are arranged by cognitive levels using the Marzano and Kendall taxonomy, and provide students with the opportunity to demonstrate knowledge and application of the subject matter at the following levels:

Module review—retrieval, comprehension and analysis

Chapter review—retrieval, comprehension, analysis and knowledge utilisation

Unit review—retrieval, comprehension, analysis and knowledge utilisation.

CHART A Cognitive processes as arranged by Marzano and Kendall

Cognitive processes—levels of thinking			
Retrieval	**Comprehension**	**Analysis**	**Knowledge utilisation**
Level 1—basic level of thinking • involves remembering, recalling, recognising and executing information	**Level 2**—higher level of thinking than retrieval • involves understanding and identifying key information	**Level 3**—more complex thinking than comprehension • involves examination of information and the identification and separation into its separate parts	**Level 4**—most complex thinking level • involves applying information to investigate, experiment, problem-solve and make decisions

Increasing complexity of thinking
Each level of thinking builds upon lower levels. For example, you must be able to retrieve information and comprehend it before you can analyse it.

CHART B Cognitive processes, associated verbs with sample questions and instructions

Cognitive processes, associated verbs and sample questions			
Retrieval	**Comprehension**	**Analysis**	**Knowledge utilisation**
Processes: • recognising • recalling • symbolising	**Processes:** • recognising • recalling • symbolising	**Processes:** • recognising • recalling • symbolising	**Processes:** • recognising • recalling • symbolising
Cognitive verbs	**Cognitive verbs**	**Cognitive verbs**	**Cognitive verbs**
define demonstrate describe identify indicate label list name paraphrase recall recognise (e.g. features) select show state use	calculate (e.g. numerical answer; mathematical processes) clarify comprehend (e.g. meaning) construct (e.g. a diagram) demonstrate describe determine develop discuss draw (e.g. visual depiction) explain illustrate implement (e.g. plan or proposal) recognise (e.g. features) represent select show sketch summarise symbolise (e.g. through diagram, illustration or model) understand use	analyse apply assess calculate (e.g. numerical answer; mathematical processes) categorise classify compare conclude consider contrast critique deduce derive determine diagnose differentiate discriminate distinguish edit evaluate extrapolate explore identify infer interpret (e.g. meaning) judge organise predict reflect (on) sort scrutinise	adapt appraise appreciate argue assess comment (make a judgement) conduct (e.g. investigations) conclude construct (e.g. an argument) convince create design (e.g. a methodology, an artefact or a proposal) decide determine develop (e.g. a strategy, product or process) devise discuss/explore evaluate experiment/test (e.g. hypotheses) extrapolate (e.g. information, ideas, components) into a whole, in order to create new meaning generate/test (e.g. hypotheses) hypothesise/propose (e.g. arguments or concepts) investigate/examine (e.g. an argument, statement or conclusion) judge justify/prove (e.g. an argument, statement or conclusion) manipulate (e.g. language texts, skills or technologies) modify persuade predict (e.g. a result) propose prove research realise/resolve (e.g. artistic works) solve (e.g. problems) synthesise (e.g. information, ideas or components) test

Note that some cognitive verbs appear in more than one cognitive level.

Note that a question may not necessarily include a cognitive verb.

CHART B *continued*

Cognitive processes, associated verbs and sample questions			
Sample instruction and question	**Sample instruction and question**	**Sample instruction and question**	**Sample instruction and question**
Identify the electron configuration of Cr and Cu. What is the electron configuration of Cr and Cu?	**Explain** how successive ionisation energy data is related to the electron configuration of an atom. How is the electron configuration of an atom related to successive ionisation energy data?	**Compare** and **explain** the metallic and non-metallic behaviour of elements for Li–Cs and F–I. What are the similarities and differences between the metallic and non-metallic behaviours of elements?	**Make predictions** based on supplied solubility curves. What prediction can you make from the solubility curve with which you are supplied?

UNDERSTANDING THE QUESTION OR INSTRUCTION

The cognitive verb alone is not a sufficient guide to understanding what the question or instruction requires as a response. Questions may not include a cognitive verb. In addition, a cognitive verb may apply to more than one level of thinking. Consider the following examples.

Examples	Use of the cognitive verb 'explain'	Scope and context of the instruction or question
	What is the question asking?	**How much do I write?**
Example 1a: Explain diffusion. What is diffusion?	The key aspect/s of the question: **a** definition response—retrieval **b** paraphrase response—comprehension	A question that focuses on: **a** one key term—'diffusion'
Example 1b: Explain convection. What is convection?		A question that focuses on: **b** one concept—'convection'
Example 2a: Explain the **difference** between simple and facilitated diffusion. What is **different** between simple and facilitated diffusion?	The key aspect/s of the question: **a** compare and contrast—analysis	A question that focuses on: **a** two terms—'simple diffusion' and 'facilitated diffusion' **b** differences between the two terms
Example 2b: Explain the **difference** between convection and conduction. What is **different** between convection and conduction?		A question that focuses on: **a** two terms—'convection' and 'conduction' **b** differences between the two terms
Example 3a: Explain how you would conduct an experiment using chromatography to **analyse** proteins. What experimental procedure would you use to **analyse** proteins using chromatography?	The key aspect/s of the question: **a** create, design, experiment **b** knowledge utilisation	A question that focuses on: **a** two terms—'proteins' and 'chromotography' **b** their analysis **c** design of an experiment
Example 3b: Explain how you would conduct an experiment using convection to **analyse** the specific heat capacity of a metal. What experimental procedure would you use to **analyse** the specific heat capacity of a metal using convection?		A question that focuses on: **a** two terms—'convection' and 'specific heat capacity' **b** their analysis **c** design of an experiment

Strategies for understanding the question or instruction

As you can see, analysing a question or instruction can be quite challenging. This particularly applies when more complex cognitive processes are required.

The following steps provide a framework for understanding and analysing questions and instructions.

Strategies for understanding the question or instruction	**Example** Element X forms a compound with oxygen in which the ratio of the number of atoms of X to the number of atoms of oxygen is 2:5. Element X makes up 59.7% of the mass of the compound. Calculate the molar mass of X and use it to identify this element.
1 Underline the cognitive verb/s and identify a plausible thinking level for the verb.	'Calculate the molar mass of X and use it to identify this element.' **Calculate** involves assessment and deductive thinking, so has **analysis** thinking level qualities. **Identify** is found on the list for both **retrieval** and **analysis**.
2 Determine the scope and context of the question and its thinking level.	The scope of the question involves calculations using given data and matching against the periodic table. The context is the understanding and analysing of the data. This targets the analysis cognitive level.
3 Consider whether some cognitive actions from Chart B are required to complete the question.	The question is complex. It asks for **analysis** of the data provided then deduction based on that analysed data.
4 Make sure you know the meaning of every word in the question or instruction.	**Calculate** means to 'determine or find (e.g. a number, answer) by using mathematical processes; obtain a numerical answer showing the relevant stages in the working; ascertain/determine from given facts, figures or information'. **Identify** means to 'distinguish, locate, recognise and name; establish or indicate who or what someone or something is; provide an answer from a number of possibilities; recognise and state a distinguishing factor or feature'.
5 Rephrase the question or instruction in your own words, elaborating on all details required.	Rephrasing may be in the form of a question or instruction. For example: 'I can look up the molar mass of oxygen and I know oxygen makes up 40.3% of this compound and the unknown element is 59.7% of the compound. Use this to work out the molar mass of the unknown element.'

ASSESSMENT TASKS AND COGNITIVE PROCESSES

Pearson Chemistry 12 Queensland Student Book provides a solid foundation for undertaking all assessment tasks in the syllabus. Comprehensive sets of key instructions and tasks, arranged by cognitive thinking levels, and mirroring the instruction types of the examination, are provided at the end of each module and chapter.

Module reviews have tasks listed under the cognitive processes of retrieval, comprehension and analysis.

Chapter reviews cover the three levels of cognitive processes, as well as knowledge utilisation.

Unit reviews provide the opportunity to consolidate and test you on a broader area of subject matter.

Mandatory practicals provide support in this skill area through practice at this cognitive level.

This approach will support you in developing the skills and level of application required to complete the assessment tasks.

You are required to complete the following assessment tasks:

a Data test (IA1)
b Student experiment (IA2)
c Research investigation (IA3)
d Examination (EA)

The following charts provide an indication of the cognitive processes you should expect to encounter in each type of assessment task. Note that the student experiment and research investigation assessment tasks are designed for thinking at the highest cognitive levels. While retrieval, comprehension and analysis are required to complete the tasks, they are the underlying thinking levels necessary to complete the tasks. Hence the differences in the sizes of the ticks, with the largest tick indicating the focal cognitive thinking level.

Data test (IA1)				
Retrieval	**Comprehension**	**Analysis**	**Knowledge utilisation**	The task requires you to demonstrate thinking that is complex and at the higher levels of analysis and knowledge utilisation. Retrieval and comprehension underlie the thinking so data can be analysed in the test.
✔	✔	✔	✔	

Student experiment (IA2)				
Retrieval	**Comprehension**	**Analysis**	**Knowledge utilisation**	The task requires you to demonstrate thinking that is complex and at a high level. Retrieval, comprehension and analysis underlie the experimenting and problem-solving required for this task.
✔	✔	✔	✔	

Research investigation (IA3)				
Retrieval	**Comprehension**	**Analysis**	**Knowledge utilisation**	The task requires you to demonstrate thinking that is complex and at a high level. Retrieval, comprehension and analysis underlie the investigation and decision-making required for this task.
✔	✔	✔	✔	

The examination will include two papers. Each paper consists of a number of different types of items, including short and combination responses.

Examination (EA)					
	Retrieval	**Comprehension**	**Analysis**	**Knowledge utilisation**	
Short response: • multiple choice • single word • calculating using algorithms.	✔	✔	✔	✔	Short responses generally draw on factual subject matter in the retrieval and comprehension areas of cognitive processes but may require analysis where calculations and data interpretation are involved.
Combination response: • short items requiring single-word, single-sentence or short paragraph responses • calculating using algorithms • interpreting graphs, tables or diagrams • responding to unseen data and/or stimulus.	✔	✔	✔	✔	The calculations and responses to unseen data move the cognitive processes required to the highest levels of thinking.

DEFINITIONS OF COGNITIVE VERBS

The following list provides definitions for cognitive verbs. Where available, the definitions are taken from the QCAA syllabus. Those verbs whose definitions are not in the QCAA syllabus appear in grey text. Refer to the list to clarify exactly what is required when any of these verbs appear in a question or instruction. Verbs are organised according to cognitive levels of thinking.

Increasing complexity of thinking

Level of thinking	Cognitive verb	Definition of cognitive verb
Retrieval—processes of recognising, recalling, symbolising	define	give the meaning of a word, phrase, concept or physical quantity; state meaning and identify or describe qualities
	demonstrate	prove or make clear by argument, reasoning or evidence, illustrating with practical examples; show by example; give a practical exhibition
	describe	give an account (written or spoken) of a situation, event, pattern or process, or of the characteristics or features of something
	identify	distinguish; locate, recognise and name; establish or indicate who or what someone or something is; provide an answer from a number of possibilities; recognise and state a distinguishing factor or feature
	indicate	suggest, show or recommend a course of action
	label	identify by applying a name to an object or person
	list	write the names of connected items, usually one below the other
	name	specify or give a label to an object or person
	paraphrase	use different words to convey the same meaning
	recall	remember; present remembered ideas, facts or experiences; bring something back into thought, attention or one's mind
	recognise	identify or recall particular features of information from knowledge; identify that an item, characteristic or quality exists; perceive as existing or true; be aware of or acknowledge
	select	choose in preference to another or others; pick out
	show	provide the relevant reasoning to support a response
	state	express something definitely and clearly
	use	operate or put into effect; apply knowledge or rules to put theory into practice

Increasing complexity of thinking

Level of thinking	Cognitive verb	Definition of cognitive verb
Comprehension—processes of integrating, symbolising	calculate (e.g. numerical answer, mathematical processes)	work out using mathematical processes and determine by reasoning
	clarify	make clear or intelligible; explain; make a statement or situation less confused or more comprehensible
	comprehend (meaning)	understand the meaning or nature of; grasp mentally
	construct	create or put together (e.g. an argument) by arranging ideas or items; display information in a diagrammatic or logical form; make; build
	demonstrate	prove or make clear by argument, reasoning or evidence, illustrating with practical examples; show by example; give a practical exhibition
	describe	give an account (written or spoken) of a situation, event, pattern or process, or of the characteristics or features of something
	determine	establish, conclude or ascertain after consideration, observation or calculation; decide or come to a resolution
	develop	elaborate, expand or enlarge in detail; add detail and fullness to; cause to become more complex or intricate
	discuss	examine by argument; sift the considerations for and against; debate; talk or write about a topic, including a range of arguments, factors or hypotheses; consider, taking into account different issues and ideas, points for and/or against, and supporting opinions or conclusions with evidence
	draw (visual depiction)	produce a picture, diagram or other visual representation
	explain	make an idea or situation plain or clear by describing it in more detail or revealing relevant facts; give an account; provide additional information
	illustrate	provide pictures; provide an example for a point being made
	implement	put something into effect (e.g. a plan or proposal)
	recognise	identify or recall particular features from knowledge; identify that an item, characteristic or quality exists; perceive as existing or true; be aware of or acknowledge
	represent	scientific representations are a verbal, physical or mathematical demonstration of understanding of a science concept or concepts; a concept can be represented in a range of ways and using multiple models (ACARA 2015c)
	select	choose in preference to another or others; pick out
	show	provide the relevant reasoning to support a response
	sketch	execute a drawing or painting in simple form, giving essential features but not necessarily with detail or accuracy
	summarise	give a brief statement of a general theme or major point/s; present ideas and information in fewer words and in sequence
	symbolise	represent or identify by a symbol or symbols
	understand	perceive what is meant by something; grasp; be familiar with (e.g. an idea); construct meaning from messages, including oral, written and graphic communication
	use	operate or put into effect; apply knowledge or rules to put theory into practice

Increasing complexity of thinking

Level of thinking	Cognitive verb	Definition of cognitive verb
Analysis—processes of matching, classifying, analysing errors, generalising, specifying	analyse	dissect to ascertain and examine constituent parts and/or their relationships; break down or examine in order to identify the essential elements, features, components or structure; determine the logic and reasonableness of information; examine or consider something in order to explain and interpret it, for the purpose of finding meaning or relationships and identifying patterns, similarities and differences
	apply	use knowledge and understanding in response to a given situation or circumstance; carry out or use a procedure in a given or particular situation
	assess	measure, determine, evaluate, estimate or make a judgement about the value, quality, outcomes, results, size, significance, nature or extent of something
	calculate	work out using mathematical processes and determine by reasoning
	categorise	place in or assign to a particular class or group; arrange or order by classes or categories; classify; sort; separate
	classify	arrange, distribute or order in classes or categories according to shared qualities or characteristics
	compare	display recognition of similarities and differences and recognise the significance of these similarities and differences
	conclude	form a judgement based on evidence
	consider	think deliberately and carefully about something, typically before making a decision; taking something into account when making a judgement; view attentively or scrutinise; reflect on
	contrast	display recognition of differences by deliberate juxtaposition of contrary elements; show how things are different or opposite; give an account of the differences between two or more items or situations, referring to both or all of them throughout
	critique	review (e.g. a theory, practice or performance) in a detailed, analytical and critical way
	deduce	reach a conclusion that is necessarily true, provided a given set of assumptions is true; arrive at, reach or draw a logical conclusion from reasoning and the information given
	derive	arrive at a reasoning; manipulate a mathematical relationship to give a new equation or relationship; in mathematics, obtain the derivative of a function
	determine	establish, conclude or ascertain after consideration, observation, investigation or calculation; decide or come to a resolution
	diagnose	identify the nature of a problem or illness
	differentiate	identify the difference/s in or between two or more things; distinguish; discriminate; recognise or ascertain what makes something distinct from similar things; in mathematics, obtain the derivative of a function
	discriminate	note, observe or recognise a difference; make or constitute a distinction in or between; differentiate; note or distinguish as different
	distinguish	recognise as distinct or different; note points of difference between; discriminate; discern; make clear a difference/s between two or more concepts or items
	edit	correct written material by careful checking
	evaluate	make an appraisal by weighing up or assessing strengths, implications and limitations; make judgements about ideas, works, solutions or methods in relation to selected criteria; examine and determine the merit, value or significance of something based on criteria
	extrapolate	infer or estimate by extending or projecting known information; conjecture; infer from what is known; extend the application of something (e.g. a method or conclusion) to an unknown situation by assuming that existing trends will continue or similar methods will be applicable
	explore	look into both closely and broadly; scrutinise; inquire into or discuss something in detail
	identify	recognise and establish things such as groupings of similar items, mistakes or issues

Increasing complexity of thinking

Analysis—processes of matching, classifying, analysing errors, generalising, specifying *(continued)*	infer	derive or conclude something from evidence and reasoning, rather than from explicit statements; listen or read beyond what has been literally expressed; imply or hint at
	interpret	use knowledge and understanding to recognise trends and draw conclusions from given information; make clear or explicit; elucidate or understand in a particular way; bring out the meaning of, e.g. a dramatic or musical work, by performance or execution; bring out the meaning of an artwork by artistic representation or performance; give one's own interpretation of; identify or draw meaning from, or give meaning to, information presented in various forms, such as words, symbols, pictures or graphs
	judge	form an opinion or conclusion about; apply both procedural and deliberative operations to make a determination
	organise/ sequence/ structure	arrange; order; form as or into a whole consisting of interdependent or coordinated parts, especially for harmonious or united action
	predict	give an expected result of an upcoming action or event; suggest what may happen based on available information
	reflect on	think about deeply and carefully
	scrutinise	examine closely or critically
	sort	arrange in prescribed groupings or order

Increasing complexity of thinking

Level of thinking	Cognitive verb	Definition of cognitive verb
Knowledge utilisation—processes of investigating, experimenting, decision-making, problem-solving	adapt	modify or change something for a new purpose or use
	appraise	evaluate the worth, significance or status of something; judge or consider a text or piece of work
	appreciate	recognise or make a judgement about the value or worth of something; understand fully; grasp the full implications of
	argue	give reasons for or against something; challenge or debate an issue or idea; persuade, prove or try to prove by giving reasons
	assess	measure, determine, evaluate, estimate or make a judgement about the value, quality, outcomes, results, size, significance, nature or extent of something
	comment	express an opinion, observation or reaction in speech or writing; give a judgement based on a given statement or result of a calculation
	conduct	direct an action or course; manage; organise; carry out
	conclude (conclusion)	form a judgement based on evidence
	construct	create or pull together (e.g. an argument) by arranging ideas or items; display information in a diagrammatic or logical form; make; build
	convince (convincing)	persuade by argument or proof; leaving no margin of doubt; clear; capable of causing someone to believe that something is true or real; persuading or assuring by argument or evidence; appearing worthy of belief; credible or plausible
	create	bring something into being or existence; produce or evolve from one's own thought or imagination; reorganise or put elements together into a new pattern or structure or to form a coherent or functional whole
	decide	reach a resolution as a result of consideration; make a choice from a number of alternatives
	design	produce a plan, simulation, model or similar; plan, form or conceive in the mind; in English, select, organise and use particular elements in the process of text construction for particular purposes; these elements may be linguistic (words), visual (images), audio (sounds), gestural (body language), spatial (arrangement on the page or screen) and multimodal (a combination of more than one)
	determine	establish, conclude or ascertain after consideration, observation, investigation or calculation; decide or come to a resolution
	develop	elaborate, expand or enlarge in detail; add detail and fullness to; cause to become more complex or intricate

Increasing complexity of thinking

Knowledge utilisation—processes of investigating, experimenting, decision-making, problem-solving *(continued)*	devise	think out; plan; contrive; invent
	discuss/explore	examine by argument; sift the considerations for and against; debate; talk or write about a topic, including a range of arguments, factors or hypotheses; consider, taking into account different issues and ideas, points for and/or against, and supporting opinions or conclusions with evidence
	draw conclusions (conclusion)	form a judgement based on evidence
	evaluate	make an appraisal by weighing up or assessing strengths, implications and limitations; make judgements about ideas, works, solutions or methods in relation to selected criteria; examine and determine the merit, value or significance of something, based on criteria
	experiment/test	try out or test new ideas or methods, especially in order to discover or prove something; undertake or perform a scientific procedure to test a hypothesis, make a discovery or demonstrate a known fact
	explore	inquire into something or discuss in detail
	generate	produce; create; bring into existence
	hypothesise	formulate a supposition to account for known facts or observed occurrences; conjecture, theorise, speculate, especially on uncertain or tentative grounds
	investigate	carry out an examination or formal inquiry in order to establish or obtain facts and reach new conclusions; search, inquire into, interpret and draw conclusions about data and information
	judge	form an opinion or conclusion about; apply both procedural and deliberative operations to make a determination
	justify	give reasons or evidence to support an answer, response or conclusion; show or prove how an argument, statement or conclusion is right or reasonable
	make decisions	select from available options; weigh up positives and negatives of each option and consider all the alternatives to arrive at a position
	manipulate	adapt or change to suit one's purpose
	modify	change the form or qualities of; make partial or minor changes to something
	persuade (persuasive)	capable of changing someone's ideas, opinions or beliefs; appearing worthy of approval or acceptance (of an argument or statement); communicating reasonably or credibly
	predict	give an expected result of an upcoming action or event; suggest what may happen based on available information
	propose	put forward (e.g. a point of view, idea, argument or suggestion) for consideration or action
	prove	use a sequence of steps to obtain the required result in a formal way
	realise/resolve	consolidate and communicate intent through a synthesis of ideas and application of media to express meaning
	research	locate, gather, record, attribute and analyse information in order to develop understanding
	solve	find an answer to, explanation for, or means of dealing with (e.g. a problem); work out the answer or solution to (e.g. a mathematical problem); obtain the answer/s using algebraic, numerical and/or graphical methods
	synthesise	combine different parts or elements
	test	take measures to check the quality, performance or reliability of something


Copper
29
Cu
63.546(3)
Silver
47
Ag
65.38(2)
Cadmium
48
Cd
100:1
±1 In 20°C
ml 100
90
80
NH
HO
O
N
H

CHAPTER

01 Chemistry Skills and Assessment Toolkit

This chapter provides important information and support in the study of the QCAA Chemistry 2019 General Senior Syllabus for Units 3 and 4.

The Chemistry Skills and Assessment Toolkit is designed to be used as a reference tool. It should be consulted on a need-to-know basis, where relevant, during this course of study. It is not intended that this chapter be worked through as a whole.

Chapter focus

This chapter focuses on providing support and guidance in:

- successful learning in chemistry
  - barriers to learning
  - strategies for effective learning
  - representations in chemistry.
- development and application of scientific skills
  - mathematical and statistical processes used in chemistry
  - Standard International (SI) units
  - visual representations
  - graphical representations
  - measurement errors and uncertainty.
- responding to assessment tasks
  - Data test (IA1)
    - understanding, analysing and interpreting data and statistics
  - Student experiment (IA2)
    - developing the research question or hypothesis
    - considering variables, risks, types of data
    - planning methodology
    - presenting, analysing and interpreting data
    - writing the scientific report.
  - Research investigation (IA3)
    - understanding and analysing claims
    - developing research questions
    - strategies for evaluating resources
    - note-taking
    - writing a scientific report.
  - Examination (EA)
    - understanding the features and conditions of each of the two papers
    - strategies to apply through the course, to enhance learning
    - strategies for revising and consolidating learning
    - techniques and hints when sitting the exam.



Chapter organisation

The chapter is arranged in four parts:

- Part A: Working scientifically
- Part B: Student experiment
- Part C: Research investigation
- Part D: Examination.

An outline of these parts is provided below.

Please note: The examples provided in this chapter assist in modelling how students may arrive at a testable hypothesis or research question. All summative assessment tasks will need to be officially endorsed prior to being undertaken, and should be checked to make sure they address the QCAA ISMG criteria. Experiments must also be carefully reviewed in consultation with your science teacher or school laboratory technician.

QCAA Chemistry General Senior Syllabus objectives

Students will:

- describe and explain scientific concepts, theories, models and systems and their limitations
- apply understanding of scientific concepts, theories, models and systems within their limitations
- analyse evidence
- interpret evidence
- investigate phenomena
- evaluate processes, claims and conclusions
- communicate understandings, findings, arguments and conclusions.

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

Part A: Working scientifically

The focus of Part A is on basic mathematical skills and their applications to chemistry. It features many worked examples and opportunities to apply these examples yourself. These skills are engaged with throughout the course. They are assessed, directly and indirectly, in assessment tasks and drawn on to analyse data in experiments and investigations.

Explore Part A to help prepare yourself with the skills you will draw on for the Data test (IA1), and when undertaking a range of mandatory and suggested practicals. You will also find these skills useful when completing sections of the Student experiment (IA2), Research investigation (IA3) and the Examination (EA).

Refer to the following outline of Part A: Working scientifically to learn, revise and practise the skills in the areas in which you need help.

Module	Look here for:	eBook page
1.2 Orders of magnitude	• scientific notation • transforming decimal notations to scientific notation • converting values from decimal to scientific notation • converting between scientific notation and scientific units • orders of magnitude and prefixes • SI prefixes • examples of such calculations	e18
1.3 Mathematical basics for chemistry	• examples of maths used in chemistry • analysing straight line graphs	e24
1.4 Units	• measurement and units • the correct use of unit symbols • SI units • unit conversions	e27
1.5 Uncertainties in measurement and error	• explanations of the terms uncertainty, error, accuracy and precision • causes of errors • calculations with uncertainty and error • writing measurements with uncertainty and error values • writing measurement and calculations to the correct significant figure • determining the absolute uncertainty of a value • converting between absolute and percentage uncertainties • calculating a value along with the associated uncertainty	e31
1.6 Tables and graphs	• arranging and recording data in tables • converting data from tables to graphs • types of graphs—scatterplots, line graphs, bar and column graphs, pie charts • outliers and how they are represented on graphs • representing missing data on graphs	e45
1.7 Statistics	• calculating mean, median, mode and range • statistical significance of standard deviation • regression, linear regression and R^2 values	e53

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Part B: Student experiment (IA2)

The focus of Part B is on the Student experiment (IA2). This internal assessment requires you to follow the full scientific method over an extended and defined period of time. You need to develop your own research question or hypothesis to investigate, based on an initial practical already completed in class.

Part B supports you through all aspects of the student experiment. The QCAA objectives and instrument-specific marking guide (ISMG) for the assessment are explained.

Explore Part B for examples of how to modify, extend, refine or redirect the class practical and write a research question or hypothesis. Follow the step-by-step guide to evaluate the quality of your hypothesis or research question. Delve into particular sections of Part B, when needed, to reinforce your knowledge and understanding of scientific methodology.

Refer to Part B for support on data types, data collection and analysis of data to draw valid conclusions. This includes how to identify errors in data, validity and relationships between data. Be guided in the write-up of your scientific report by support material on scientific writing style and the structure of the report.

Refer to the following outline of Part B: Student experiment to learn, revise and practise skills in the areas in which you need help.

Module	Look here for:	eBook page
1.8 Research and planning	• types of variables • modifying, refining, extending or redirecting your initial experiment • developing an experimentally testable research question/hypothesis • evaluating the research question/hypothesis • using a scientific journal to keep a record • validity and reliability • quantitative and qualitative data • nominal, ordinal, discrete and continuous data • risk assessments • chemical hazard codes and symbols	e62
1.9 Conducting an experiment	• determining what data is relevant • determining what sufficient data is • collecting data • selecting appropriate equipment	e82
1.10 Results	• analysing raw data • identifying errors—mistakes, systematic errors and random errors • analysing precision • analysing validity and theoretical relationships • interpreting results • relating findings to a chemical concept • evaluating data • evaluating the method	e87
1.11 Communicating and writing a scientific report	• the sections of a report • scientific writing style • writing a scientific report • acknowledging sources • addressing the ISMG	e95

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Part C: Research investigation (IA3)

The focus of Part C is on the Research investigation (IA3). This internal assessment requires you to gather secondary evidence on a research question over an extended and defined period of time. You will develop your own research question to investigate based on a claim (provided by your teacher) related to the course.

Part C supports you through all aspects of the research investigation. The QCAA objectives and instrument-specific marking guide (ISMG) for the assessment are explained.

Engage with Part C to assist with writing your research question. Delve into the examples of claims, their analysis for context and elements, to guide you in developing your own research question. Be guided by the information about locating and evaluating suitable secondary sources for the research. This includes how to identify errors in data, validity and relationships between data.

Part C will assist in the writing of your scientific report and provide support material on the scientific writing style and the structure of the report. It also provides a brief overview of different ways to present the report and looks at the literature review format.

Refer to the following outline of Part C: Research investigation to learn, revise and practise skills in the areas in which you need help.

Module	Look here for:	eBook page
1.12 Developing the research question from a claim	• analysing a claim • identifying variables and measurable terms in the claim • examples of claims and questions developed from them • guidelines for developing a research question • developing a research question • refining a research question	e104
1.13 Finding and choosing suitable resources	• the difference between primary and secondary sources • locating resources • determining the reliability and validity of resources	e110
1.14 Research: taking and organising notes	• recording notes in a scientific journal • paraphrasing information • different ways to record information • recording data and results • recording information about sources	e117
1.15 Writing a report for the research investigation	• different ways to present the report • presenting the report as a literature review • features of a literature review • structure of a literature review	e124

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Part D: Examination (EA)

The focus of Part D is on the Examination (EA). This summative external assessment requires you to complete two papers. Each paper covers the whole chemistry course, Units 3 and 4. The examination constitutes 50% of the total assessment for the course.

Part D supports you through all aspects of the examination process. Refer to this section throughout the year, not just in the weeks prior to the examination. Effective exam preparation needs ongoing consolidation of learning and revision of course material at regular intervals. Effective preparation begins with a sound understanding of the course and its requirements. It is also important that you know where to go for support and what sort of support is available to you throughout the course.

The examination requires that you use particular skills and strategies that are not necessarily used in the student experiment or research investigation. The data test and examination are similar in the strategies you should apply to complete them. It is possible you will feel more anxious regarding the examination, as it accounts for 50% of your total mark in Chemistry.

Part D guides you through all aspects of preparation for the examination. Refer to it for tips on strategies to help you consolidate your learning and for revision hints and suggestions. Before doing practice exams, read through the list of strategies to use during reading and writing time. Sitting an exam successfully requires more than having subject matter understanding and skills. It is also about exam technique, as this can boost your performance.

Refer to the following outline of Part D: Examination to learn strategies and techniques to enhance your learning, revision and examination performance.

Module	Look here for:	eBook page
1.16 Examination preparation	• an overview of the two exam papers including duration, content, response items and equipment • strategies to use to consolidate learning • strategies for revising and practising • strategies to use when sitting the exam • what happens after the exam	e131

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1.1 Successful learning in chemistry

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- appreciate effective strategies for high-impact learning
- develop your understanding of the role of scientific representations
- develop connections and provide strategies for learning
- appreciate how knowledge of the three levels of scientific representation can enhance your learning
- develop a deeper understanding of concepts and applications in chemistry
- identify barriers to your learning
- identify some strategies to use to reduce barriers to your learning.

HIGH-IMPACT LEARNING STRATEGIES

Recent research into best practice for teaching and learning has made some interesting findings. Many of the results relate to teachers and their classroom strategies. There are, however, some important strategies that you can apply to make your learning more effective and assist you in working through challenges. The high-impact learning strategies outlined in Table 1.1.1 on the following page are proven ways to improve your learning outcomes. The strategies are not exclusive to the learning of chemistry; they can be applied to your learning in all subject areas and situations. At the core of all learning is the idea that you, the learner, gain increasing regulation and control of your own learning, propelling you along the path of lifelong learning.

The high-impact learning strategies chart identifies three key characteristics—attitudes, behaviours and metacognition—that positively influence learning outcomes. Research has shown that the listed strategies are among the most highly effective in helping students directly influence their learning and achievement.

TABLE 1.1.1 Characteristics and strategies of high-impact student learning

HIGH-IMPACT STUDENT LEARNING STRATEGIES			
	Attitudes	**Behaviours**	**Metacognition**
Characteristics	Attitude relates to your frame of mind, the approach to your learning and the responses to challenges to produce your desired level of learning.	Behaviour relates to the actions you take and habits you develop and implement as learning strategies.	Metacognition relates to thinking about how you think, and the gaining of awareness of how you learn. Metacognition is very complex thinking and involves you reflecting on how you best learn.
Strategies	• **Effort.** Increasing your level of effort can improve your abilities in, and mastery of, the subject. Effort can be directed at subject matter and skill competence. • **Motivation.** Motivation is the desire to learn for learning's sake, rather than learning specifically. If your motivation is waning, try breaking tasks into smaller chunks and rewarding yourself when each task is finished. • **Concentration**, **persistence** and **engagement**. Learning is enhanced with concentration and sustained application. Create a study area that minimises distractions. The quality of study time has a greater impact on achievement than the amount of time spent studying. • **Perception.** Perceive difficult tasks as challenges to be tackled and overcome. See mistakes as opportunities to improve.	• **Practise.** Practise, practise and more practise. Few people have such natural ability that they are experts. Most people devote hours to repeating and retrying tasks to achieve expert levels in a field. • **Verbalising.** Learning is improved by speaking or verbalising material as a variation to the more common reading and writing. Try talking through the steps to complete a task. Check assessment tasks by reading them out loud. • **Seeking assistance** from classmates and/or teachers. Regularly work with a partner or in a group to discuss learning issues and subject matter. Learning is enhanced when you explain material to others. • **Summaries** of subject matter. Creating concept maps of key subject matter is an effective way of summarising material. • **Study skills.** Note-taking, underlining and highlighting are three effective examples of study skills. Use these strategies to identify key ideas and enhance your understanding. • **Memorisation** and using **mnemonics.** Some material simply needs to be memorised, such as formulas and key glossary definitions. Using mnemonics may help, as well as making charts to summarise key information.	• **Feedback.** This is a powerful tool for improvement. Carefully read feedback comments on your work. If you need more clarification, discuss the feedback with your teacher. Understanding and internalising comments on your work helps you to learn from your mistakes. It also helps you to look more critically at your own work, so you develop self-evaluation skills. • **Reciprocal teaching** involves students taking on the role of teacher. This is a very effective way of improving understanding by placing you, the learner, in an active role rather than being the passive recipient of knowledge. Create a study group of classmates and take turns teaching (revising) a concept or skill to the others. • **Evaluation** and **reflection.** Try assessing your own work against set criteria, such as ISMGs from the syllabus. This requires an understanding of task objectives and evaluation of whether the criteria have been met. This fosters growth as an independent learner. Spend some time reflecting on what you did well, what you need to focus on for improvement, and think about what actions you can take to make those improvements.

LEARNING IN CHEMISTRY

Your experience and understanding of science has developed during the junior years of science lessons and from your observations of the world. Your understanding forms through scientific experimentation, conducting investigations and learning from your textbooks and teachers.

Science is an evolving body of knowledge that can be captured and explained using different tools, such as physical and mathematical models, diagrams, explanations and equations. These tools, which can be referred to as representations, help build meaning and deepen your understanding of the science you are studying.

In order to help you improve your learning, it is useful to be able to identify the role of different representations to explain scientific concepts. These representations can be simplified into three categories—macroscopic, sub-micro and symbolic (Table 1.1.2).

TABLE 1.1.2 Representation levels

Representation level	Examples of representation
macroscopic	observable phenomena—water boiling, magnesium reacting in acid, universal indicator paper changing colour
sub-micro	images and illustrations used to show the properties or characteristics of phenomena at an atomic level—structure of the atom, electron configuration, ionic bonding
symbolic	figures, numbers or symbols used primarily in chemical equations to represent reactions, processes or properties of phenomena

BARRIERS TO LEARNING

In education, factors that prevent a person from learning something effectively are referred to as 'barriers to learning'. There are many different barriers to learning, ranging from language barriers to learning difficulties. Everyone is capable of learning, but finding the techniques and strategies that help to break down these barriers can be a challenge. Each learner has their own preferences regarding the way they learn, so the barriers differ. Within the more abstract disciplines of science, such as chemistry, there are additional barriers that come with the subject matter resulting in further challenges to learning.

To learn chemistry effectively, you need to identify your personal barriers to learning and then work towards overcoming them. Common barriers to learning in chemistry are explained for effective learning and building of connections and meaning.

Scientific literacy

'Scientific literacy' refers to the ability to make sense of and understand the scientific world in order to make informed decisions. This means having knowledge and understanding of scientific concepts and processes in order to make decisions. Literacy also applies to learning and being able to correctly apply new scientific terms in order to both understand and communicate scientific information. This includes being able to use different representations to deepen your understanding. In other words, being scientifically literate means to operate competently like a scientist.

Terminology

Science is almost like learning another language. There are many new terms to learn. Some terms, like 'polymerisation' for example, can be tricky to use appropriately as they describe a whole process in one word. Other terms, like 'diffusion' and 'cathode' for example, are less challenging to use if the processes they describe are less **complex** or the term relates to an object.

The use of representations

Chemists often talk about phenomena and objects that we cannot see. Hence chemistry requires the use of imagination and the ability to visualise. To assist this visualisation, teachers and chemists often produce representations of complex concepts, such as molecular bonding or chemical reactions. Visual aids usually take the form of symbols, diagrams or animations used to symbolise a concept (Figure 1.1.1). Developing a good understanding of science disciplines requires students to be able to effectively interpret these representations.

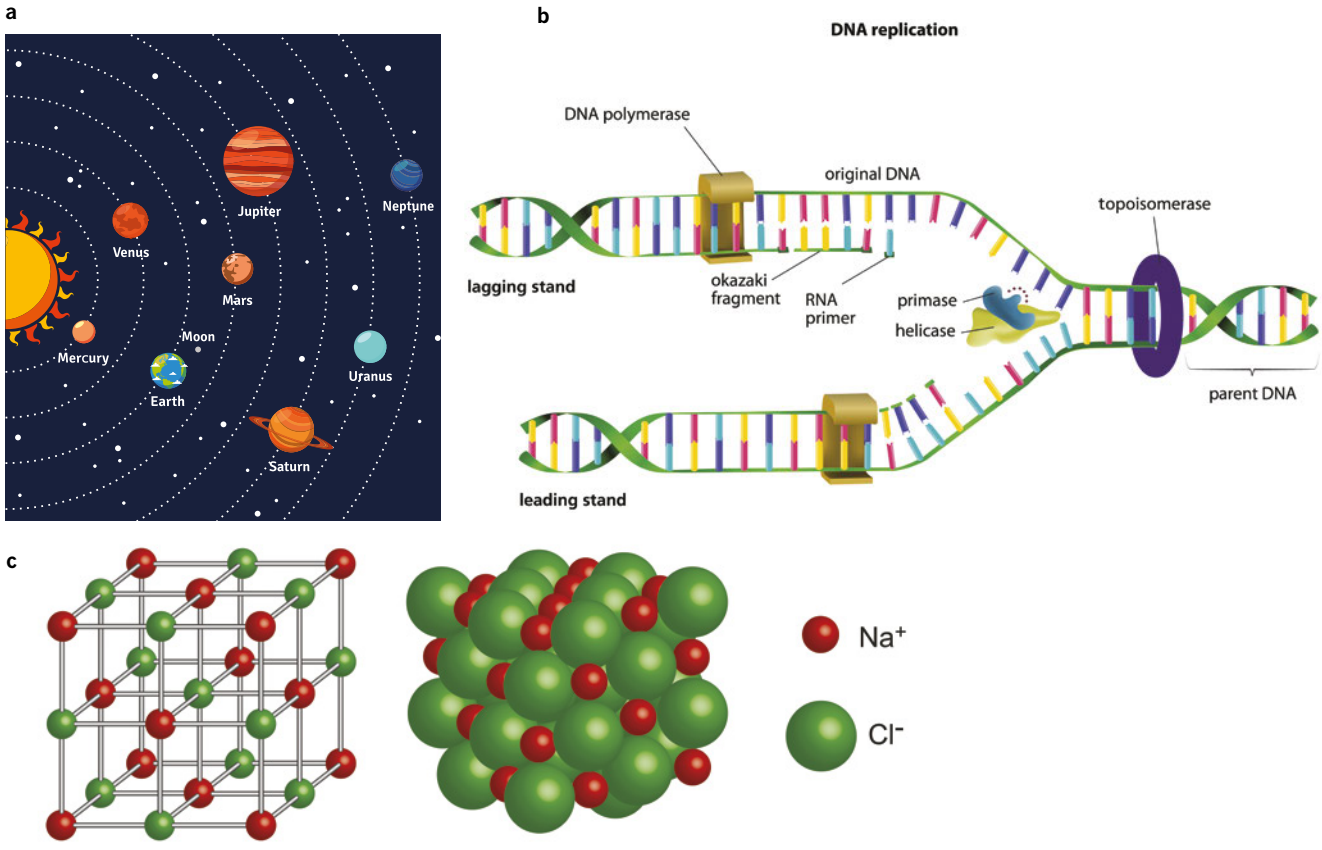


FIGURE 1.1.1 (a) A representation of our solar system (used in physics). (b) A representation of DNA replication (used in biology). (c) A representation used to show the formation of an ionic lattice (used in chemistry)

The use of representations in chemistry is essential for effective learning. Understanding chemistry requires students to engage with a variety of representations. Studies have shown that the key to learning successfully in chemistry is an awareness and understanding of the representations used to explain and model chemical concepts. Scientists have investigated these representations and, while there are variations in the exact terminology used, all the scientific studies agree that there are three levels of representation used in chemistry (Figure 1.1.2):

- the macroscopic level
- the sub-micro level
- the symbolic level.

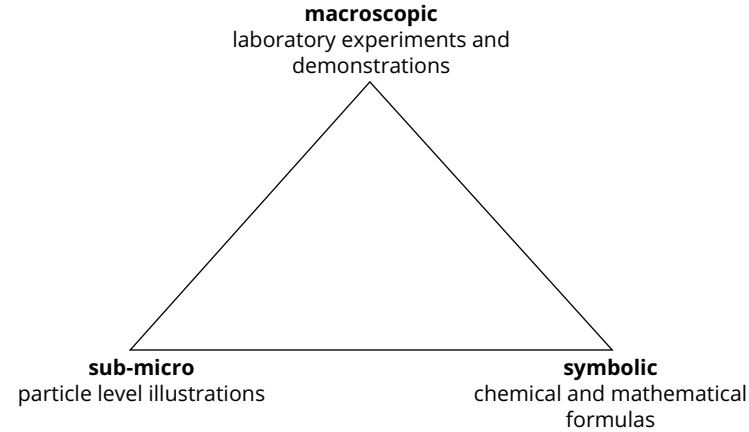


FIGURE 1.1.2 An illustration of the three levels of scientific representation, often referred to as the 'triplet relationship'

Macroscopic level

You are probably familiar with the term 'micro' as meaning something very small. 'Macro' is the opposite and as such refers to anything that is considered large (for chemistry!). In chemistry we refer to anything we can observe with our senses, or can be observed in an experiment, as macro, such as melting, dissolving and colour changes in chemical reactions. It also focuses on phenomena that can be measured such as temperature, concentration and density (Figure 1.1.3).

Macroscopic phenomena can be observed first-hand and are usually the first way that a concept or idea is experienced, introduced or learnt. Macroscopic representations are usually simple; additional and more complex representations are often needed to help explain what is happening at a molecular level. This is where sub-micro and symbolic representations are used.

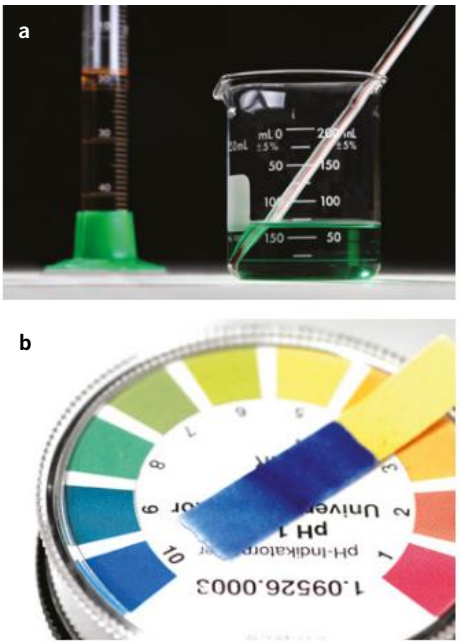


FIGURE 1.1.3 Two examples of macroscopic representations: (a) temperature changes in chemical reactions (measured phenomena) and (b) the reaction that indicator paper goes through to help us determine pH (observed phenomena)

Sub-micro level

The sub-micro level refers to phenomena that are too small to see, even with a microscope (with 'micro' meaning small and 'sub' meaning under/beneath). This level is used to represent extremely small entities such as atoms and ions. Chemical activity at the molecular level can be organised using two levels:

- level 2 sub-micro—qualitative representations such as diagrams, illustrations and animations
- level 3 symbolic—quantitative representations such as equations and stoichiometry.

For the sub-micro type of representation, models are usually introduced as an aid to understanding (Figure 1.1.4).

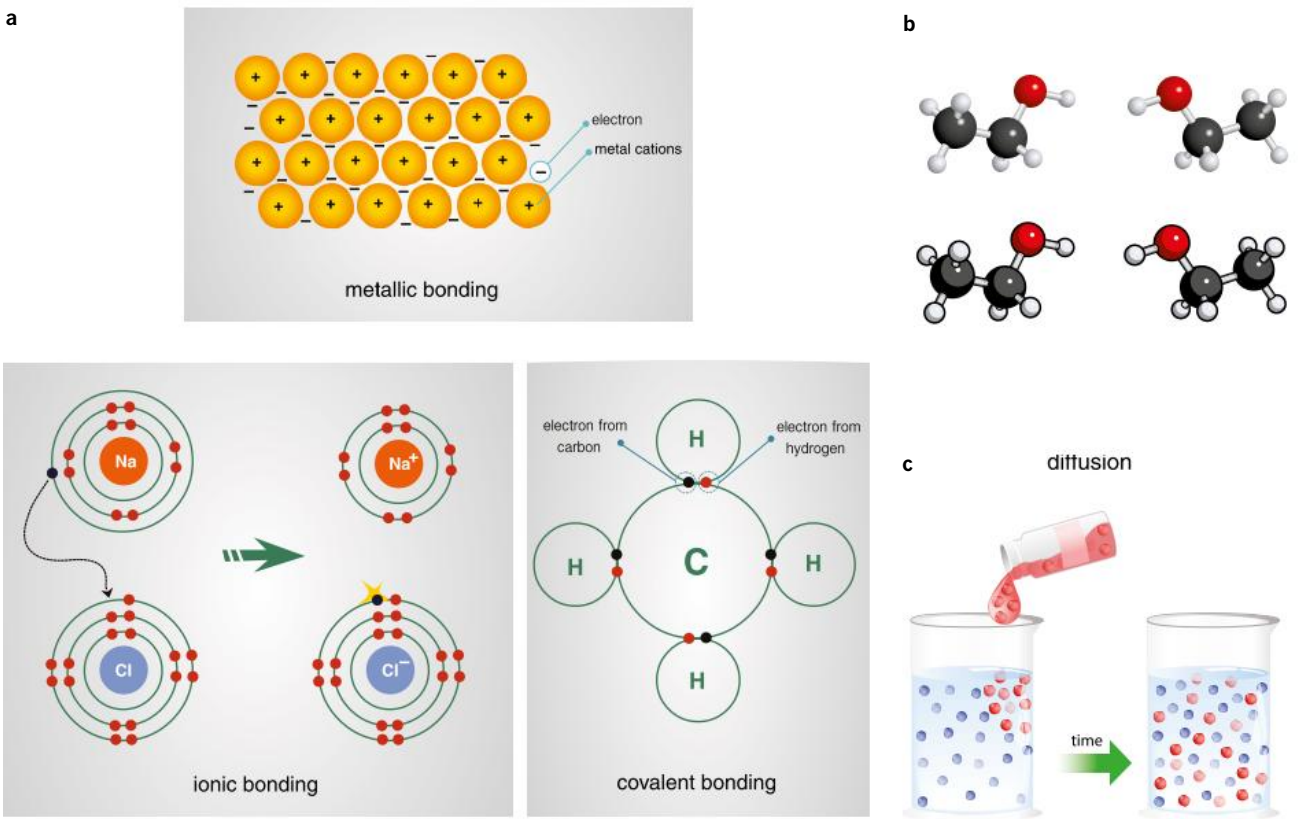


FIGURE 1.1.4 Examples of models being used to explain (a) the different types of molecular bonding, (b) molecular structure, and (c) chemical processes (in this example, diffusion)

Rather than focusing on observations and measurements as in the macroscopic level, sub-micro representations consider properties and characteristics of atoms or molecules to aid understanding of their behaviour.

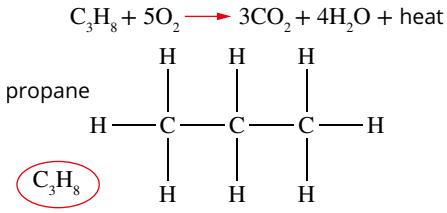


FIGURE 1.1.5 This illustration shows examples of symbolic representation such as the structural formula, molecular formula, subscripts, symbolic equation and even the arrow in the chemical equation to show the complete combustion of propane.

Symbolic level

The symbolic level involves the use of a variety of different symbols—everything from chemical formulas and the use of subscript, to symbols indicating charge or polarity. All chemical symbols fall under the symbolic level (Figure 1.1.5).

While sub-micro level representations focus on the properties or characteristics of sub-microscopic phenomena, symbolic level representations, such as chemical equations (Figure 1.1.5), focus on ways to easily illustrate these properties or characteristics without having to write long passages of text.

The triplet relationship

The three levels of representation are often referred to as the triplet relationship because they are all interconnected and it is very rare to study a topic in chemistry without reference to multiple levels. Figure 1.1.6 shows the relationship between the three levels of representation.

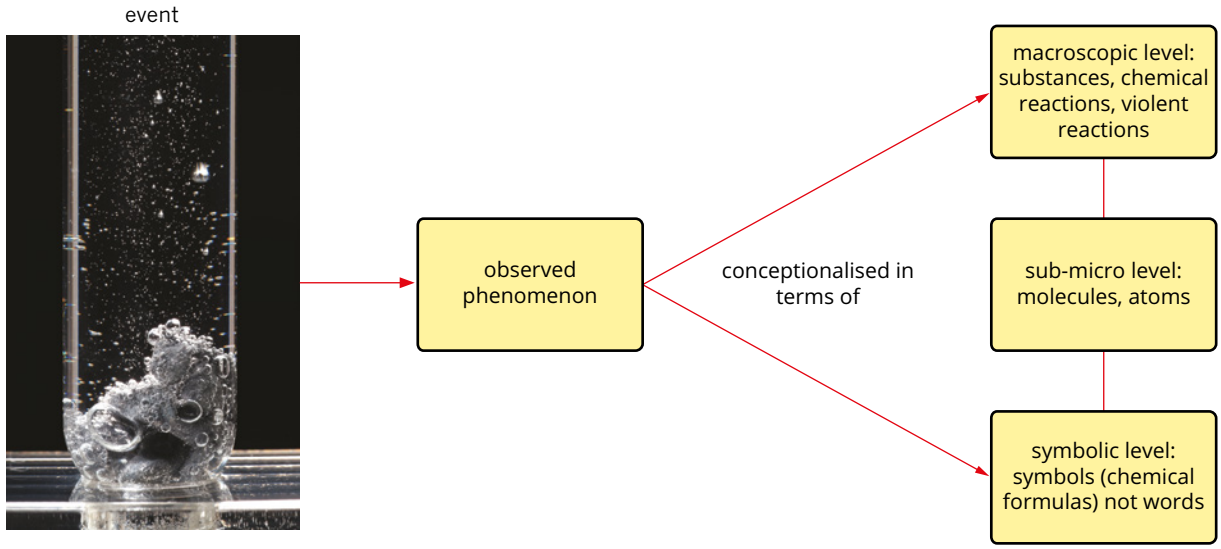


FIGURE 1.1.6 The interconnection between an event or chemical phenomenon and the three levels of representation. The example shows the chemical reaction when zinc comes in contact with hydrochloric acid.

Problems with interpreting the triplet relationship

Numerous studies have shown that students encounter difficulty in understanding these levels individually and in building links between levels. The largest area of difficulty is understanding the representations used in the sub-micro level. The majority of students understand macroscopic and symbolic representations fairly well, but the sub-micro representation level requires something the other two do not—the use of imagination. If a topic has been taught incorporating all three representations, and if correct chemical terminology has been used, this can enhance the learner's ability to correctly depict sub-micro representations, resulting in a better understanding of a concept. Figure 1.1.7a demonstrates a misleading representation that blocks learning, and an accurate representation that aids learning.

Two-dimensional representations have limitations and they can often be misleading. Studies have highlighted that beakers containing liquids are often represented with a handful of molecules drawn in them, when in reality there are hundreds of thousands of molecules. A horizontal line is often used to show the surface of the liquid, inferring that the liquid molecules are stored in some medium, rather than the medium being actually composed of the molecules. An easy way to avoid this confusion is to more accurately draw diagrams as shown in Figure 1.1.7b.

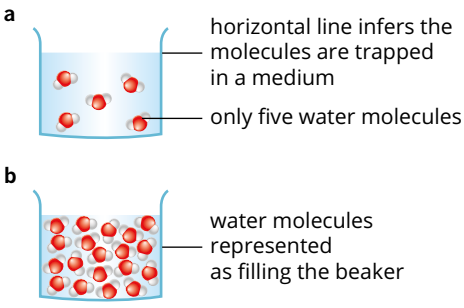


FIGURE 1.1.7 (a) A misleading representation of water molecules in a beaker, and (b) a more accurate representation

Shifting between representation levels

It is problematic for learners when a teacher shifts between the macroscopic level and the sub-micro level to help explain a concept or process. Teachers are accustomed to effortlessly shifting between the levels and often wrongly assume that their learners can do the same.

When students try to explain what has happened in a chemical reaction, they often use macroscopic representations and explanations (which rely on observations). Students who use sub-micro explanations are able to show their teacher that they possess a deeper understanding of a concept or process, because this level requires students to visualise reactions at a molecular level, which is a skill all chemists need to develop. Try explaining some simple chemical reactions using sub-micro representations and slowly build up to explaining most chemical reactions in this way. Table 1.1.3 shows some examples of macroscopic observations and the equivalent sub-micro explanations.

TABLE 1.1.3 Examples of how a macroscopic observation can be worded as a sub-micro explanation

Macroscopic behaviour	Sub-micro explanation
pressure of a gas	collisions of rapidly moving particles on vessel walls
melting	temperature is high enough that the particles have enough energy to overcome some intermolecular forces
sodium chloride dissolves in water	ion–dipole forces of attraction between water molecules and ions are sufficient to overcome the forces between oppositely charged ions in the solid lattice
reactions proceed more quickly at a higher temperature	a higher fraction of collisions have total energy of colliding particles greater than the activation energy required for the reaction
a substance displays optical activity	molecules of the substance are asymmetrical; interactions between the molecules and electromagnetic radiation are such that the plane of polarisation of the radiation are always rotated in the same direction

Using representations to ensure effective learning

It is very important that you understand representations in chemistry and the barriers they can create for some learners. It is important to be proactive in trying to overcome these barriers and have some strategies to get over your learning blocks.

Potential strategies include:

- using concept maps; focus on a process or concept in the middle and then branch out into the three ways it can be represented (macroscopic, sub-micro and symbolic)
- finding multiple examples of each representation (Figure 1.1.8)

- using tables to identify gaps in knowledge
  - identify parts of your chemistry course that you have found difficult and try to identify types of representations that have been used to help explain it
  - if one type of representation is missing, try to create your own
  - if you know of a representation that you do not understand, reflect on what the barrier might be
  - create your own representation for it
  - approach your teacher for assistance if necessary.

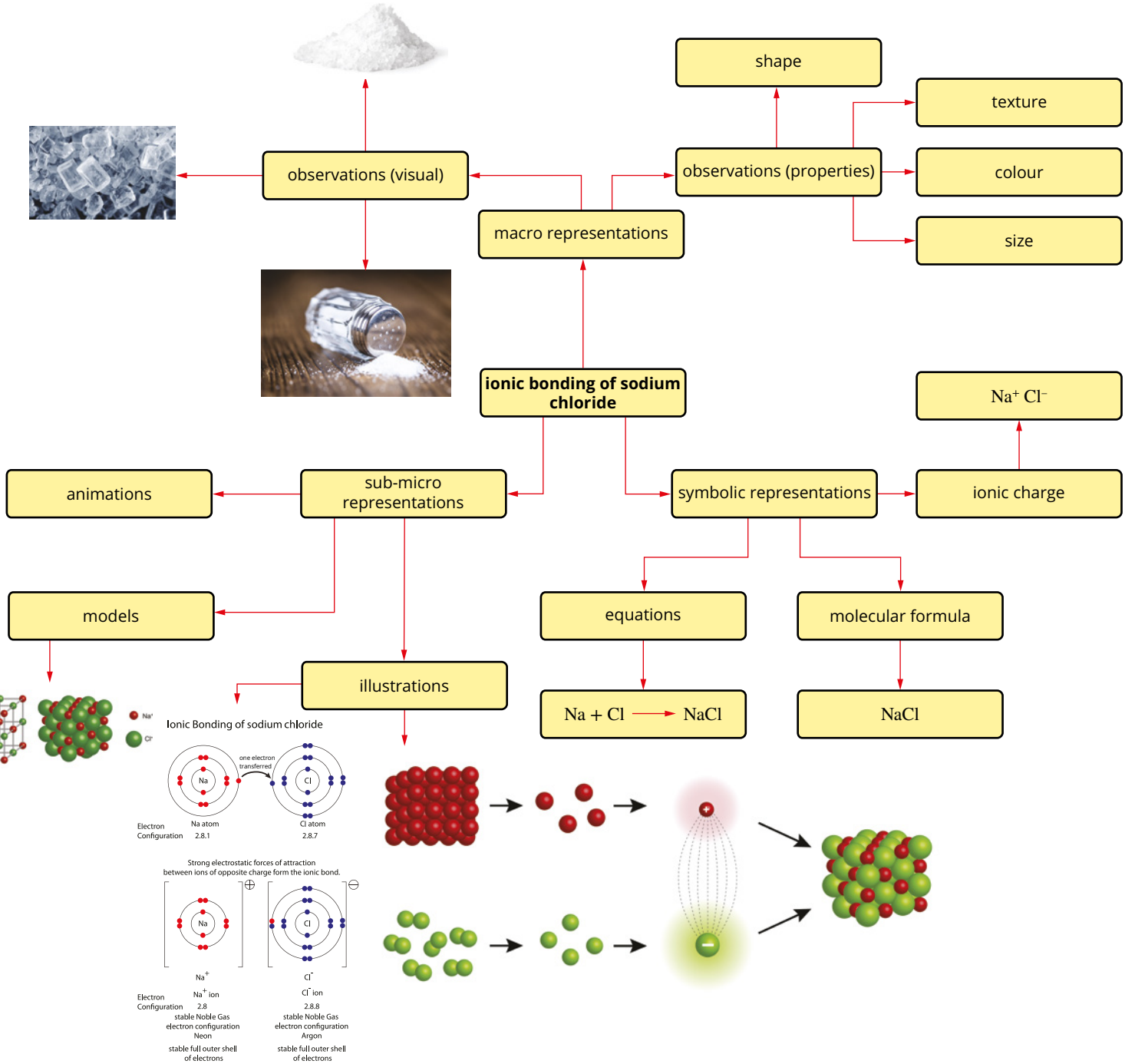


FIGURE 1.1.8 Examples of different scientific representations

In addition to these strategies, this student book contains other examples of the different representation levels that you can use. Table 1.1.4 outlines the application and purpose of these features. The list is not exhaustive; you may find additional examples of features that address the different levels of representation.

TABLE 1.1.4 Representation levels found in the Pearson Chemistry Queensland series features

Representation level	Pearson Chemistry series feature	Resource	Application/purpose
literacy	glossary	student book	definitions of key scientific terms
	preliminary material such as Marzano and Kendall's cognitive verbs list	student book	unpacking meaning behind instruction and enabling understanding of the type of response required
	literacy review worksheets	skills and assessment book	building language and meaning of discourse terminology
macroscopic	mandatory practicals	student book	requires use of observation skills to record results
	additional practicals	skills and assessment book	requires use of observation skills to record results
sub-micro	diagrams	student book and skills and assessment book	illustrations help to visualise complex chemical processes and concepts
	interactives	Reader+	animations help to visualise complex chemical processes and concepts
	videos	Reader+	help illustrate complex chemical processes and concepts
	module, chapter and unit reviews	student book	practise applying learnt terminology in answering questions
symbolic	chemical equations	student book	a simpler and often shorter representation of a chemical reaction
	structural formula	student book and skills and assessment book	a more efficient way of illustrating the structure of a molecule
	mandatory practicals	student book	requires use of observation skills to record results
	additional practicals	skills and assessment book	requires use of observation skills to record results

Teachers and textbooks use chemical representations to assist students in their learning. Having an understanding of the use of these representations allows you as a learner to proactively identify how you learn best. By identifying the types of representations that cause difficulty in your learning, you can be proactive in overcoming the learning barrier. Use the strategies mentioned to ensure effective learning throughout your chemistry course.

1.1 Review

SUMMARY

- Scientific concepts are expressed by different representations.
- Scientific representations can be placed into three categories—macroscopic, sub-micro and symbolic.
- The macroscopic level deals with observable or 'large' events in chemistry.
- The sub-micro level deals with events that are too small to be seen by the naked eye—the atomic scale.
- The symbolic level also deals with the atomic scale and the symbols that represent the chemical events.
- The three levels of representation are connected to each other—the chemical event is observed, the event is explained in atomic terms, and the atomic changes are represented by symbols.
- Effective learning in chemistry involves understanding representations used in the subject, identifying your own personal barriers to learning and working to overcome them.

KEY QUESTIONS

Retrieval

1 List the different representation levels used in chemistry.

Comprehension

2 Demonstrate your understanding of each representation level by providing an example of each.

Analysis

3 Reflect on your learning in chemistry.

a Identify any barriers that block your learning.

b Explain how you might overcome this barrier to your learning.

PART A WORKING SCIENTIFICALLY

Part A will consider the basic mathematical skills and applications that will be required for the data test, a range of mandatory and suggested experiments, as well as for the student experiment.

THE DATA TEST (IA1)

The Data test (IA1) is completed at the end of Unit 3 and relates only to material in that part of the course. The data test is completed in conditions similar to those of the examination at the end of Unit 4, although the focus of the data test is wholly on understanding, analysing and interpreting data and drawing evidence-based conclusions.

The following table outlines some important information about the data test, such as the types of response items, the test conditions and the equipment that can be used.

	Data test
Types of items	• short answers: single sentences or short paragraphs • longer paragraphs (50–250 words per item) • other items involving calculations and/or interpretations
Syllabus coverage	• Unit 3
Assessment objectives	• apply understanding • analyse evidence • interpret evidence and draw conclusions
Conditions	• perusal (reading) time: 10 minutes • writing time: 60 minutes
Equipment	• QCAA-approved graphics calculator • seen formula and data booklet provided • unseen stimulus material
Marks	• constitutes 10% of total assessment

Studying for the data test cannot be rushed in the hours and days before the test. It is not a memory-style test where you can cram at the last minute. The skills and thinking required to effectively complete the data test are best acquired over an extended period of time, with practice and more practice. Part A outlines many of the skills that will enhance your performance when working with data. Refer to Part A on a need-to-know basis to develop your skills.

1.2 Orders of magnitude

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- convert numbers into scientific notation, and vice versa
- estimate the value of a quantity using its order of magnitude
- estimate the value of a quantity of calculation.

SCIENTIFIC NOTATION

In scientific research and literature, measurements are often written in **scientific notation** to overcome confusion or ambiguity. Quantities are written as a number between one and 10 and then multiplied by an appropriate power of 10. Note that 'scientific notation', 'standard notation' and 'standard form' all have the same meaning.

Examples of some values written in scientific notation are:

6.02×10^{23} particles

$25.25\,\text{mL} = 2.525 \times 10^{-2}\,\text{L}$

$0.00302\,\text{mol} = 3.02 \times 10^{-3}\,\text{mol}$

Values given in scientific notation show the significant numbers and indicate the precision of measurement during experimentation by the instrument. Uncertainties in measurement and error are covered in more detail in Module 1.5.

SKILLBUILDER 1.2.1

Transforming decimal notation to scientific notation

Scientists use scientific notation to handle very large and very small numbers. For example, instead of writing 0.000 000 035, scientists would write 3.5×10^{-8}.

A number in scientific notation (also called standard form or power of 10 notation) is written as:

$a \times 10^b$

where:

- a is called the coefficient and is a real number between 1 and 10, that is $1 \leq a < 10$
- b is called the exponent and is an integer (a positive or negative whole number). b is the power that 10 is raised to and is called the index value.

Note that if b is positive, then the number is larger than one and if b is negative, then the number is less than 1.

To transform a very large or very small number into scientific notation, perform the following steps.

1. Show the original number as a decimal number greater than or equal to 1 but less than 10.
2. Multiply the decimal number by the appropriate power of 10.

The index value is determined by counting the number of places the decimal point needs to be moved to form the original number again (Figure 1.2.1 and Table 1.2.1).

- If the decimal point is moved b places to the left, b will be a positive number; for example $510 = 5.1 \times 10^2$.
- If the decimal point is moved b places to the right, b will be a negative number; for example $0.051 = 5.1 \times 10^{-2}$.

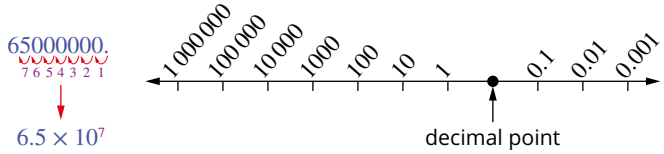


FIGURE 1.2.1 The index value is determined by counting the number of places the decimal point needs to be moved.

TABLE 1.2.1 Converting from scientific notation

Scientific notation	Number (expanded form)
1×10^{-9}	0.000 000 001
1×10^{-6}	0.000 001
1×10^{-3}	0.001
1×10^{-1}	0.1
1	1
1×10^{1}	10
1×10^{3}	1000
1×10^{6}	1 000 000
1×10^{9}	1 000 000 000

You will notice from these examples that when large numbers are written in scientific notation, the 10 has a positive index value. Numbers smaller than 1 are written with 10 to a negative index.

Test the skill

Convert 121 000 to scientific notation.

Worked example 1.2.1

CONVERTING TO SCIENTIFIC NOTATION

Calculate the number of molecules present in a 0.350 g sample of heptane (C_7H_{16}).	
Thinking	**Working**
Calculate the molar mass of heptane.	C = 12.01; H = 1.01 $M_r = 7 \times 12.01 + 16 \times 1.01$ $= 100.23\,g$
Convert to scientific notation.	
Move the decimal place to after the first digit.	100.23 $= 1.0023$
Count the number of places the decimal place was moved.	2
Use the number of decimal places moved as the power index to base 10.	1.0023×10^2
Determine whether the decimal was moved left or right.	left
Do not place a negative symbol (–) in front of the power index, 10.	$1.0023 \times 10^2\,g$
Convert 0.350 g to scientific notation (using the same steps as before).	$0.350\,g = 3.50 \times 10^{-1}\,g$
Calculate the number of moles of heptane used by dividing mass of heptane by its molar mass.	$\frac{3.50 \times 10^{-1}}{1.0023 \times 10^2}$ $= 3.492 \times 10^{-3}$
State Avogadro's number.	6.02×10^{23}
Calculate the number of individual heptane molecules present in 100 g by multiplying the number of moles of heptane by Avogadro's number.	number $= (3.492 \times 10^{-3}) \times 6.02 \times 10^{23}$ $= 2.10321 \times 10^{21}$
Write to 3 significant figures.	2.10×10^{21} molecules

➤ Try yourself 1.2.1

CONVERTING TO SCIENTIFIC NOTATION

In 2009, the average mass of carbon dioxide generated by each person was 44 900 kg. Calculate how many molecules of carbon dioxide this is equal to.

You should be routinely using scientific notation to express very large and small numbers. This also involves learning to use your calculator intelligently. Scientific and graphics calculators can be put into a mode whereby all numbers are displayed in scientific notation. It is useful when doing calculations to use this mode rather than attempting to convert to scientific notation by counting digits on the calculator display.

An important reason for using scientific notation is that it removes ambiguity about the precision of some measurements. For example, a measurement recorded as 240 g could be a measurement to the nearest gram; that is, somewhere between 239.5 g and 240.5 g, or it could have been rounded up to the nearest 10 g. By writing this quantity as 2.40×10^2 g, it makes the accuracy of the value clear (in this case, 3 **significant figures**).

Writing numbers without scientific notation

To write a number into long form from scientific notation, follow these rules.

- If the exponent is positive, write the coefficient without the decimal point. Continue to write zeros after the last digit in the coefficient so that the number of placeholders after the first digit is equal to the exponent.
- If the exponent is negative, write a zero in the units placeholder, then a decimal point. Continue to write zeros until the total number of zeros (including the zero in the units placeholder) is equal to the positive value of the exponent. Then write the coefficient without the decimal place.

Worked example 1.2.2

WRITING QUANTITIES FROM SCIENTIFIC NOTATION

The speed of light is $2.998 \times 10^8\,m\,s^{-1}$. Represent this value in long form.

Thinking	Working
The exponent is positive, which means the number in long form will be greater than 1. Write the number down without the 10^8 and then move the decimal point eight spaces to the right. When you run out of figures in the number, add a zero for each additional movement to the right.	$299\,800\,000\,m\,s^{-1}$

➤ Try yourself 1.2.2

WRITING QUANTITIES FROM SCIENTIFIC NOTATION

Represent the following values in long form.

a The concentration of a solution was determined to be $1.5 \times 10^{-4}\,mol\,L^{-1}$.

b The rate of a reaction was calculated to be $2.4 \times 10^{-5}\,mol\,dm^{-3}\,s^{-1}$.

Scientific notation is the preferred way of communicating very large and very small measurements and information in chemistry. Often for convenience and ease of use, quantities in chemistry problems should first be converted into scientific notation before any calculations can be carried out.

ORDERS OF MAGNITUDE AND PREFIXES

As stated above, scientists often work with very large or very small numbers due to the measurements made during experimentation. Physicists can measure astronomical distances between stars billions and billions of kilometres away. Biologists can measure the number of DNA bases in a genome in the millions, or the size of biological molecules a millionth or a billionth the size of a metre. Chemists can measure the number of atoms in a solution to the millions or billions of molecules. It is important to understand the numbers in scientific notation, their order of magnitude and to be able to convert them into other units.

Scientific notation is common for most sciences displaying numbers with magnitude, for example 2.56×10^{-4}. The other form of communicating measured results is to use units that represent the order of magnitude. If $2.56 \times 10^{-4}\,m$ were measured, it could be written either in the scientific notation as it is already, or as $256\,\mu m$. The symbol μ represents the prefix 'micro-' (Table 1.2.2), which means 'one millionth of the measured unit'. So when 'micro-' is placed in front of metre, it becomes micrometre, meaning 'one millionth of a metre', therefore $256\,\mu m$ becomes 256 millionths of a metre. Again, these are very small measurements and numbers.

SI PREFIXES

In order to write down a physical measurement, two methods are used: prefixes and scientific notation.

An SI **prefix** is a symbol written at the front of a unit to indicate that the measurement is a power of 10 higher or lower than the unit itself.

There are 20 SI prefixes in use and most of them denote units that are 1000 (10^3) times larger or smaller than the previous prefix. Table 1.2.2 lists the SI prefixes commonly used in chemistry.

Each prefix represents an order of magnitude. You should become familiar with both scientific notation and prefixes for units of measurement. You should also be able to interchange them. Table 1.2.2 will help.

When units are displayed with a negative exponent, such as mol L^{-1}, the negative value of the exponent signifies the division of the units; in other words, per unit. In this case, mol L^{-1} is the same as mol/L, or moles per litre.

TABLE 1.2.2 SI prefixes used in chemistry

Prefix	Symbol	Multiplier	Description	Decimal	Example
tera	T	10^{12}	trillion	1 000 000 000 000	Electricity generation provides over 20 000 terawatt-hours of energy a year.
giga	G	10^{9}	billion	1 000 000 000	Over 10 gigatonnes of carbon dioxide is produced from burning coal.
mega	M	10^{6}	million	1 000 000	1 MHz is close to the frequencies at which TV stations broadcast.
kilo	k	10^{3}	thousand	1000	1 kg is 1000 g.
hecto	h	10^{2}	hundred	100	1 hPa is a unit used in meteorology used to describe atmospheric pressure.
–	–	1	unit	1	–
deci	d	10^{-1}	tenth	0.1	1 L = 1 dm^3.
centi	c	10^{-2}	hundredth	0.01	There are 100 cm in 1 m
milli	m	10^{-3}	thousandth	0.001	There are 1000 mm in 1 m.
micro	μ	10^{-6}	millionth	0.000 001	μg are commonly used as the unit for medicine dosage.
nano	n	10^{-9}	billionth	0.000 000 001	The wavelength of yellow sodium streetlights is 550 nm.
pico	p	10^{-12}	trillionth	0.000 000 000 001	The diameter of the hydrogen atom is about 100 pm.
femto	f	10^{-15}	quadrillionth	0.000 000 000 000 001	Some lasers emit a pulse of light that lasts for 1 fs.

SI prefixes are used to avoid writing very small or very large numbers with lots of zeros. The prefix is added directly to the name of a unit and a prefix symbol attaches directly to the symbol for a unit.

The larger prefixes are written as a capital letter, while the smaller prefixes are written using a lowercase letter.

Note that the fundamental unit kilogram has itself a prefix, but all multiples of mass are written with the base unit grams. As an example, one million kilograms is not written as one megakilogram, but as one gigagram (Gg).

Before any measurements with a prefix can be substituted into a formula, they must be converted into SI units without the prefix, i.e. in scientific notation.

Converting between units

Often in science you may need to convert from one unit to another to complete a calculation. Knowing how to change between units is an important skill; however, conversion factors should be used carefully. As some units of measurement are difficult to visualise, knowing the size of different units in relation to each other will aid your understanding and help you avoid errors in your calculations.

- The most common mistake made with conversion factors is multiplying rather than dividing.
- Do not put spaces between the prefixes and the unit symbols.
- It is important to give a symbol the correct case (uppercase or lowercase). There is a big difference between 1 mm and 1 Mm.

About 720 kJ is required to drive a car 1 km. To put this into context it is useful to calculate the amount of fuel that is required.

The enthalpy of combustion of octane is $-5471\,\text{kJ mol}^{-1}$.

Since a typical combustion engine is only about 25% efficient, you only get $0.25 \times 5471 = 1368\,\text{kJ}$ per mole of octane that is burnt.

This means that in order to drive 1 km you need to burn $720/1368 = 0.526$ moles of octane.

This is not a very useful or practical value and so this needs to be converted into a volume. To do this you need to convert the number of moles into a mass by multiplying by the molar mass (M_r octane = 114.26 g). So 0.526 moles weighs $0.526 \times 114.26\,\text{g} = 60.10\,\text{g}$. Again this is not terribly useful when standing at a petrol pump so the mass is converted to volume by dividing by the density of octane (0.702 g/mL). Therefore, the volume of octane required to drive a car 1 km is about 86 mL. This equates to 8.6 L/100 km, which is a unit often quoted by car manufacturers to highlight the fuel efficiency of a particular car.

Worked example 1.2.3

CONVERTING BETWEEN UNITS

Convert 60 micrograms to grams.	
Thinking	**Working**
Convert the units from micrograms to grams.	$= \frac{\mu g}{} \times \frac{g}{\mu g}$ $= \frac{\cancel{\mu g}}{} \times \frac{g}{\cancel{\mu g}}$ $= g$
To convert micrograms to grams, multiply 60 by the number of grams in a microgram (i.e. grams/micrograms).	$= \frac{60}{} \times \frac{g}{\mu g}$ $= \frac{60}{} \times \frac{1}{1000000}$ $= 0.00006\,g$

➤ Try yourself 1.2.3

CONVERTING BETWEEN UNITS

The concentration of cortisol in an athlete's blood was measured to be $4 \times 10^{-8}\,\text{mol L}^{-1}$. Convert this concentration to nmol L^{-1}.

When converting from one unit to another it is essential that you check that the answer makes sense. For instance, if converting from μm to km, you would expect that there are many μm in a km. Multiplying by 1000 000 000 rather than dividing by 1000 000 000 during prefix conversions is one of the most common mistakes made by students.

1.2 Review

SUMMARY

- Scientific notation, standard notation and standard form all have the same meaning.
- A number in scientific notation (also called standard form or power of 10 notation) is written as $a \times 10^n$, where:
  - a is called the coefficient and is a real number between 1 and 10; that is, $1 \leq a < 10$
  - b is called the exponent and is an integer (positive or negative).

KEY QUESTIONS

Retrieval

1 State why chemists need to write numbers in scientific notation instead of long form.

2 Identify the two numbers between which the coefficient of a number expressed in scientific notation has to lie.

3 State what the unit Tg means.

Comprehension

4 Determine the following values in scientific notation.
a 637 nm
b 319 s

5 Represent the following numbers in long form.
a 1.1×10^{-10} m
b 7.031×10^{6} ms^{-2}

6 Determine the order of magnitude of the following values.
a 6.41×10^{9} m
b 1.201×10^{-3} m^3

7 Select the correct scientific notation for each number below.

Number	Scientific notation
0.002	2×10^{3}
2000	1.234×10^{-1}
0.1234	2×10^{-3}
12.34	1.234×10^{1}
123.4	1.234×10^{2}

Analysis

8 Convert the following lengths into the unit in brackets, presenting the information in scientific notation.
a 1.56 mm (μm)
b 8.35 nm (cm)

9 A human hair is about 50 μm wide, whereas a virus is 2×10^{-8} m wide. Determine how many times wider is the width of a human hair than the width of the virus.

10 Calculate the surface area, volume and surface area to volume ratio for the following shapes.

Shape	Surface area (cm^2)	Volume (cm^3)	Surface area : volume (cm^{-1})
cube (3 cm)			
sphere (radius 1.5 cm)			
cylinder (radius 1.2 cm; height 2 cm)			

1.3 Mathematical basics for chemistry

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand that the rules of mathematics apply for solving mathematical operations or calculations in chemistry
- perform basic mathematical operations using percentages and fractions
- rearrange and substitute formulas using algebraic rules
- use the equation of a straight line to determine its gradient and *y*-intercept.

Science uses mathematics in working with data. The evidence can be quantified, measured and analysed. This is known as statistical analysis (a branch of mathematics).

When conducting mathematical operations or calculations, remember all the rules of mathematics apply, including:

- order of operations
- rules for transposing formulas and working with fractions
- substitutions
- approximations.

EXAMPLES OF MATHEMATICAL BASICS FOR CHEMISTRY

Worked example 1.3.1 demonstrates examples of mathematics in chemistry.

Worked example 1.3.1

MATHEMATICAL BASICS IN CHEMISTRY

The equilibrium of the reaction between two chemicals is given by the expression:

$K_{eq} = \frac{[B]^2}{[A]}$

Calculate the equilibrium constant for the reaction when the concentrations of A and B at equilibrium are measured to be 2.50 mol L^{-1} and 0.100 mol L^{-1} respectively.

Thinking	Working
Convert the units and prefixes into SI units and scientific notation (if required). Do not write the answer to more than the maximum number of significant figures in the question.	$[A] = 2.50\,mol\,L^{-1}$ $[B] = 1.00 \times 10^{-1}\,mol\,L^{-1}$
Write down the equation.	$K_{eq} = \frac{[B]^2}{[A]}$
Substitute in the values.	$K_{eq} = \frac{[1.00 \times 10^{-1}]^2}{[2.50]}$ $= 4 \times 10^{-3}$
Express to the lowest number of significant figures in the data (3 significant figures).	$K_{eq} = 4.00 \times 10^{-3}\,mol L^{-1}$

➤ Try yourself 1.3.1

MATHEMATICAL BASICS IN CHEMISTRY

Calculate the concentration of 4.20 g of sodium chloride (NaCl) in 250 mL of water.

ANALYSING STRAIGHT LINES

A straight line is the simplest relationship between two variables. The **dependent variable** is plotted on the *y*-axis and the **independent variable** is plotted on the *x*-axis. The relationship between the two variables is represented by the gradient. The *y*-intercept and gradient can be easily calculated by hand or with technology. Figure 1.3.1 shows a typical straight line relationship.

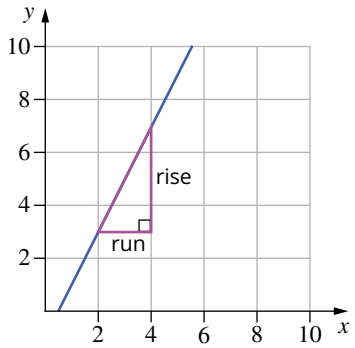


FIGURE 1.3.1 A graph representing a simple relationship between two variables

The gradient of any straight line is calculated using:

$$\text{gradient, } m = \frac{\text{rise}}{\text{run}} = \frac{\Delta y}{\Delta x}$$

The *y*-intercept, *c*, is read off the *y*-axis.

The equation of any straight line is determined by the gradient and *y*-intercept:

$$y = mx + c$$

In the example in Figure 1.3.1, the equation of the straight line is $y = 2x - 1$ with a gradient of 2 and *y*-intercept of −1.

SKILLBUILDER 1.3.1

Interpreting the slope of a linear graph

Scientists often represent a relationship between two variables as a graph. For directly proportional relationships, the variables are connected by a straight line, where the slope (or gradient) of the line represents the constant of proportionality between the two variables.

The slope or gradient of the line is defined as the ratio of change between two points in the vertical axis (Δy), divided by the change between two points in the horizontal axis (Δx). In other words, it measures the rate at which one variable (the dependent variable) changes with respect to the other (the independent variable).

Figure 1.3.2 has two straight lines with different slopes. The steeper slope (blue line) indicates that the rate of change is larger. This means the change is happening more quickly.

The flatter slope (purple line) indicates that the rate of change is smaller. This means the change is happening more slowly.

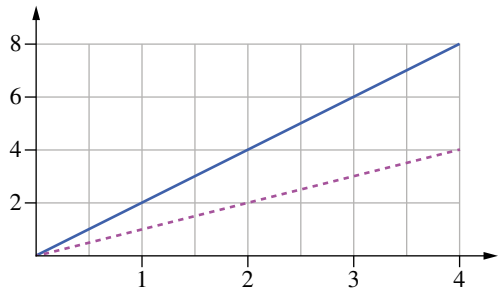


FIGURE 1.3.2 Different rates of change on a linear graph

Worked example 1.3.2

INTERPRETING THE SLOPE OF A LINEAR GRAPH

On a graph with two sloped lines, determine what the steeper sloped line indicates.

A a faster rate of change
B a slower rate of change
C the same rate of change
D a much slower rate of change

Thinking	Working
The slope or gradient of the line is defined as the ratio of change between two points in the vertical axis (Δy), divided by the change between two points in the horizontal axis (Δx).	A is correct. The steepness of the slope indicates the rate of change. A line with a steeper slope indicates a faster rate of change.

➤ Try yourself 1.3.2

INTERPRETING THE SLOPE OF A LINEAR GRAPH

Determine which of the following options indicates the rate of change of a straight line on a graph.

A area under the graph
B *x*-intercept
C gradient
D *y*-intercept

1.3 Review

SUMMARY

- When conducting mathematical operations or calculations, remember all the rules of mathematics apply, including:
  - order of operations
  - rules for transposing formulas and working with fractions
  - substitutions
  - approximations.

KEY QUESTIONS

Retrieval

1 State the formula for calculating the gradient of a straight line on a graph.

Comprehension

2 Determine the following quantities.

a the mass of 75 mL of ethanol (density of ethanol is $0.789\,g\,mL^{-1}$)

b the volume of 24.5 g of ethanol

Analysis

3 A student recorded the following temperatures of water.

Time (min)	Temperature (°C)
0	22
2	34
4	43
5	50
8	64
10	78

a Calculate the average temperature change per minute during the experiment.

b Determine whether the increase was constant throughout the experiment by drawing a graph of the data.

1.4 Units

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- appreciate that chemistry uses the Standard International (SI) of units
- recall fundamental units, their symbols and definitions
- understand that the SI prefixes are multipliers of powers of 10 of the base units
- convert between various units of the same type using SI and some non-SI units.

Sciences need a common system of units in order to describe measurements. In chemistry, measurements are made using the **Standard International (SI)** system of units. Most countries around the world use and understand these units as they are internationally accepted in science, commerce, sport and everyday life.

MEASUREMENT AND UNITS

When taking measurements, make sure the units you measure or observe are accurate and remember to use common or SI units when recording your evidence. Table 1.4.1 presents common quantities and SI units used in chemistry.

TABLE 1.4.1 Common quantities and SI units used in chemistry

Quantity	Symbol for quantity	Unit
mass	m	gram (g) kilogram (kg)
volume	V	litre (L) millilitre (mL)
amount of substance	n	mole (mol)
molar mass	M	grams per mole ($g\,mol^{-1}$)
relative molecular or formula mass	M_r	no units; relative to one atom of ^{12}C exactly
relative atomic mass	A_r	no units; relative to one atom of ^{12}C exactly
relative isotopic mass	I_r	no units; relative to one atom of ^{12}C exactly
energy	E	joule (J) kilojoule (kJ)
concentration (molarity)	c	moles per litre ($mol\,L^{-1}$ or $mol\,dm^{-3}$)
density	d	$g\,mL^{-1}$ or $kg\,L^{-1}$
temperature	T	°C, K
pressure	P	atm, Pa

Correct use of unit symbols

The correct use of unit symbols removes ambiguity, as symbols are recognised internationally. Some important points to keep in mind when writing units and recording measurements and numbers are given in Table 1.4.2.

Uppercase letters are used only for the symbols of the units that are named after people. For example, the unit of energy is joule and the symbol is J. The joule was named after James Joule who was famous for studies into energy conversions. The exception to this rule is 'L' for litre. Uppercase L is used because a lowercase 'l' looks like the numeral '1'.

The product of a number of units is shown by separating the symbol for each unit with a space. The division or ratio of two or more units can be shown in fraction form, using a slash, or using negative indices. Prefixes should not be separated by a space.

TABLE 1.4.2 Examples of correct and incorrect use of symbols for derived units

Rule	✓	✗
Numbers and symbols should not be mixed.	thirty grams 30 g	thirty g 30 grams
Do not put spaces between prefixes and unit symbols.	kg mL kPa	k g m L k Pa
Write the correct case for symbols (uppercase or lowercase).	1 mm 84 kg 5.2 mL	1 Mm 84 KG 5.2 ml
SI units should not be followed by a full stop unless they are at the end of a sentence. The symbols for units are not abbreviations.		
Only use uppercase letters for unit symbols named after people. The exception is 'L' to avoid confusion because 'l' looks like the numeral '1'.	J (the unit of energy is joule, named after James Joule)	
Units named after people can take the plural form by adding an 's' when used with numbers greater than one. Never do this with the unit symbols.	two kilojoules	2 kJs
The product of a number of units is shown by separating the symbol for each unit with a space.	0.1 mol dm^{-3}	0.1 mol dm^{-3}
The division or ratio of two or more units can be shown in fraction form, using a slash, or using negative indices.	0.1 mol dm^{-3} J g^{-1} °C^{-1}	0.1 mol dm^{-3} J g^{-1} °C^{-1}
When units are displayed with a negative exponent such as g mL^{-1}, the negative value of the exponent signifies the division of the units, or per unit. In this case, g mL^{1} is the same as g/mL, or grams per decilitre.	1000 kJ mol^{-1} 13 °C/g	1000 kJ/mol^{-1} 13 °C/g^{-1}

Table 1.4.3 provides some examples of correct and incorrect use of symbols for derived units.

TABLE 1.4.3 Examples of the use of symbols for derived units

Correct symbol ✓	Incorrect symbol ✗
J g^{-1} °C^{-1}	Jg^{-1} °C^{-1}
g mol L^{-1}	gmol^{-1}
kPa	K Pa

Worked example 1.4.1

UNIT CONVERSIONS

Calculate the number of litres in one cubic kilometre.	
Thinking	**Working**
State each unit in terms of m^3. Remember that a km^3 is a cube that has sides of 1000 m by 1000 m by 1000 m.	$1\,L = 0.001\,m^3$ and $1\,km^3 = 1000\,m \times 1000\,m \times 1000\,m = 10^9\,m^3$
Take the inverse of each equation to find the equivalent volume in m^3.	$1\,m^3 = \frac{1}{10^9} = 10^{-9}\,km^3$ and $1\,m^3 = \frac{1}{0.001} = 10^3\,L$
Now equate them since they are both equal to $1\,m^3$.	$10^{-9}\,km^3 = 10^3\,L$ $\therefore \frac{10^3\,L}{10^{-9}\,km^3} = 10^{12}\,L/km^3$
State the answer.	There are 10^{12} or one trillion litres in 1 cubic kilometre.

➤ Try yourself 1.4.1

UNIT CONVERSIONS

The concentration of paracetamol in a children's cough syrup was 120 mg/5 mL. The usual dosage for children is $15\,mg\,kg^{-1}$ of weight. Calculate the number of mL that a 10 kg child should receive.

1.4 Review

SUMMARY

- Scientists use conventional ways of writing numerical measurements such as using Standard International (SI) units.
- Units with a prefix need to be converted into scientific notation before they can be used in a chemistry formula.
- When converting units, it is very useful to write the conversions as fractions and then cross cancel out to ensure that the conversion is done correctly.
- When units are displayed with a negative exponent, the negative value of the exponent signifies the division of the units. For example, $g\,mL^{-1}$ is the same as g/mL or grams per millilitre.
- When writing and recording measurements, remember:
  - numbers and symbols should not be mixed
  - do not put spaces between prefixes and unit symbols
  - write the correct case for symbols (uppercase or lowercase).

KEY QUESTIONS

Retrieval

1 State the standard unit of measurement, and the symbol, for the following quantities.
- **a** time
- **b** thermodynamic temperature
- **c** length
- **d** mass

2 List the following units from largest to smallest.
centi, milli, mega, kilo, nano, micro

Comprehension

3 Explain why general members of society, not just the scientific community, need a systematic and consistent set of units for measurement.

Analysis

4 Identify any errors in the recordings below and correct them.
- **a** $23\,mL/gh^{-1}$
- **b** $79\,kl\,s^{-1}$
- **c** four litres
- **d** 1.56 grams

5 Determine how many metres there are in the 656 nm wavelength of red light emitted from hydrogen.

6 Determine how many atoms there are in 5.3 g of helium.

1.5 Uncertainties in measurement and error

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- explain the difference between accuracy and precision
- explain the difference between uncertainty and error
- calculate uncertainty and error values for measurements
- show measurements with uncertainty and error values
- show measurements and calculations to the correct number of significant figures
- perform calculations that contain uncertainty or error values
- understand that all measurements made in chemistry experiments are subject to a level of uncertainty
- differentiate between accuracy and precision and know how to express these quantitatively using significant figures
- perform calculations using significant figures
- explain the difference between mistakes, systematic uncertainties and random uncertainties
- determine the absolute uncertainty of a value based on the precision of the instrument
- convert between absolute and percentage uncertainties
- calculate a value along with the associated uncertainty.

All measurements are limited by the instrument used and the observer. Accuracy of the measurements and results are therefore affected. Instruments have a prescribed level of precision and cannot measure within the smallest increment of the device. In addition, a scientist's technique and experience with the instrument influences the precision with which the reading can be made. In science, it is impossible to measure the **true value**, as there will always be some degree of **uncertainty**.

Some experiments can measure closer to the true value than others and experimentation in closed systems enables more accurate and precise measurements. The results may have **errors** and uncertainty in the values measured or observed. Therefore, science can be thought of as developing evidence-based results that have some limitations. Measurements with uncertainty and errors are normal in science and so results are always presented with a **range** (e.g. ±0.25) indicating possible precision, or processed through statistical calculations.

ACCURACY AND PRECISION

In science and statistics, the terms 'accuracy' and 'precision' have very specific and different meanings.

- **Accuracy** is the ability to obtain the correct measurement. To obtain accurate results, you must minimise **systematic errors**.
- **Precision** is the ability to consistently obtain the same measurement. To obtain precise results, you must minimise **random errors**.

To understand more clearly the difference between accuracy and precision, think about throwing darts at a dartboard (Figure 1.5.1). Accuracy is being able to hit the bullseye, whereas precision is being able to hit the same spot every time you shoot.

Any measurement made in chemistry needs to be both accurate and precise.

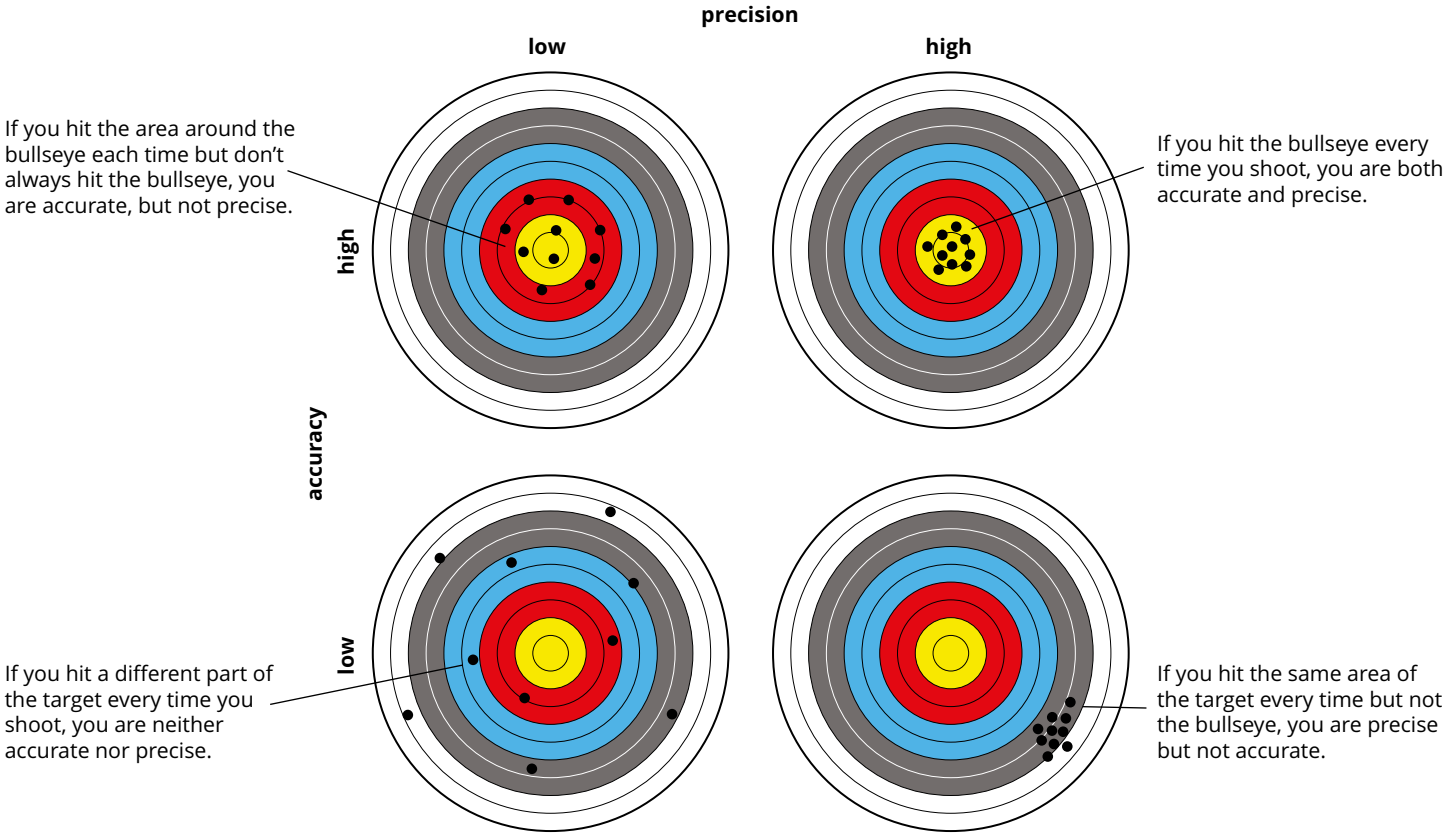


FIGURE 1.5.1 Using a dartboard with darts illustrates the difference between accuracy and precision. In summary, measurements should be both as precise and as accurate as you can make them.

Recording numerical data

When using instruments to measure data, the number of significant figures (or digits) and decimal places you use is determined by how precise your measurements are.

The overall precision of the measurement depends on the scale, accuracy and precision of the instrument and technique you are using (Figure 1.5.2). For example, a beaker may be used to measure volumes approximately and has limited accuracy, for example ±5%; however, a graduated pipette is much more accurate, with accuracies of ±0.1% or ±0.2%. Your pipette may be accurate but if your technique using the pipette is variable, the overall accuracy and precision will be limited.

When you record **raw data** and report processed data, you must use the number of significant figures available from your equipment or **observation**. This is discussed in more detail in Module 1.10. Using either a greater or smaller number of significant figures can be misleading. For example, Table 1.5.1 shows measurements of five mass samples taken using an electronic balance accurate to 2 decimal places. The data was entered into a spreadsheet to calculate the mean, which was displayed with 4 decimal places. You would record the mean as 20.83 g, not 20.8260 g, because 2 decimal places is the precision limit of the instrument. Recording 20.8260 g would be an example of false precision.

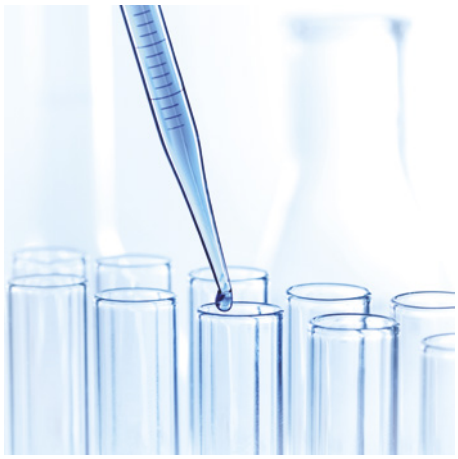


FIGURE 1.5.2 A 5 mL graduated pipette can measure volumes to an accuracy of one-tenth of a millilitre, or 5 mL ± 0.1 mL. The pipette has major divisions of 1 mL and minor divisions of 0.1 mL. You can estimate to 0.05 mL and record volumes to 2 decimal places; for example, 3.80 mL or 4.55 mL.

TABLE 1.5.1 An example of false precision in a data calculation

Sample	1	2	3	4	5	mean
Mass (g)	20.13	20.62	21.22	20.99	21.17	20.8260

UNCERTAINTY AND ERROR

Uncertainty and errors arise from various different sources. Uncertainty is a range of measurements from the experiment in which the true value is expected to lie. Due to variations, an estimation is made to suggest where the true value should be found among the measurements. Uncertainty is one indicator of limitations.

Error is the difference between a measurement and the true value. This is not an indication of human error or mistakes. It is due to an inability to achieve the true value. Error cannot be eliminated and therefore it is important to understand and record the error and report it. Two types of errors can occur—systematic and random (Table 1.5.2).

TABLE 1.5.2 Systematic and random errors

Error	Definition	Cause	Example
systematic	An error in measurements caused by the design of a system (e.g. methodology) or instrument (e.g. uncalibrated), which results in the measurements shifting in a systemic direction. The mean may be displaced or varied in a predictable way affecting the accuracy of the measurement.	• instrument calibration • choice of instrument • precision of instrument (increments) • precision of instrument (sample rate—per second) • sampling	The balance used for weighing out samples reads 0.05 g too high for all your masses because it was improperly tared (set to zero) at the start of the experiment.
			Using a standard hydrochloric acid solution for a series of titrations that is not 1.0 mol L^{-1}. As long as the actual concentration of the acidic solution is determined, the number of moles of base required to neutralise it in each titration can be corrected for.
random	An error that affects the measurement in an unpredictable way resulting in an uneven variation (fluctuation) in measurements above and below the expected true value. This affects the precision of the measurement.	• estimation (measuring between increments) • sampling (frequency, spread, increments) • parallax • instrument sensitivity • noise	Using universal indicator to determine the pH of a solution, in which the pH must be estimated by the shade and colour of the paper (e.g. yellow/orange versus bright orange).
			Measuring the time taken for a reaction to occur has a random error associated with the identification of when the reaction is judged to be complete.

Uncertainties and errors should always be calculated or measured and then reported. They then form part of the analysis and interpretation (see Module 1.7 Statistics and Module 1.10 Results) as well as the evaluation. Also, it is a good idea to consider uncertainty and error when planning experiments (see Module 1.8 Research and planning and Module 1.9 Conducting an experiment).

Calculating uncertainty in measurement

The goal when taking measurements is to get as close as possible to the 'true' or 'correct' value. For example, when using a measuring cylinder for the volume of solution, the reading may be between two increments on the instrument. The uncertainty can be calculated, or estimated, and is often represented as a percentage or expressed based on the unit of measurement, i.e. if measuring to the nearest mm and the value lies between the divisions then the uncertainty is expressed as ± 0.5 mm.

If the uncertainty was described as ±1%, it means that the measurement taken is likely to be no more than 1% above or below the 'true' value of the quantity that is being measured.

When averaging repeat measurements, the uncertainty should be reported alongside your average. Uncertainty represents a realistic range within which the true value is likely to be. The following equation is a simple way to calculate the uncertainty.

$$\text{uncertainty} = \pm \frac{\text{upper value} - \text{lowest value}}{2}$$

Worked example 1.5.1

CALCULATING UNCERTAINTY

A titration was performed three times and the volume of acid required to neutralise the solution was 25.8 mL, 26.0 mL and 24.8 mL. Calculate the uncertainty.

Thinking	Working
Calculate the average volume of acid required.	$\text{average} = \frac{25.8 + 26.0 + 24.8}{3}$ $= 25.533$
Write down the formula.	$\text{uncertainty} = \pm\frac{\text{upper value} - \text{lowest value}}{2}$
Insert the values then calculate.	$\text{uncertainty} = \pm\frac{26.0 - 24.8}{2}$ $= \pm\frac{(1.2)}{2}$ $= 0.6\ \text{mL}$
Combine measurement with uncertainty.	25.3 mL ± 0.6 mL

➤ Try yourself 1.5.1

CALCULATING UNCERTAINTY

The mass of acetaminophen in five tablets is 440 mg, 436 mg, 453 mg, 443 mg and 429 mg. Calculate the average mass of acetaminophen in a tablet and the uncertainty.

Another example of uncertainty is instrumental error or uncertainty in measurement. This is the precision of an instrument and is limited by the smallest increment the instrument can measure. The uncertainty of an instrument is half the smallest increment. This is known as **absolute uncertainty**. The following equation is a simple way to calculate the absolute uncertainty of a measurement.

$$\text{uncertainty} = \pm\frac{\text{smallest increment}}{2}$$

SKILLBUILDER 1.5.1

Calculating absolute uncertainty

Calculate the absolute uncertainty for instrumental error during an experiment where the temperature was measured at 32°C using a glass thermometer with increments of 1°C and a digital thermometer with increments of 0.1°C.

For the glass thermometer:

1 Write down the formula.

$\text{uncertainty} = \pm\frac{\text{smallest increment}}{2}$

2 Insert the values and calculate.

$\text{uncertainty} = \pm\frac{1}{2}$
$= \pm 0.5°\text{C}$

3 Combine the measurement with the uncertainty.

32°C ± 0.5°C

For the digital thermometer:

1 Write down the formula.

$\text{uncertainty} = \pm\frac{\text{smallest increment}}{2}$

2 Insert the values and calculate.

$\text{uncertainty} = \pm\frac{0.1}{2}$
$= \pm 0.05°\text{C}$

3 Combine the measurement with the uncertainty.

32°C ± 0.05°C

Uncertainty can also be reported as a percentage of the measurement. This is known as **relative uncertainty**. The following equation is a simple way to calculate the relative uncertainty of a measurement.

$$\text{relative uncertainty} = \pm\left(\frac{\text{absolute uncertainty}}{\text{measurement}}\right) \times 100$$

Worked example 1.5.2

CALCULATING RELATIVE UNCERTAINTY FOR INSTRUMENTAL ERROR

The temperature during an experiment was measured and then reported at 25.3°C ± 0.1°C. Calculate the relative uncertainty.	
Thinking	**Working**
Write the formula for relative uncertainty.	$\text{relative uncertainty} = \pm\left(\frac{\text{absolute uncertainty}}{\text{measurement}}\right) \times 100$
Insert the values and calculate.	$\text{relative uncertainty} = \pm\left(\frac{0.1}{25.3}\right) \times 100$ $= 0.395\%$
For the digital thermometer, combine the measurement with the relative uncertainty and express to the appropriate number of significant figures.	25.3°C ± 0.40%

➤ Try yourself 1.5.2

CALCULATING RELATIVE UNCERTAINTY FOR INSTRUMENTAL ERROR

The mass of copper sulfate used to make up a solution was 20.14 ± 0.05 g. Calculate the relative uncertainty.

Significant figures

When measuring phenomena during experimentation, the precision of the instruments determines the number of significant figures and decimal places you record in the data.

Significant figures convey meaning and precision and the number of significant figures used depends on the scale of the instrument. You should record data using the number of significant figures available from the equipment or observation. Using either a greater or smaller number of significant figures is misleading.

When writing an answer to the correct number of significant figures, you may need to use rounding if the initial answer has more figures (digits) than you need. These extra figures are called 'non-significant figures'. If the first non-significant figure is ≥5, round up the number. If the first non-significant figure is <5, then do not round up. For example, if the initial answer for a calculation was 2.1259 but you only needed an answer to 3 significant figures, you would round it to 2.13. If the initial answer was 2.1241, then to 3 significant figures this becomes 2.12.

SKILLBUILDER 1.5.2

Identifying significant figures

When giving an answer to a calculation, it is important to take note of the number of significant figures that you use.

You should give an answer that is as accurate as possible. However, an answer cannot be more accurate than the data or the measuring device used to calculate it. For example, if an electronic balance that measures to the nearest gram shows that an object has a mass of 56 g, then the mass should be recorded as 56 g, not 56.0 g. This is because you do not know whether it is 56.0 g, or 56.1 g, or 56.2 g or 55.8 g.

The number 56 has 2 significant figures. Recording to three significant figures (e.g. 56.0 g or 55.8 g) would not be scientifically 'honest'.

If this mass of 56 g is used to calculate another value, it would also not be 'honest' to give an answer that has more than 2 significant figures.

Determining the number of significant figures to give an answer to depends on the kind of calculation you are doing.

- If you are multiplying or dividing, use the smallest number of significant figures provided in the initial values.
- If you are adding or subtracting, use the smallest number of decimal places provided in the initial values.

Working out the number of significant figures

The following rules should be followed to avoid confusion in determining how many significant figures are in a number.

- All non-zero digits are always significant; for example, 21.7 has 3 significant figures.
- All zeros between two non-zero digits are significant; for example, 3015 has 4 significant figures.
- A zero to the right of a decimal point and following a non-zero digit is significant; for example, 0.5700 has 4 significant figures.
- Any other zero is not significant, as it will be used only for locating decimal places; for example, 0.005 has just 1 significant figure.

Worked example 1.5.3

IDENTIFYING SIGNIFICANT FIGURES

a Show which of the following is written to 2 significant figures.

A 30.1
B 0.00040
C 0.5
D 5.12

b George multiplied 1.22 by 1.364. Select from the options below the result of this multiplication with the correct number of significant figures.

A 1.66
B 1.664
C 1.65
D 1.7

Thinking	Working
a Zeros that come before the integer 4 are not significant, whereas those that follow the integer are significant.	B is correct. A has 3 significant figures. C has 1 significant figure. D has 3 significant figures.
b 1.22×1.364 $= 1.66408$	A is correct. When two numbers are multiplied, use the smallest number of significant figures in the initial values to report your answer. In George's multiplication, the answer is 1.66408, but since 1.22 has 3 significant figures, the correct answer is 1.66.

➤ Try yourself 1.5.3

IDENTIFYING SIGNIFICANT FIGURES

Show which of the following is 0.003452 written to 3 significant figures.

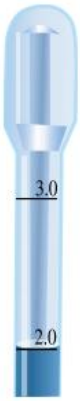
A 345
B 3.45
C 0.003
D 0.00345

Worked example 1.5.4

DETERMINING THE SIGNIFICANT FIGURES OF A MEASUREMENT FROM AN INSTRUMENT

When measuring the amount of solution for an acid–base experiment, you need to record the figures accurately.

a using a plastic pipette



b using a glass pipette



Thinking	Working
a If the plastic pipette is used to measure the solution, the increments will determine the significant figures.	
If you measured 1 mL, you need to record the amount accurately.	Record the increment of the measured amount to the precision of the instrument = 1 mL.
Determine the significant figures. Because the pipette (measuring instrument) only measured in millilitres, you can only record in full millilitres.	The measurement of 1 mL has 1 significant figure—the number 1.
b If the glass pipette is used to measure the solution, the increments will determine the significant figures.	
If you measured 1 mL, you would need to record the amount accurately.	Record the increment and the measured amount to the precision of the instrument = 1.0 mL.
Determine the significant figures. Because the pipette (measuring instrument) measured in tenths of millilitres, you can only record to the tenth of a millilitre.	The measurement of 1.0 mL has 2 significant figures—the number 1 and the number 0.

➤ Try yourself 1.5.4

DETERMINING THE SIGNIFICANT FIGURES OF A MEASUREMENT FROM AN INSTRUMENT

When measuring the temperature for a calorimeter experiment, you need to record the figures accurately.

a using a glass alcohol thermometer



b using a digital thermometer



Significant figures are the exact digits observed when recording the results of an observation or experiment. For example, if the volume of O_2 gas produced and measured from the electrolysis of water was 6.0 mL because exactly 6.0 mL was observed, then the measurement is 6.0 mL with 2 significant figures, not 6 mL.

Table 1.5.3 shows some examples of measurements and how many significant figures they have.

TABLE 1.5.3 Measurements and significant figures

Measurement	Number of significant figures
15	2
3.5	2
3.50	3
0.0**37**	2
1401	4
1400	4

> It is important to record the exact numbers measured during an experiment. This determines the significant figures and later the accuracy and precision of the analysis. If a zero is observed, record it, it is the exact amount measured. This includes all zeros before and after decimal places.

Using either a greater or smaller number of significant figures can be misleading. For example, Table 1.5.4 shows three measurements to 2 decimal places (4 significant figures). The data was entered into a spreadsheet to calculate the **mean**, which was displayed with 3 decimal places. You would record the mean as 19.52 mL, not 19.517 mL, because 2 decimal places is the precision limit of the instrument. Recording 19.517 mL would be an example of false precision.

TABLE 1.5.4 An example of false precision in a data calculation

Trial	1	2	3	mean
Volume (mL)	19.45	19.55	19.55	19.517

Calculations with uncertainties

There are a few rules when conducting calculations with numbers (or measurements) that have uncertainties. It is important to record the correct uncertainty once all the calculations are done so that the appropriate accuracy is reported. Table 1.5.5 outlines the rules for undertaking calculations with data and its associated uncertainty.

Keep in mind that the rules for significant figures apply to all numerical reporting, including the uncertainties.

TABLE 1.5.5 Rules for calculations involving uncertainty

Calculation	Rule	Examples
addition and subtraction	add the uncertainties	$5.4 \pm 0.05 + 3.2 \pm 0.05 = 8.6 \pm 0.1$ $5.4 \pm 0.05 + 3.2 \pm 0.1 = 8.6 \pm 0.15$ $5.4 \pm 0.05 - 3.2 \pm 0.05 = 2.2 \pm 0.1$ $5.4 \pm 0.05 - 3.2 \pm 0.1 = 8.6 \pm 0.15$
multiplication and division	add the relative uncertainties	$3.0 \pm 0.05 \times 1.5 \pm 0.05$ $= 3.0 \pm 1.6\% \times 1.5 \pm 5\% = 4.5 \pm 6.6\%$ $3.0 \pm 0.05 \div 1.5 \pm 0.05$ $= 3.0 \pm 1.6\% \div 1.5 \pm 5\% = 2.0 \pm 6.6\%$
multiplying by a constant (absolute uncertainty)	multiple the uncertainty	$3.14 \times (4.1 \pm 0.05) = 12.9 \pm 0.16$
multiplying by a constant (relative uncertainty)	maintain the uncertainty	$3.14 \times (4.1 \pm 1.6\%) = 12.9 \pm 1.6\%$

Determining an uncertainty in a single measurement

When using an instrument to measure a property of an object, there will always be a limit as to how precise the reading can be.

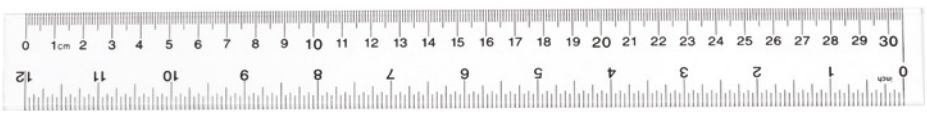
The precision that can be read off a single instrument is called the limit of reading. This is the smallest visible graduation on an analogue instrument, or, if a digital instrument is used, then the limit of reading is usually the smallest decimal place given on the screen.

For most analogue instruments, the absolute uncertainty, Δx, in a measurement of x is exactly half of the limit of reading for each part of the measured object that has to be lined up. This means that the actual measurement could be anywhere from *half* of the smallest graduation too big to *half* of the smallest graduation too small.

Some analogue instruments have a zero mark and a reading mark, such as a ruler shown in Figure 1.5.3a. The object to be measured has to be lined up at *both* ends, thus doubling the absolute uncertainty. For instance, when using rulers or burettes, the absolute uncertainty is equal to the limit of reading, rather than half of it.

In a digital instrument, Δx is typically the limit of reading, or the smallest decimal place given on the screen. An example of this is a high precision electronic balance as shown in Figure 1.5.3b.

a



b



FIGURE 1.5.3 (a) A ruler with a limit of reading of 1 millimetre, and (b) an electronic balance with a limit of reading of 0.001 g

For analogue instruments that have one scale to line up (such as a measuring cylinder, thermometer or voltmeter), the absolute uncertainty is half of the smallest graduation scale, or limit of reading.

For analogue instruments that have two scales to line up (such as rulers and burettes), the absolute uncertainty is equal to the smallest graduation scale, or limit of reading.

For digital instruments, the absolute uncertainty is equal to the smallest decimal place displayed.

Usually, the absolute uncertainty in a measurement will have 1 significant figure, or 2 significant figures if the first digit is 1. This is done because the uncertainty of a measurement is meant to be an estimate and writing more than 2 significant figures is therefore meaningless.

When the absolute uncertainty has been determined, the measurement should be rounded so that it and the absolute uncertainty have the same number of decimal places. This is to keep the measurement and its uncertainty to the same precision. Examples of measurements and their absolute uncertainties are shown in Table 1.5.6.

TABLE 1.5.6 Examples of writing a measurement and its absolute uncertainty

Measurement and absolute uncertainty	Comments
48.2 ± 1.0°C	The absolute uncertainty is written to 2 significant figures because the first digit is 1. The measurement and uncertainty have the same number of decimal places.
99.99 ± 0.01 s	The measurement and absolute uncertainty are written to 2 decimal places, with 1 significant figure for the uncertainty. This measurement of time may have been recorded using a digital device, such as a data logger, since the precision is quite high.
0.000000031 ± 0.000000005 kg	This is technically a correct way of writing a measurement and its absolute uncertainty, but it is normally written in scientific notation so that the measurement and uncertainty have the same power of 10, i.e. $(3.1 \pm 0.5) \times 10^{-8}$ kg

The limit of reading and absolute uncertainties of common equipment used in a chemistry laboratory are shown in Table 1.5.7.

TABLE 1.5.7 A summary of common instruments and their uncertainties

Instrument	Type of instrument	Limit of reading	Absolute uncertainty	Example	Notes
mm ruler	analogue	1 mm	± 1.0 mm	123.8 ± 1.0 mm	Half of the limit of reading is 0.50 mm, but since the object to be measured has to be lined up at both ends, the uncertainty is double this, or ±1.0 mm.
cm ruler	analogue	1 cm	± 1.0 cm	31.4 ± 1.0 cm	Half of the limit of reading is 0.50 cm, but since the object to be measured has to be lined up at both ends, the uncertainty is double this, or ±1.0 cm.
thermometer	analogue	1.0 °C	± 0.5 °C	24.4 ± 0.5 °C	Only the top part of the liquid in the thermometer has an uncertainty, so the uncertainty is exactly half of the limit of reading.
measuring cylinder	analogue	1.0 mL	± 0.5 mL	15.7 ± 0.5 mL	The limit of reading and absolute uncertainty depend on the size of the measuring cylinder.
burette	analogue	0.1 mL	± 0.1 mL	20.1 ± 0.1 mL	Half of the limit of reading is 0.05 mL, but since the object to be measured has to be lined up at both ends, the uncertainty is double this, or ±0.1 mL.
volumetric pipette	analogue		varies ± 0.03 mL	25.00 ± 0.03 mL	The uncertainty for the pipette is based on the precision given on the pipette. The precision varies based on the size and quality of the pipette.
stopwatch	digital	0.01 s	from ± 0.1 to ± 0.4 s	9.6 ± 0.2 s	The limit of reading is not the absolute uncertainty for a stopwatch because the user's reaction time (usually between 0.1 and 0.4 s) needs to be taken into consideration.
electronic balance	digital	typically 0.01 g	± 0.01 g	7.03 ± 0.01 g	Half the limit of reading is 0.005 g, but since the scales have to be read before and after putting the object on the scales the uncertainty is double this or ± 0.01 g.

These steps will help you write a measurement and its absolute uncertainty.

1 Determine the absolute uncertainty from the type of instrument used to measure the quantity.
2 Measure the quantity, including an estimate of the final significant figure.
3 If the first digit of the absolute uncertainty is 1, then one more significant figure can be quoted. Usually this extra digit is zero.
4 The measurement is then rounded up or down to the same number of decimal places, or place value holders, as the uncertainty; however, the uncertainty should not be presented to more than 2 significant figures.
5 Do not forget the unit of measurement for the quantity.

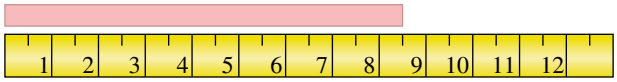
> The absolute uncertainty should be written to one or a maximum of 2 significant figures.

Worked example 1.5.5

READING MEASUREMENTS

For each of the following objects, determine its measurement and uncertainty.

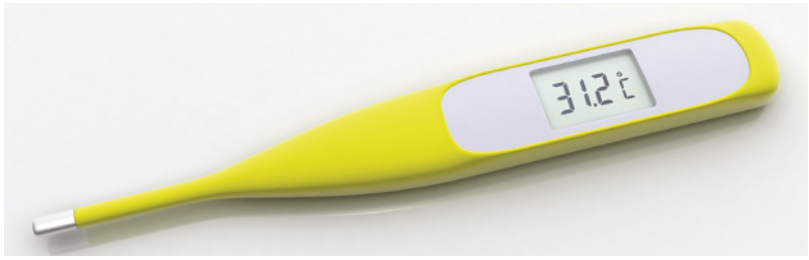
a the length of the pink rectangle measured with a ruler calibrated in centimetres



b the temperature of tap water measured using an analogue thermometer



c the temperature of tap water measured using a digital thermometer



Thinking	Working
a The pink rectangle is between 9 cm and 10 cm in length, so the best estimate for this is 9.6 cm.	length, L = 9.6 cm
The limit of reading is 1.0 cm, so this is the uncertainty in a centimetre ruler.	$\Delta L = \pm 1.0$ cm
Write the measurement and uncertainty.	length = 9.6 ± 1.0 cm

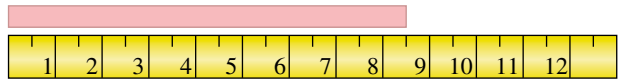
b	The temperature is between 23°C and 24°C, with the best estimate of 23.8°C.	temperature, T = 23.8°C
	The limit of reading is 1.0°C, so the uncertainty is half of this, i.e. 0.5°C.	ΔT = ±0.5°C
	Write the measurement and uncertainty.	temperature = 23.8 ± 0.5°C
c	This temperature measurement is done using a digital thermometer, so the temperature is simply read off the screen at 31.2°C.	temperature, T = 31.2°C
	The uncertainty in this measurement is then 1 of the smallest decimal value, i.e. ±0.1°C.	ΔT = ±0.1°C
	Write the measurement and uncertainty.	temperature = 31.2 ± 0.1°C

➤ Try yourself 1.5.5

READING MEASUREMENTS

For each of the following objects, determine its measurement and uncertainty.

a the length of the pink rectangle measured with a ruler calibrated in centimetres



b a red liquid in an analogue measuring cylinder



c the mass of a doughnut measured on an electronic scale



1.5 Review

SUMMARY

- Accuracy is the ability to obtain the correct measurement. To obtain accurate results, you must minimise systematic errors.
- Precision is the ability to consistently obtain the same measurement. To obtain precise results, you must minimise random errors.
- Uncertainty is a range of measurements from the experiment in which the true value is thought to be.
- Error is the difference between a measurement and the true value; this is *not* an indication of human error or a mistake.
- Uncertainty and error values are presented as a range (e.g. ±0.25).
- A simple way to calculate uncertainty is:

  $$\text{uncertainty} = \pm\frac{(\text{upper value} - \text{lowest value})}{2}$$

  A simple way to calculate the absolute uncertainty of a measurement is:

  $$\text{uncertainty} = \pm\frac{\text{smallest increment}}{2}$$

- The relative uncertainty can be calculated using this formula:

  $$\text{relative uncertainty} = \pm\left(\frac{\text{absolute uncertainty}}{\text{measurement}}\right) \times 100$$

- The rules for calculations involving uncertainty are listed in the following table.

Calculation	Rule
addition and subtraction	add the absolute uncertainties
multiplication and division	add the relative uncertainties
multiplying with a constant (absolute uncertainty)	multiple the uncertainty
multiplying with a constant (relative uncertainty)	maintain the uncertainty

- Significant figures are a way of communicating how precise a measurement is.
- The number of significant figures used depends on the scale of the instrument.
- There are specific rules governing how many significant figures there can be in any measurement.
  - All non-zero digits are significant.
  - All zeros between non-zero digits are significant.
  - Trailing zeros (either decimal or not) if measured are significant.
  - Leading zeros are not significant (in numbers with decimals, they only inform where the decimal is placed).
- All measurements made in chemistry experiments are subject to a level of uncertainty or doubt as to the precision of that measurement.
- A measurement without an uncertainty is meaningless.
- Accuracy is a description of how close a measurement is to an accepted value.
- Precision is a description of how many digits can be written down for a single measurement, or how close together a group of measurements are.
- Systematic errors arise due to mistakes in calibrating or using equipment the wrong way for every measurement.
- Random errors are naturally occurring and cannot be eliminated.
- The limit of reading of an instrument is the smallest graduation on the device.
- The absolute uncertainty of a measurement is determined by the limit of reading of an instrument.
- Uncertainties are typically written as an absolute value or percentage.
- Propagation of uncertainties involves the mathematical combination of uncertainties from a range of variables.
- When adding or subtracting measurements, the individual absolute uncertainties always add.
- When multiplying or dividing measurements, the individual percentage uncertainties always add.
- When raising a measurement to a power, the percentage uncertainty is multiplied by the absolute value of the power.
- When using measurements in a formula, perform any addition and subtraction propagations first, followed by multiplication, division and indices.

1.5 Review *continued*

KEY QUESTIONS

Retrieval

1 Describe how values of uncertainty and error are presented.

Comprehension

2 Explain the difference between accuracy and precision.

Analysis

3 Calculate the average and uncertainty of the following data.

a 11.4, 10.9, 11.8, 10.6, 11.5, 11.1

b 25.3, 27.4, 22.0, 26.1, 28.4, 23.1

4 Determine the absolute uncertainty of the following instruments.

a a cm ruler

b a burette graduated in 0.1 mL intervals

c an electronic balance giving a reading down to the nearest 0.001 g

1.6 Tables and graphs

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- create tables to record and organise data
- present data from tables into graphs
- distinguish between types of graphs
- select appropriate graphs to represent data
- represent missing data in graphs
- explain what an outlier is and know how to represent them in graphs.

PRESENTING DATA IN TABLES

Tables record number values and allow you to organise your data. In general, tables provide more detailed data than graphs, but it is easier to observe trends and patterns in data when they are in graph form than in table form.

Presenting raw data in tables

Tables organise data into rows and columns and can vary in complexity according to the nature of your data. Tables can be used to organise raw data and **processed data**, or to summarise results.

The simplest form of a table is a two-column chart. The first column should contain the independent variable (the one you control) and the second column should contain the dependent variable (the one that may change in response to a change in the independent variable).

As you can see in Figure 1.6.1, tables should have the following features:

- a descriptive title
- column headings (including the units)
- aligned figures (align the decimal points)
- the independent variable placed in the left column.

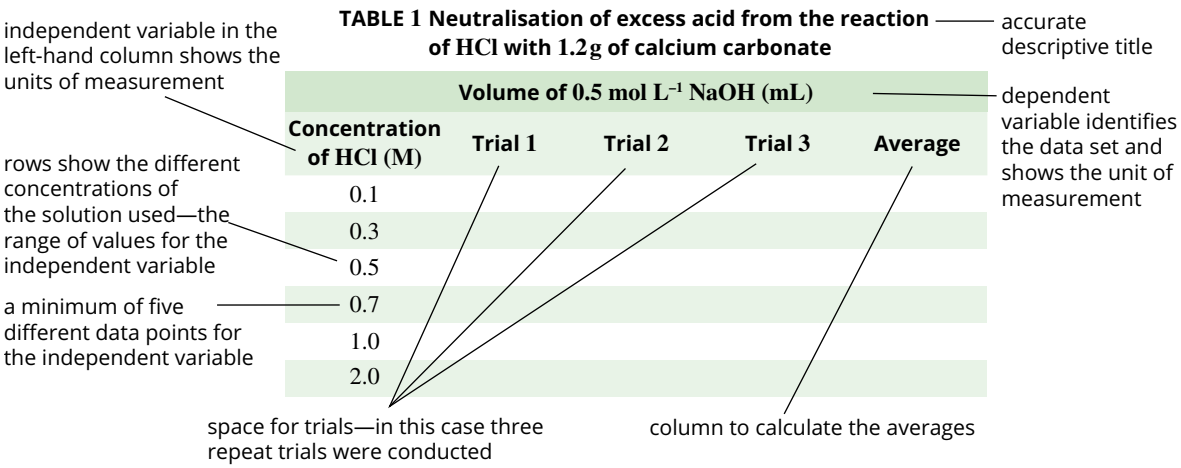


FIGURE 1.6.1 Features of a good table

Presenting processed data in tables

Table 1.6.1 shows the relationship between temperature and average reaction rate. It displays reaction rate data in a processed format, because it displays the mean of several values for each temperature. If uncertainty is to be calculated for processed data, then it has to be recorded with the raw data. To report processed data accurately the uncertainty is also displayed, which will be a requirement for assessments.

TABLE 1.6.1 Effect of temperature on mean reaction rate, including uncertainty

Temperature (°C)	Average reaction rate (mol dm^{-3} s^{-1})
15	0.038 ± 0.002
25	0.043 ± 0.001
35	0.059 ± 0.001
45	0.074 ± 0.0015

PRESENTING DATA IN GRAPHS

A **graph** is an incredibly useful tool. In chemistry, data is plotted using a line or curved graph and it is sometimes called a scatterplot. Plotting data in graphs has many advantages.

- Data can be represented visually.
- Data points that are incorrect can be ignored.
- Constants can be determined from the properties of the line or curve.
- Uncertainties can be represented as an **error bar**.
- A general **line of best fit** that matches the trend of the majority of the data points can be determined.
- Any known relationship between the dependent and independent variables can be supported or rejected, especially by the use of uncertainties.

Tables often provide more detailed data than graphs, but graphs can suggest a possible relationship between the dependent and independent variables and highlight if none exists. From the shape of the curve, it is easier to observe trends, patterns and gaps in data in graphical form than in tabular form.

Graphs, like the one shown in Figure 1.6.2, are used when two variables are being considered and one variable is dependent on the other. The graph shows the relationship between the variables.

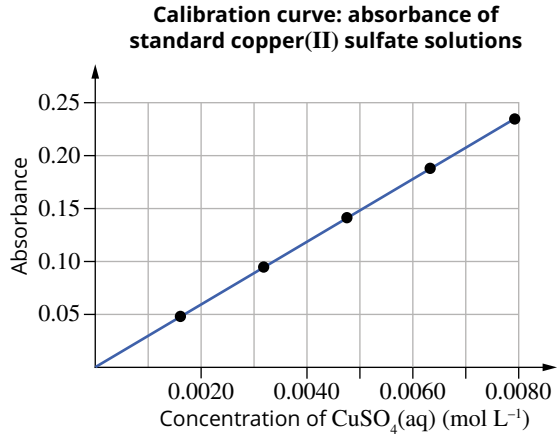


FIGURE 1.6.2 A graph showing the relationship between two variables: absorbance (dependent variable) and concentration of $CuSO_4(aq)$ (independent variable).

DRAWING GRAPHS IN CHEMISTRY

For use in chemistry, every graph must have the following features.

- The graph must have a suitable set of axes for the independent and dependent variables. Most chemistry graphs are only drawn in the first quadrant, but some graphs use all four quadrants (i.e. have negative values for the independent and dependent variables). Remember that:
  - the independent variable is the variable that you deliberately change and always goes along the *x*-axis
  - the dependent variable is the variable that changes because the independent variable was changed and always goes on the *y*-axis.

- The graph must have a suitable scale that allows information to be seen easily and quickly. For most graphs, it is important to choose a scale that is linear and has tick marks at common intervals (e.g. 2, 5, 10, 100 units).
- The graph must have a title and the axes must have labels. Make sure that the axis labels show information about the quantity and units. Give your graph a descriptive title that is not just a repeat of the labels of the axes.
- Data points should be plotted as a small circle or small cross indicating their position. Use different symbols for different sets of data.
- Error bars should be drawn for each point. These indicate the absolute uncertainties in the independent (a horizontal line) and dependent (a vertical line) values. They are drawn as a horizontal line centred on the data point indicating the independent variable's uncertainty left and right of the value and as a vertical line centred on the data point above and below the value, indicating the dependent variable's uncertainty. Combining the *x* and *y* error bars forms an error rectangle that the true measurement is located within (Figure 1.6.3). The smaller the error bar for a given point, the more precise the measurement is.

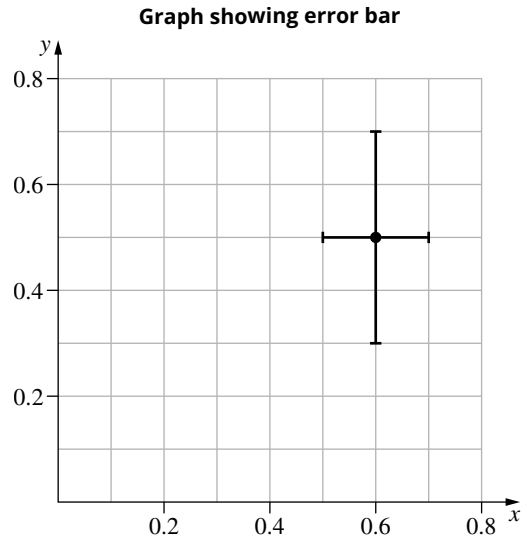


FIGURE 1.6.3 This error bar has an *x*-value of 0.6 ± 0.1 and a *y*-value of 0.5 ± 0.2.

Error bars are the graphical representation of the uncertainties in the independent and dependent variables.

The line of best fit

This is the straight line or a curve that best summarises the data. This line does not have to pass through every point nor the origin, but does have to be one smooth continuous line or curve and *not* a 'join the dots' line (Figure 1.6.4). Typically, the line of best fit should have as many points on the line as possible, but if this is not possible then it should have as many points above the line as there are below the line.

The line of best fit is a straight line or curved line that best summarises the general pattern of the data on the graph.

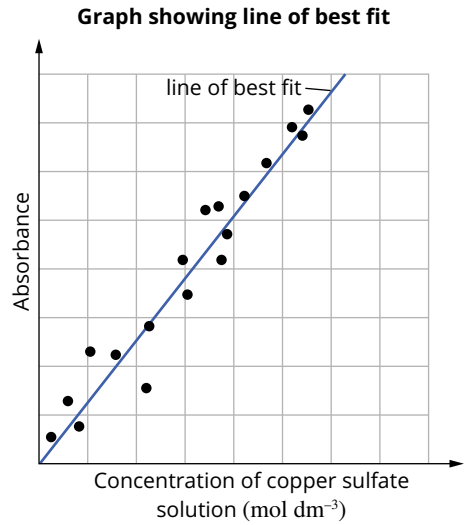


FIGURE 1.6.4 This graph shows that the line of best fit should normally pass through the error bars of each point and be extrapolated so that it intersects the *y*-axis.

TYPES OF GRAPHS SEEN IN CHEMISTRY

There are several types of graphs, including line graphs, bar graphs and pie charts. The best one to use will depend on the nature of the data. In chemistry, many relationships in the form of formulas and graphs are seen that exist between two variables. Each graph below shows some particular relationship between the independent and dependent variables that occur often in chemistry.

You will encounter all of these graphs at some stage during your chemistry course.

Scatterplots and line graphs

Scatterplots are commonly used to display data in the form of a graph and can be used to plot raw or processed data. They are used to show the relationship between two variables when one variable is dependent on the other.

The independent variable, which is set by the experimenter, is always shown on the *x*-axis. The dependent variable, which is the variable measured in the experiment, is always shown on the *y*-axis. The data is plotted on the graph as a series of points. Each point should be drawn in pencil as a small circle or cross. Alternatively, you can use a computer program to generate your graphs.

A **line graph** is a good way of representing continuous quantitative data. In a line graph, the values are plotted as a series of points on the graph. A line can then be drawn from each point to the next, as shown in Figure 1.6.5. This line shows the change in data from one point to the next but does not predict the value of a point between the plotted data.

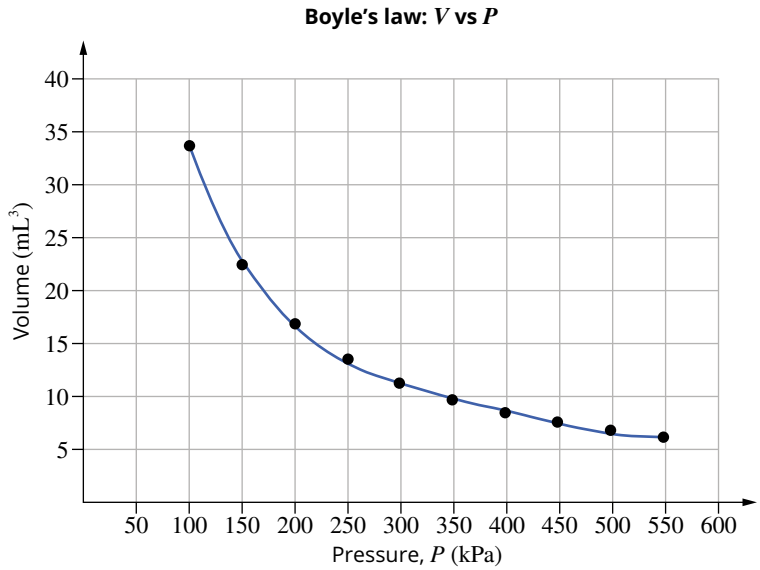


FIGURE 1.6.5 A line graph showing the change in volume of a gas in a syringe against the mass compressing the syringe

Alternatively, a single straight or curved line can be drawn, as shown in Figure 1.6.6, which is a **trend line**, or a line of best fit. It is used to show the overall trend in the data and can be used to predict values between the data points. A line of best fit usually does not pass through every data point. Its position can be estimated by eye (ensuring equal number of data points above and below the line when drawn) but mathematical or graphing programs can be used to determine the line of best fit more accurately. This will be covered in more detail in Module 1.7.

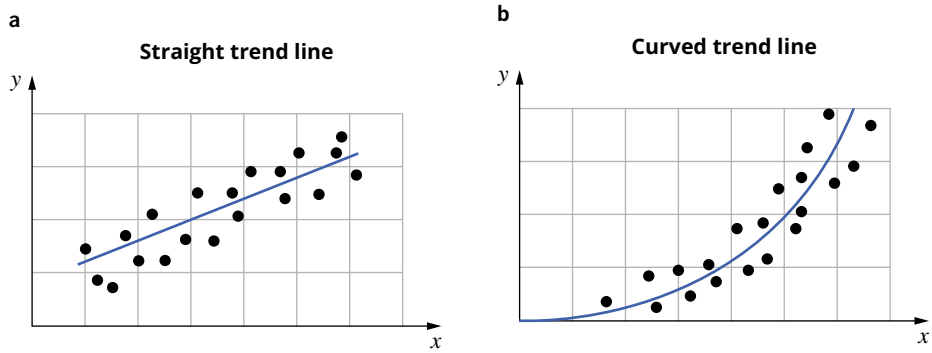


FIGURE 1.6.6 Scatterplots showing (a) straight and (b) curved trend lines

Bar and column graphs

Bar and column graphs are used to show categories and discrete (discontinuous) data.

- A **column graph** shows the value of the dependent variable by the height of the column; the categories are labelled across the *x*-axis.
- A **bar graph** shows the value of the dependent variable by the length of the horizontal bar; the categories are labelled up the *y*-axis.

Bar and column graphs are commonly used when the independent variable is categorical rather than numerical, or when the numerical data is discrete. The bars or columns are always the same width and the same distance apart.

Bar and column graphs are very useful for graphing qualitative and discrete data, such as the water quality data from various locations along a waterway (Figure 1.6.7).

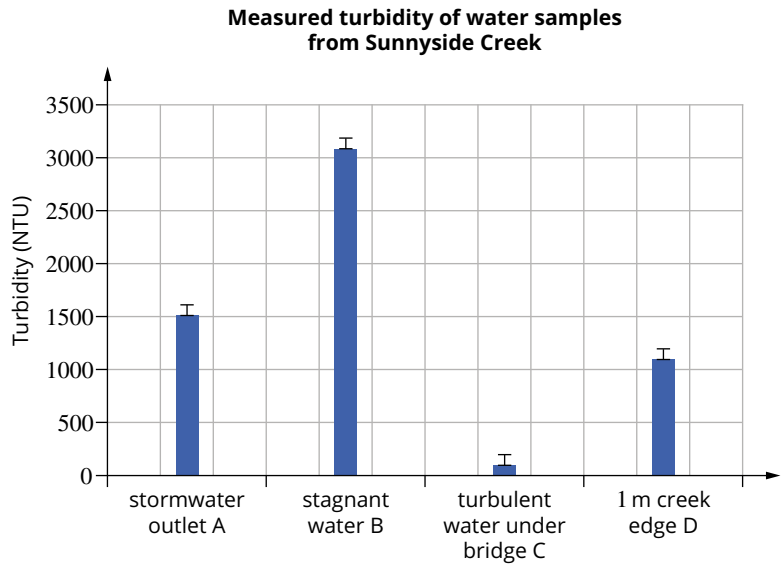


FIGURE 1.6.7 A bar graph can be used to compare data. This graph shows the measured turbidity of water samples taken from various locations along Sunnyside Creek.

Pie charts

A **pie chart** is a way of presenting qualitative or discrete quantitative data. It shows each category of data as a proportion of the total data. The chart is a circle divided into sections according to the proportions of each category, like slices of a pie (Figure 1.6.8). Each category is coloured or shaded differently so that it can be distinguished clearly from the other categories. It is recommended to use pie charts only when there are few categories.

A circle is equal to 360°. To draw a pie chart you must find how many degrees are needed for each category. This can be done as follows:

1. Add the amounts in each category to find the total.
2. Divide 360° by the total (this will tell you how many degrees of the circle one value is worth).
3. Multiply the answer by the amount in the first category. Your answer will be in degrees, which can then be marked for the first category using a protractor on the circle.
4. Repeat for each category.

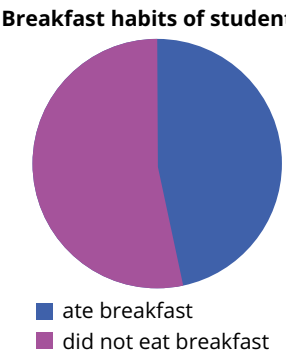


FIGURE 1.6.8 A pie chart presenting data on the breakfast habits of students

Missing data

When you have missing data, leave a gap for it, as shown in Figure 1.6.9. Ensure that the axes are complete (do not skip values), and do not join the data points that have missing data points between them.

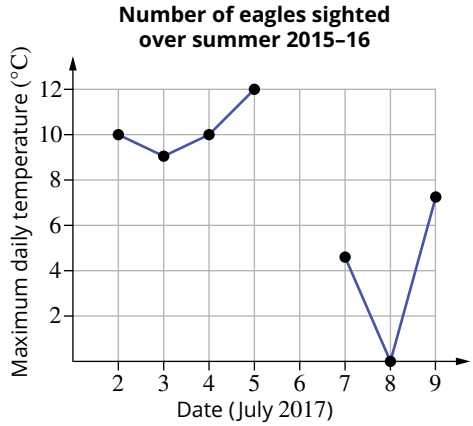


FIGURE 1.6.9 A line graph with data missing

Outliers

Sometimes when you collect data, there may be one point that does not fit the trend and may be an error. This is called an **outlier**. An outlier is often caused by a mistake made in measuring or recording data, or from a random error in the measuring equipment. This is covered in more detail later in this module. If you have an outlier in your results, you include it in your graph but ignore it when drawing the line of best fit, as in Figure 1.6.10 where the point (0.48, 0.08) is an outlier.

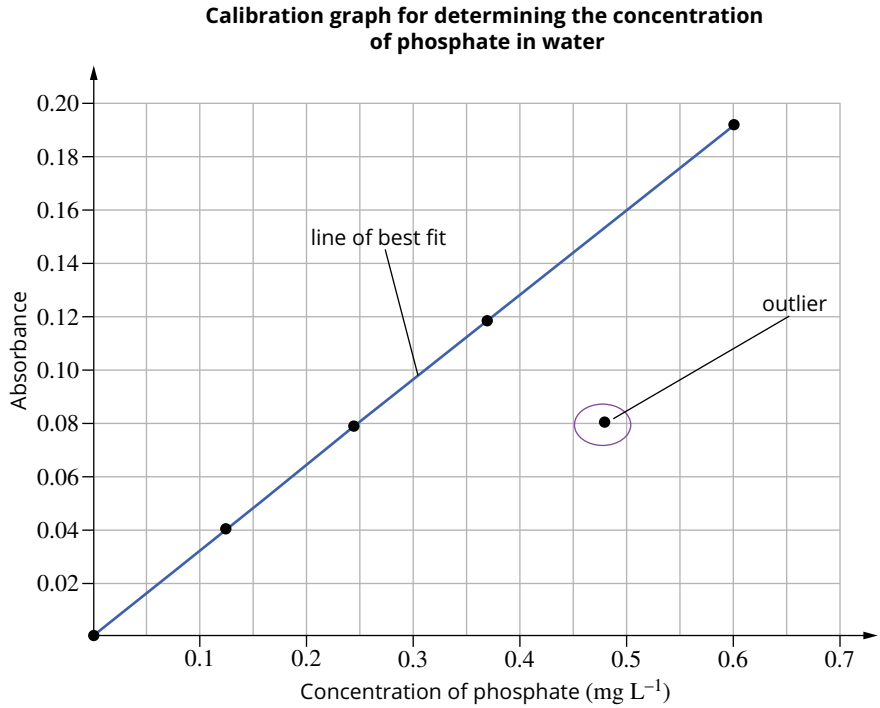


FIGURE 1.6.10 The graph is a calibration graph for determining the concentration of phosphate in water. A line graph shows an outlier, which has been ignored when adding the line of best fit.

Distorting the truth

Poorly constructed graphs can distort the truth. For example, in Figure 1.6.11 you can see two graphs that show the same data—the test results of two groups of students. One group of students did not eat breakfast before doing the test and scored an average of 42 marks out of 50. The other group of students did eat breakfast and scored an average of 48 marks out of 50. One graph distorts the difference in marks between the two groups by using a scale of only 40 to 50 marks on the *y*-axis. It is important to make sure the graphs you create do not distort your data. You should also be wary of distorted data when interpreting graphs in other publications.

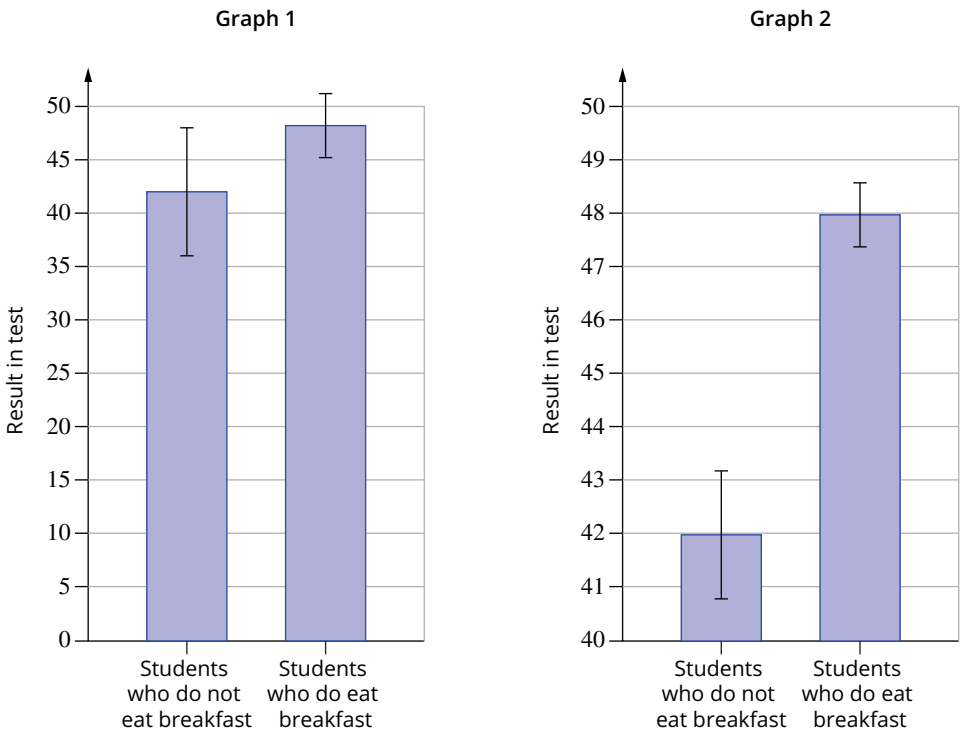


FIGURE 1.6.11 Graph 1 shows the difference between two groups of students out of the total 50 marks on the *y*-axis. Graph 2 shows the difference between the two groups within only a narrow range of marks on the *y*-axis, which distorts the difference and makes it appear larger than it really is.

1.6 Review

SUMMARY

- Tables and graphs are used to represent scientific data.
- In general, tables provide more detailed data than graphs, but it is easier to observe trends and patterns in data in graph form than in table form.
- Tables organise data into rows and columns and can vary in complexity according to the nature of your data.
- Tables should have the following features:
  - a descriptive title
  - column headings (including the units)
  - aligned figures (align the decimal points)
  - the independent variable placed in the left column
  - the dependent variable placed in the right column.
- Graphs are used to display relationships, trends and patterns between two variables with one proposed to be dependent on the other.
- There are several types of graphs, including line graphs, bar graphs and pie charts. The best one to use will depend on the nature of the data.
- Scatterplots are commonly used to display data in the form of a graph and can be used to plot raw or processed data.
- A trend line, or line of best fit, is used to show the overall trend in the data and can be used to predict values between the data points.
- A line graph is a good way of representing continuous quantitative data.
- Bar and column graphs are used to show categories and discrete (discontinuous) data.
  - A column graph shows the value of the dependent variable by the height of the column; the categories are labelled across the *x*-axis.
  - A bar graph shows the value of the dependent variable by the length of the horizontal bar; the categories are labelled up the *y*-axis.
- A pie chart is a way of presenting qualitative or discrete quantitative data.
- Missing data is represented in graphs by leaving a gap.
- An outlier is a data point that does not fit the trend and may be caused by an error.

KEY QUESTIONS

Retrieval

1 State the purpose of a trend line.

2 State the relationship that exists if one variable decreases as the other increases.

Comprehension

3 Explain what outliers are.

4 Describe the relationship between the variables indicated by a sloping linear graph.

5 Explain how the general pattern (trend) of a graph can be represented once the points are plotted.

6 Describe the relationship that exists if both variables increase or both decrease at the same rate.

Analysis

7 Antonia draws a straight line graph of data, including error bars, from an experiment she has just completed. She finds that it is not possible to draw a straight line of best fit through every error bar. Analyse the problem and advise Antonia on what to do.

8 If theory suggests that the *y*-intercept of a line is zero, deduce what this should look like on a linear graph.

9 Explain when it is more appropriate to use a graph showing a line of best fit rather than a ruled line graph joining the line from point to point.

10 Use the data below to draw a graph of the relationship between atmospheric pressure and altitude. Describe the trend and draw a line of best fit through the data.

Pressure (atm)	1.00	0.79	0.52	0.23	0.11	4.5×10^{-2}	1.3×10^{-2}	6.0×10^{-3}	2.1×10^{-3}
Altitude (km)	0	2.0	5.0	10.0	15.0	20.0	30.0	40.0	50.0

1.7 Statistics

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- calculate and interpret the range, mean, median and mode of a set of data
- evaluate the statistical significance of standard deviation
- use the R^2 values to evaluate the fit of a trend to a set of data.

One of the difficulties in chemistry is that direct measurements of phenomena, or measurements within a closed system, are challenging to obtain. Therefore, the limitations and uncertainty in the data include uncertainties in the accuracy and precision of the measurements that were recorded as well as errors related to reliability and validity of the experimental procedure. To address this problem, chemists perform statistical analysis to help understand the quality of the measurements, the results and their meaning.

This section will outline a basic understanding of common statistical analysis used in chemistry relevant to the QCAA Chemistry General Senior Syllabus.

STATISTICAL MEASURES

There are a number of common statistical measures that help describe data accurately.

Range

The range is the difference between the highest and lowest values in a data set. Table 1.7.1 shows the measurements taken for a reaction between sodium thiosulfate and sulfuric acid.

TABLE 1.7.1 Time for the cross to disappear in the reaction between sodium thiosulfate and sulfuric acid at 20°C and 50°C

Temperature	1	2	3	4	5	Mean	Range
20°C	253	158	201	169	187	187.6	253 – 158 = 95
50°C	69	85	70	91	75	78	91 – 69 = 22

To determine the range for values in Table 1.7.1, you would subtract the smallest value from the largest value. Notice how an abnormally large or abnormally small value in the data set makes the variability appear high. If one value appears way out of range, such as the time taken for the cross to disappear the first time the reaction was performed at 20°C, it may be an outlier. This illustrates the importance of observation during experiments and recording all details in a journal as experimentation and research is conducted.

The experiment was conducted with a smaller number of measurements taken at each temperature and the results are shown in Table 1.7.2.

TABLE 1.7.2 Time for the cross to disappear in the reaction between sodium thiosulfate and sulfuric acid at 20°C and 50°C

Temperature	1	2	3	Mean	Range
20°C	253	158	201	194	253 – 158 = 95
50°C	69	85	70	75	85 – 69 = 16

Even though the range has not changed much between Tables 1.7.1 and 1.7.2, the results at 20°C seem more random. In Table 1.7.2 at 50°C, the second reaction could be an outlier as the other two results show excellent agreement. The range simply outlines the total variation in measured results; no other analysis or interpretation can be achieved.

A larger **sample size** will strengthen the **validity** of the range as described above with results that may be errors.

Measures of central tendency

Measures of central tendency are single values that allow you to describe the central position in a set of data. Measures of central tendency are sometimes also called measures of central location. The mean, median and mode are all measures of central tendency.

Consider the following data set: 3, 5, 7, 8, 8, 8, 10.

- The mean (or average) is the sum of the values divided by the number of values, which in this case is (3 + 5 + 7 + 8 + 8 + 8 + 10) ÷ 7 = 7.

$$\text{mean} = \frac{\sum(x_1 + x_2 + x_3 + \ldots)}{n}$$

where Σ = sum of

$x_1 + x_2 + x_3$ = measurement$_1$ + measurement$_2$ + measurement$_3$

n = total number of measurements

- The **median** is the 'middle' value in an ordered list of values, which in this case is the fourth value, which is 8.
- The **mode** is the value that occurs most often in a list of values, which in this case is 8. This measure is particularly useful for describing qualitative or discrete data.

The appropriate measure of central tendency to use depends on the type of data you are working with (Table 1.7.3).

TABLE 1.7.3 When to use the different measures of central tendency

Type of data	Mean	Median	Mode
nominal (qualitative)	✓	✗	✗
ordinal (qualitative)	✓	✓	maybe
discrete or continuous (quantitative)	✓	✓	✓

Graphically representing data using central tendency provides a clear and succinct display of results. As there are many measured values and results in raw data, it can be difficult to analyse and interpret. It is much easier and less complicated to analyse and interpret processed data compared to raw data. Raw data includes all the measured results and usually a large number of measurements or observations. Processed data is usually a smaller number of results that represent all the measured raw data. These representative results are calculated using statistical methods such as mean, median and mode. Therefore, an analysis can be conducted to compare results using three results (e.g. three means) rather than nine results (e.g. nine individual measurements in the raw data). Interpreting a relationship is also much easier and less complicated when using fewer numbers. It is important to realise that statistical calculations do not produce the true value, rather a single value (or smaller number of values) that is meant to represent many.

Analyse the mass of two alcohols burnt in a calorimetry experiment, shown in Table 1.7.4. The average has been calculated for each alcohol; however, you will notice that the mean value was not measured during the experiment and is not in the raw data.

TABLE 1.7.4 Mass of ethanol and hexanol burnt

Ethanol (l)	Hexanol (l)
0.77 0.78 0.72 0.73 0.76 0.74	1.60 1.82 1.67 1.72 1.71 1.80
mean 0.75	mean 1.72

Standard deviation

Standard deviation specifically estimates the spread of data in a population or set of values. It calculates the spread or dispersion of data and its distance from the mean.

The standard deviation statistical calculation assumes that the data being used is from a set in which a normal curve (or normal distribution) exists. A normal distribution of data forms a 'bell' curve or a normal curve as seen in Figure 1.7.1.

A normal curve on a graph has a characteristic distribution of data.

- Approximately 68.2% of all the data lies within 1 standard deviation (1σ) of the mean. That is, 34.1% of data lies above the mean and 34.1% below the mean.
- Approximately 27.2% of all the data lies between the 1st and 2nd standard deviation (between 1σ and 2σ). That is, 13.6% of data lies above 1σ and 13.6% below 1σ.
- Approximately 4.2% of all data lies between the 2nd and 3rd standard deviation (between 2σ and 3σ). That is, 2.1% of data lies above 2σ and 2.1% below 2σ.
- The final 0.2% of data lies above and below 3σ, 0.1% on either side.

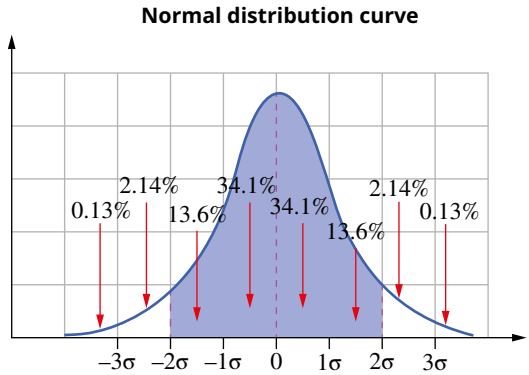


FIGURE 1.7.1 Normal distribution curve showing how far each standard deviation (σ) is from the mean (0)

When using standard deviation to analyse data, it is important to understand what has been calculated. If a measured phenomenon is expected to be equivalent from one test to another, then it would be expected that all measurements would be very close to the mean, except for unusual results like an error. You could decide that all accurate measurements should be within two standard deviations (2σ) of the mean. Therefore, any measurement outside (greater than) 2σ from the mean would be considered as an outlier (measurements that have a value outside of the expected calculation).

If standard deviation was used for a set of data in which variation is expected, it could be used to demonstrate the variation. For example, according to the Australian Bureau of Statistics, the average height of an adult female in Australia is 161.8 cm. If the height of all the female students in the chemistry class were measured with the following results (Table 1.7.5), you could use standard deviation to estimate where individuals fit into the assumed normal curve for the height of adult females in Australia.

Using the formula to calculate standard deviation:

$$\text{SD} = \sqrt{\frac{\sum(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + (x_3 - \bar{x})^2}{n-1}}$$

$\sum$ = sum of

x_1 = first measurement

$\bar{x}$ = mean

$n - 1$ = number of measurements − 1

The standard deviation for the set of data is ± 8.5 cm. Student 4 at 180.6 cm is more than 2σ away from the mean, therefore it can be said that this student is estimated to be in the top 3% of the adult female population for height. This is not an outlier because variation is expected, so standard deviation was used to understand the variance of female students in the class.

TABLE 1.7.5 Height of female students in the chemistry class

Sample	Height (cm)
student 1	164.5
student 2	156.7
student 3	172.2
student 4	180.6
student 5	163.4
student 6	158.8
student 7	153.9
student 8	150.7
student 9	160.4
student 10	156.8
mean	161.8

REGRESSION

Regression is the term used to state that the independent variable causes the result in the dependent variable during a scientific investigation. Some relationships between variables are causal, meaning that there is a cause and effect relationship. The independent variable is the cause and the change dependent variable is the effect.

There are numerous statistical calculations that estimate the causal relationship between variables; some calculations provide a value that indicates how directly an independent variable causes the dependent variable result. This attempts to show the strength of the relationship, to identify if the change in the dependent variable is entirely due to the independent variable.

In chemistry, not all relationships are direct or straightforward cause and effect. Often there are many variables that influence the dependent variable and it is helpful to try and predict how much of an effect the independent has on the dependent, while other variables are also influential.

Coefficient of determination (R^2)

The **coefficient of determination** (R^2) can calculate a value that indicates the predictability between the variables based on how much the results vary. The coefficient of determination produces a value that is an estimate as to how well you can predict the dependent variable based on the independent variable considering the variations in the results. In the examples in Figure 1.7.2, the data of group 1 does not follow the linear trend line exactly, and therefore as the concentration intensity changes (the independent variable), the absorbance (dependent variable) does not always change consistently. Sometimes it changes by 5, sometimes by 2 or even by 10 or more. The coefficient of determination (R^2) is a calculation that considers the variation in the results to estimate the predictability.

For example, a laboratory has used two different analytical techniques to determine the concentration of a performance-enhancing drug in a blood sample from an athlete suspected of cheating. The calibration curves for each technique and the R^2 value for each are shown in Figure 1.7.2.

Based on the lines of best fit and R^2 values, the second method was chosen to analyse the athlete's blood sample.

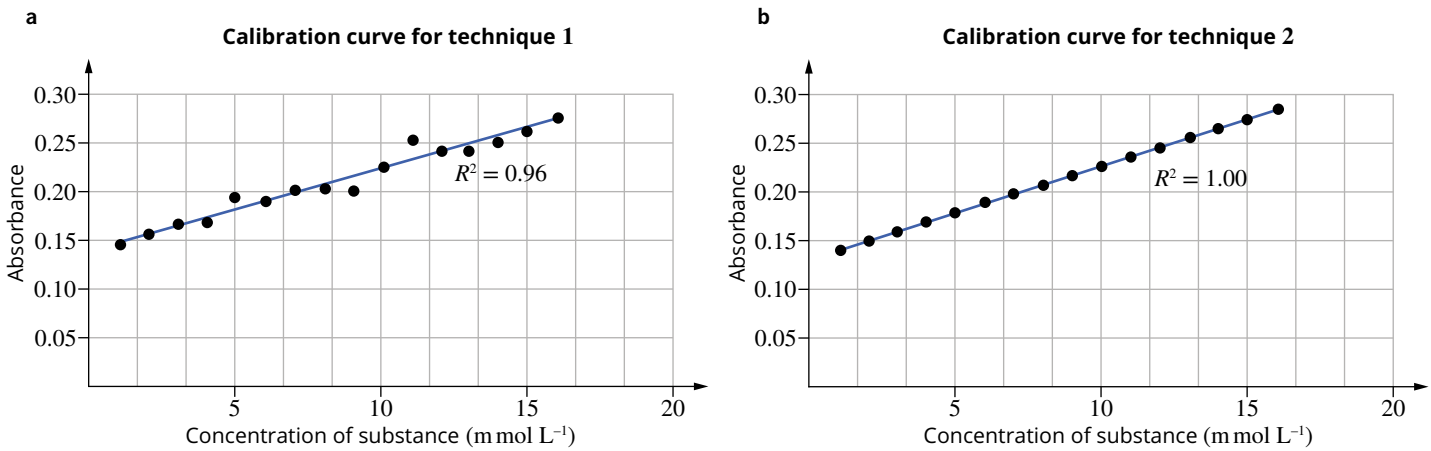


FIGURE 1.7.2 (a) The calibration curve for technique 1: linear regression was used to establish a line of best fit. (b) The calibration curve for technique 2: linear regression was used to establish a line of best fit.

Even though both techniques measured the same samples, the data is different. As can be seen in the graphs, the linear trend line is very similar with a similar slope; however, technique 1 has an R^2 value of 0.96 and technique 2 has an R^2 value of 1.00.

The coefficient of determination produces a value between 0 and 1. If the value is 0, it is unable to predict the change in the dependent variable from the independent variable due to so much variation in the results. If the value is 1, then it can predict the change in the dependent variable 100% of the time without error. Any other number between 0 and 1 is considered a percentage; for example 0.76 means that the coefficient of determination can predict 76% of the dependent variable results due to the independent variable. It is interpreted as 76% of the variation in the dependent variable can be explained by the independent variable.

In Figure 1.7.2b, the absorbance of the sample was perfectly correlated without error with the concentration of the species. This suggests that the results from technique 2, including error, **bias** and instrumental precision, are highly reliable.

Figure 1.7.2a shows that the absorbance of the sample was not precisely correlated with the concentration. The R^2 value for technique 1 is lower than the R^2 value for the data from technique 2, meaning the results are less predictable due to more variation. Technique 1 was less precise compared to technique 2; therefore, technique 2 is the preferred technique to determine the concentration in the actual sample.

1.7 Review

SUMMARY

- The range is the difference between the highest and lowest values in a data set.
- The mean, $\bar{x}$, is the average of a data set. It is calculated using the formula:
  $\bar{x} = \frac{\sum x_1 + x_2 + x_3 \ldots}{n}$, where
  $\sum$ = sum of $x_1 + x_2 + x_3$
  = measurement$_1$ + measurement$_2$ + measurement$_3$
  n = total number of measurements.
- The median is the 'middle' value in an ordered list of values.
- The mode is the value that occurs most often in a data set. The mode is particularly useful for describing qualitative or discrete data.
- Standard deviation is a measure of the spread or dispersion of data from the mean.
- Regression is the term used to state that the independent variable causes the result in the dependent variable during an experiment.
- Linear regression is a calculation that estimates a direct linear relationship between the independent and dependent variables.
- The coefficient of determination estimates how well you can predict the dependent variable based on the change in the independent variable.
- The coefficient of determination produces an R^2 value between 0 and 1.
  - The closer R^2 is to 0 the less predictable the dependent result is based on the independent value.
  - The closer the R^2 is to 1 the more predictable the dependent result is based on the independent value.

KEY QUESTIONS

Retrieval

1 Define the terms 'mean', 'median' and 'mode'.

Comprehension

2 Describe what the standard deviation informs scientists about in the data set.

Analysis

3 For the data set {21, 28, 19, 19, 25, 24, 20}, calculate the:
- **a** range
- **b** median
- **c** mode
- **d** mean
- **e** standard deviation.

4 Determine which statistical measurement—mean, mode or median—is generally most affected by an outlier.

PART B STUDENT EXPERIMENT (IA2)

The QCAA stipulates that you complete the Student experiment (IA2) in Unit 3.

The student experiment requires you to research a question or **hypothesis**. You will use research conventions to investigate the question or hypothesis by collecting and analysing primary data to draw conclusions about your research question and critically appraise your methodology. The experiment requires you to locate and use information beyond the scope of your knowledge and what you have been given in class. The student experiment requires you to undertake the full scientific method.

The QCAA Chemistry General Senior Syllabus states that this process begins with a practical conducted during class (either a mandatory or suggested practical). This in-class practical will be altered to conduct your own experiment. It is recommended that during the class practical you record your observations, queries and thoughts in a logbook. These notes can then be used to formulate a research question for the student experiment.

The student experiment constitutes 20% of the total assessment in chemistry.

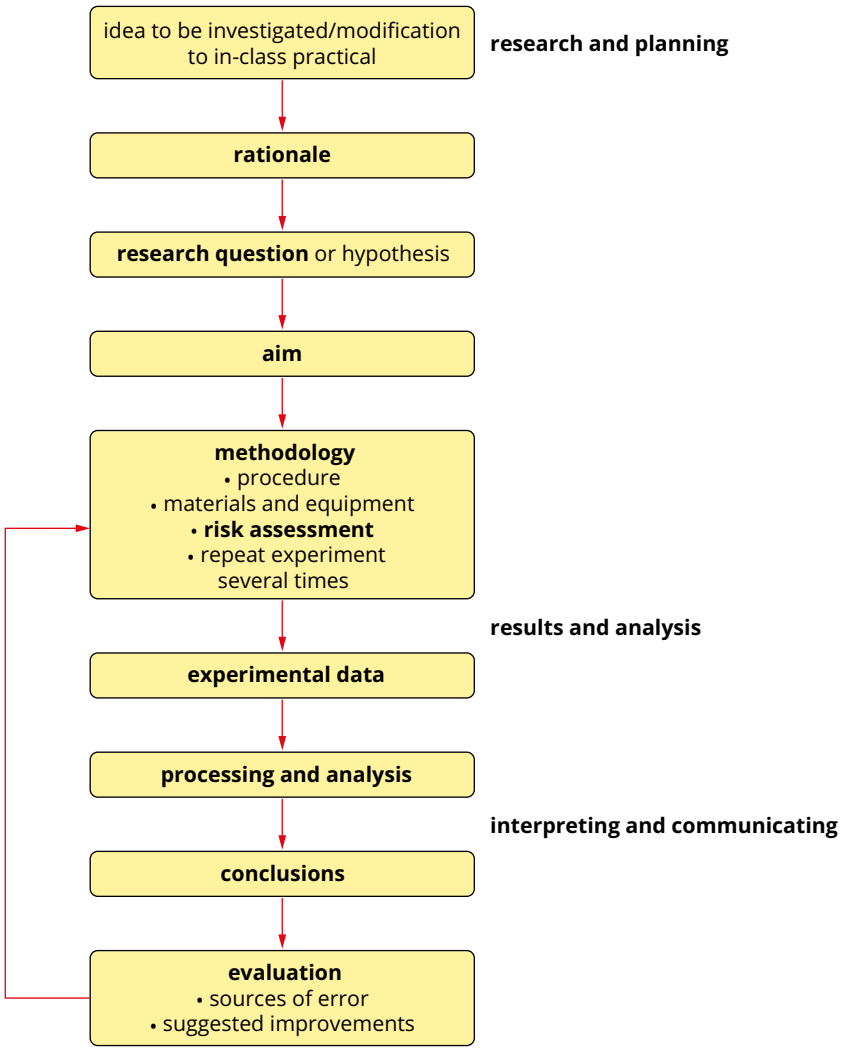
The student experiment may be presented in:

- written form (e.g. scientific report), 1500–2000 words, or
- multimodal form (e.g. poster presentation), 9–11 minutes.

A summary of the instrument-specific marking guide (ISMG) for the student experiment is provided below. It includes the objectives and marking for this summative internal assessment.

Criteria	Assessment objectives	Demonstrated by	Marks
Research and planning	• apply understanding • investigate	• a considered rationale for the experiment • justification for the changes made to the original experiment • a research question that is specific and relevant • collected data that is sufficient and relevant • consideration of risks and issues (ethical and environmental) and their management	6
Analysis of evidence	• apply understanding • analyse evidence • investigate through experimentation	• use of relevant algorithms and correct data processing • detailed and careful coverage of relevant trends, patterns and relationships in the evidence • detailed and careful coverage of uncertainty and limitations of the evidence • collection of sufficient and relevant raw data	6
Interpretation and evaluation	• interpret experiment evidence • evaluate experimental processes and conclusions	• a conclusion that is justified and addresses the research question • a discussion about the reliability and validity of the experiment that is supported by evidence • providing possible improvements and extensions to the experiment based on examination of evidence	6
Communication	• present the experiment's findings, including methodology, conclusions and evaluation	• scientific language and representations that are concise and fluent • suitable use of genre conventions • appropriate referencing conventions to acknowledge sources.	2
Total			20

The scientific inquiry is not a linear process. Scientists will not necessarily complete these steps in the stated order and some steps may need to be repeated or altered in order to more accurately address the research question, as demonstrated below.



Note that although protocol dictates that a scientific report should include an aim, for the purposes of the student experiment the inclusion of an aim will not be awarded any marks and inclusion will count against the assessment piece word count.

INSTRUMENT-SPECIFIC MARKING GUIDE

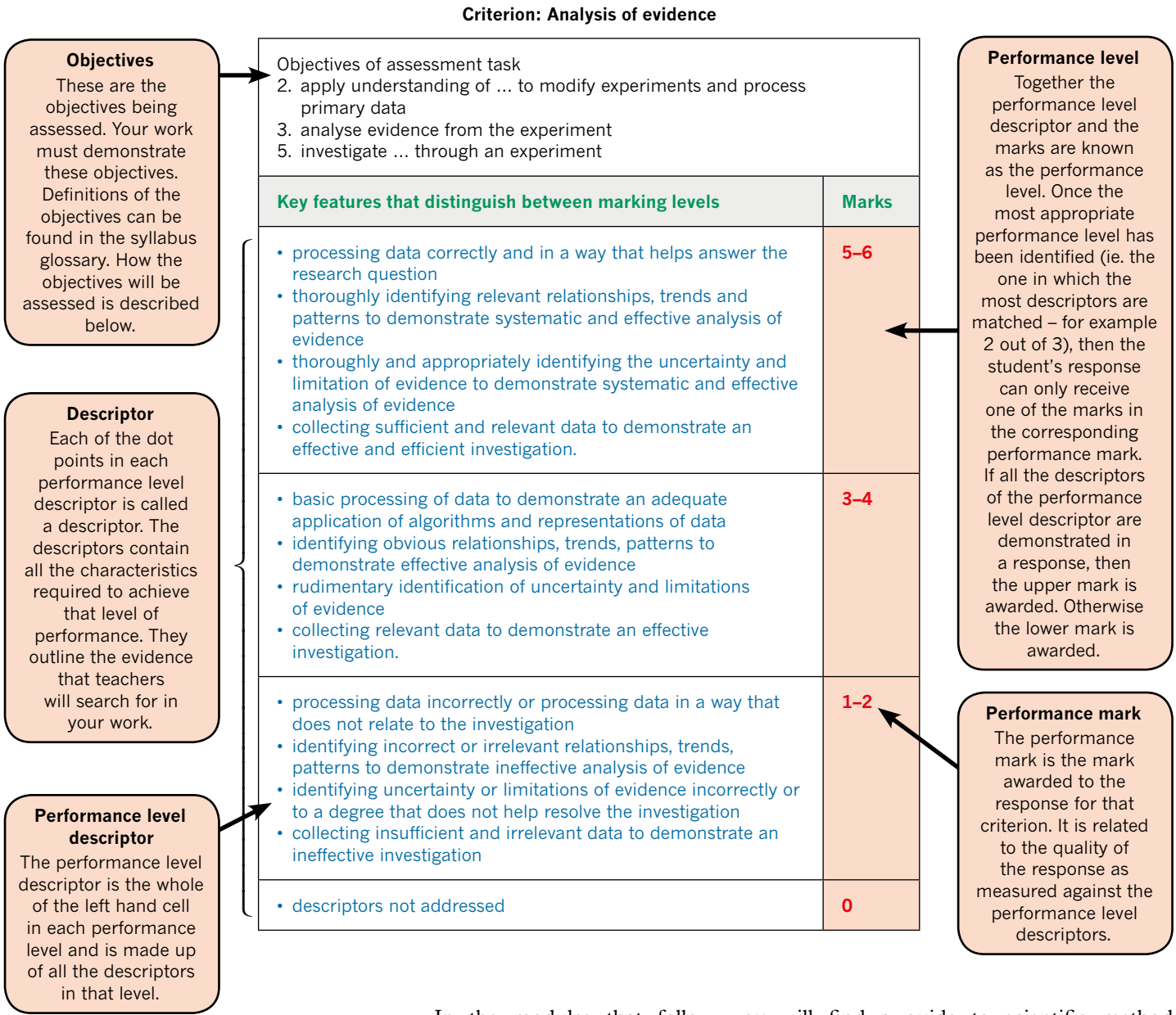
Student responses are assessed against an instrument-specific marking guide (ISMG). In developing your experiment and planning your response it is important to always have in mind the assessment objectives and in particular the characteristics that are described in the performance level descriptors.

The major features of the ISMG are outlined below and shown for the Analysis of evidence criterion.

- The ISMG has four criteria: research and planning, analysis of evidence, interpretation and evaluation and communication.
- Criteria are differentiated into performance levels, against which the qualities of the response are assessed.
- A performance level comprises a performance level mark, which may be a single mark or two-mark range, and a performance level descriptor.
- The performance level descriptor describes the characteristics that are demonstrated by a response at this quality.

The QCAA criterion 'Analysis of evidence' stipulates the characteristics of the top performance level. The interpretation of these characteristics is shown in the following figure.

In order to be awarded a mark of 5 or 6 for this criterion, you need to show a thorough, thoughtful and comprehensive engagement with the task. For example, appropriately applying algorithms and representations of data through correct and relevant data processing is working at the highest performance level. However, showing adequate application and basic data processing is working in the lower performance level. If the application is rudimentary and data is incorrect or irrelevant, the performance level will be lower again.



In the modules that follow, you will find a guide to scientific method (Modules 1.8–1.10), followed by an outline for producing a **scientific report** (Module 1.11).

TYPES OF INVESTIGATIONS

There are many different types of investigations that can be conducted in chemistry. You are probably most familiar with practical investigations or experiments. Other types of investigations involve researching and evaluating primary and/or secondary sources of information to answer a question. Examples of the types of different investigations are listed in the two tables below.

Examples of primary research	Example tasks
conducting experiments in a laboratory	• planning a valid experiment • conducting a risk assessment • working safely • recording observations and results • analysing and evaluating data and information
conducting field work	• conducting a risk assessment • working safely • recording observations and results • analysing and evaluating data and information
conducting surveys	• writing questions • collecting data • analysing data and information
designing a model	• identifying a problem to be modelled • summarising key findings • identifying advantages and limitations of the model

Examples of secondary research	Example tasks
researching published data from primary and secondary sources	• finding published information in scientific magazines and journals, books, databases, media texts, labels of commercially available products • analysing and evaluating data and information

Before you are able to start the practical side of your investigation, you first need to understand the theory behind it. This module is a guide to some of the key steps that should be taken when first developing your research questions and hypotheses.

Taking the time to carefully plan and design a practical investigation before you begin will help you to maintain a clear and concise focus throughout. Preparation is essential. It is important to have both a solid understanding of the theory behind your investigation and a detailed plan for the practical components of your investigation. In the following module, you will learn about the key steps you should take when planning and designing a practical investigation.

1.8 Research and planning

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- identify and explain the difference between controlled, measured, independent and dependent variables
- develop a research question
- evaluate research questions
- use a scientific journal to record experiments and experimental data
- plan, evaluate and refine scientific experiments
- explain what validity and reliability mean in relation to experimentation
- explain the difference between, and identify, qualitative and quantitative data
- characterise qualitative data as either nominal or ordinal
- characterise quantitative data as either discrete or continuous
- explain the difference between replication and repeat trials
- conduct risk assessments for planned experiments
- recognise common chemical GHS codes and symbols
- understand the criteria against which research and planning will be assessed.

All scientific work begins with research and planning. To conduct an experiment, as much as possible must be known about the relationship between variables. This includes understanding the relationship between controlled or measured variables as well as the independent and dependent variables. If variables are not controlled appropriately then errors and unknown quantities will influence the results. Furthermore, relationships cannot be established or observed and the experiment becomes invalid or unreliable (or both). Research and planning is the foundation of the scientific method and is always recorded in a journal.

The scientific method is non-linear and scientists should always return to previous stages of the method with new ideas or knowledge. Keeping a journal will show a chronological record of ideas, development of knowledge and understanding, and planning and refinement. Even though your journal will be in chronological order it most likely will not be entirely in a conceptually logical order. Your journal is an important ongoing draft of scientific work from which your final scientific report is written.

IDENTIFY AN EXPERIMENT AND DEVELOP A RESEARCH QUESTION

The student experiment requires you to **modify**, **refine**, **extend** or **redirect** a practical undertaken in class. Therefore, the experiment will be similar to the class practical with an alteration to investigate something slightly different, as shown in Figure 1.8.1.

Identify an experiment

When choosing a topic or observation to modify, consider the following.

- Select a topic or observation of which you already have some knowledge or understanding, or some idea about how to perform the experiment.
- Choose a topic or observation that you find interesting.

- Check that your school laboratory has the resources for you to perform the experiment or investigate the topic.
- Choose a topic that can provide clear measurable data that shows how variable y depends on variable x.

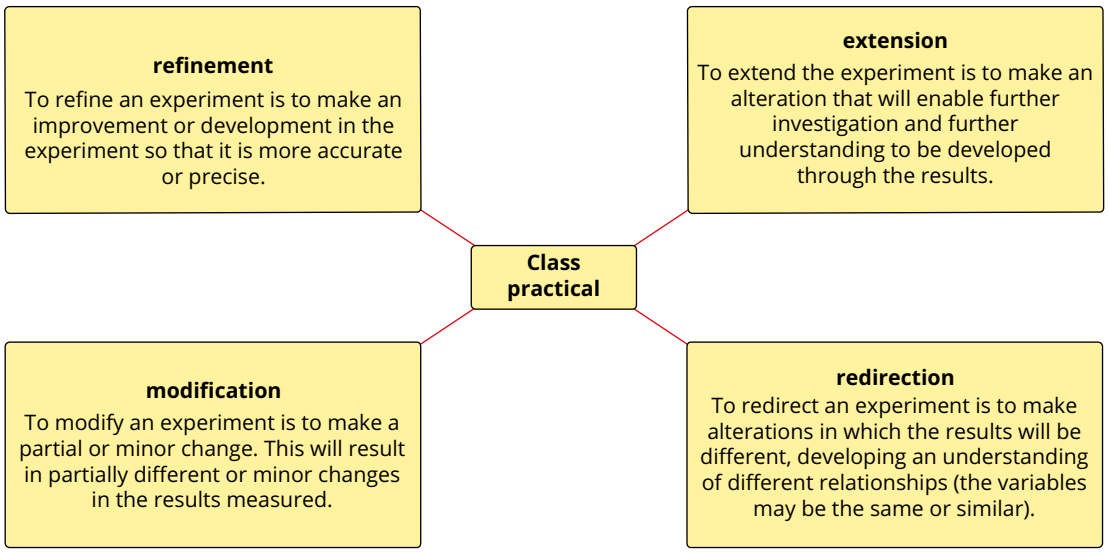


FIGURE 1.8.1 Chart showing possible changes to a class practical when developing a student experiment

Table 1.8.1 shows examples of modifying, refining, extending or redirecting practicals into a topic of interest for a student experiment.

TABLE 1.8.1 Examples for changing a practical into a student experiment

Practical	Modification, refinement, extension or redirection	Student experiment
Investigate factors that affect equilibrium.	modification and refinement	How does changing the concentration of the nitrogen dioxide affect the equilibrium position with dinitrogen tetroxide?
Investigate the electrical conductivity of strong and weak acids.	modification and refinement	How does changing the temperature of the solution affect the electrical conductivity of a 1.0 mol L^{-1} acetic acid solution?
Construct a typical galvanic cell using two metal/metal-ion half-cells.	extension	Does using a zinc electrode with a greater surface area increase the power supplied?
Carry out electrolysis of copper sulfate.	extension	How does the rate of electrolysis change because of temperature?

A justification of the alteration to the methodology of the student experiment is required by the QCAA Chemistry General Senior Syllabus. This is addressed in this module.

When altering the class practical to identify a student experiment, it is best to think of a single variable that may influence the outcome (independent variable). This may require some research. The more variables that are altered (including measured and controlled variables), the more research that is required and the more complex the task becomes. Note that some alterations of variables may require the alteration of other variables.

If only one variable is changed (the independent variable) then the class practical can be used as the control and the data collected can be used to compare results. The student experiment will need to determine its own control.

Defining the variables

The factors that can change during your experiment or investigation are called the variables. An experiment or investigation determines the relationship between variables, measuring the results. There are four categories of variables (Figure 1.8.2). You should have only one independent variable. Otherwise you could not be sure which independent variable was responsible for changes in the dependent variable (the results). If both the independent and dependent variables are altered then the data between the class practical and student experiment is not comparable.

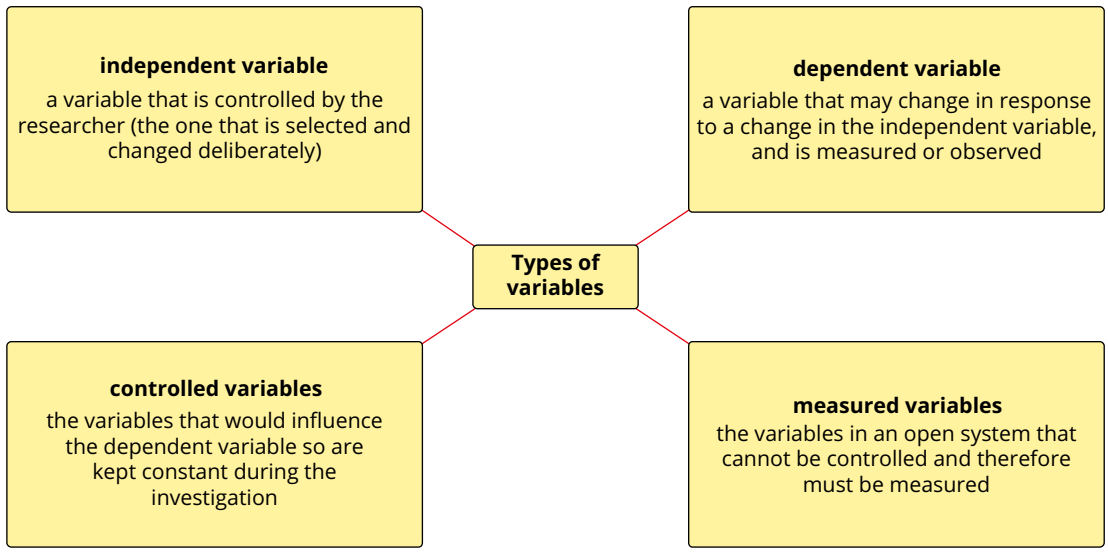


FIGURE 1.8.2 The four types of variables in experiments

Developing a research question

A research question is defined as a question that directs the scientific inquiry activity. Its purpose is to focus the research investigation or student experiment, inform the direction of the research, and guide all stages of inquiry, analysis, interpretation and evaluation.

The research question determines the experiment and the experiment is testing the question. A research question should:

- be specific and relevant to the class practical
- clearly identify the subject matter of the experiment
- specify the scope or conditions of the inquiry
- aim to find trends or patterns of relationships between two variables.

Consider the example in Figure 1.8.3.

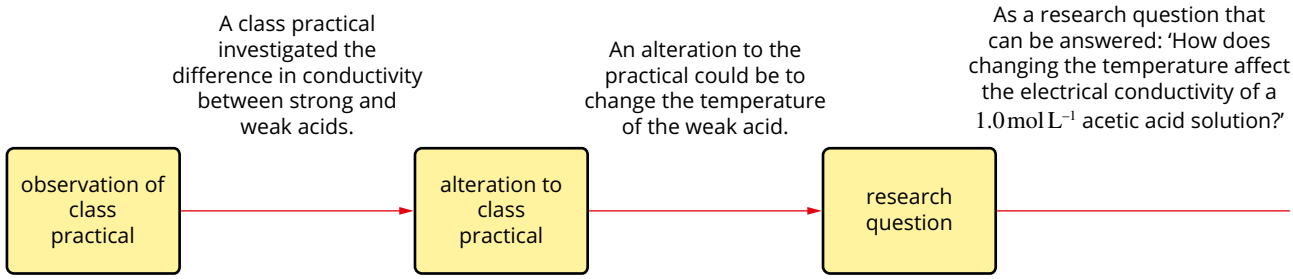


FIGURE 1.8.3 The process from class observation of a practical, to altering the practical and developing a possible research question

Background research for the student experiment would follow to refine the research question. The research could include:

- information about the variables
- correlations between variables
- ideas for refining the research question—do not reject ideas that might seem improbable at this stage.

Figure 1.8.4 demonstrates the process of question refinement and the resultant research question that will guide the student experiment.

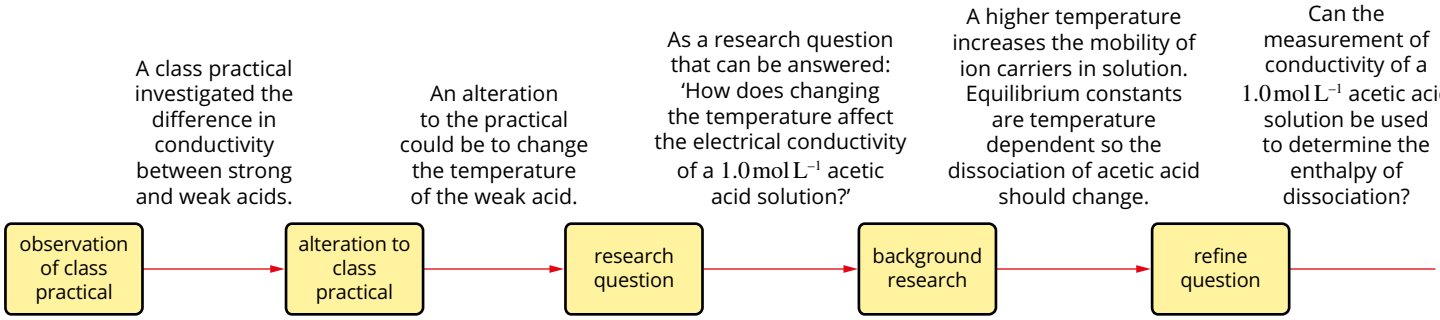


FIGURE 1.8.4 The process of refinement of the research question

The structure of a research question

All research questions should state the independent and the dependent variables. It should ask if the independent variable will affect the dependent variable. The research question must specifically outline variables in a way that is measurable; this also allows the question to be answered. See Figure 1.8.5 for example.

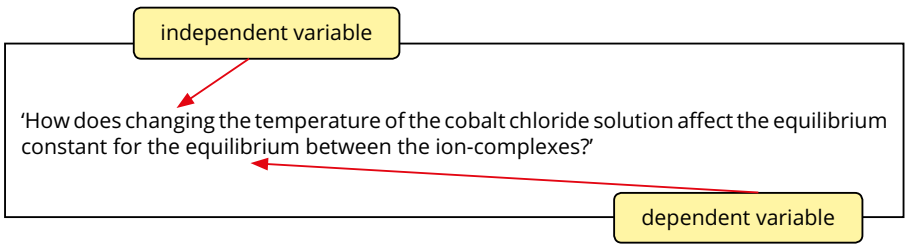


FIGURE 1.8.5 A research question stating the independent and dependent variables

A well-constructed research question should include:

- measurable variables—the independent variable and the dependent variable
- a guiding word, such as 'who', 'what', 'why' or 'will'
- a link from the guiding word to command verbs such as 'identify', 'describe', 'compare', 'distinguish', 'analyse', 'evaluate' or 'create' so that a task can be determined.

Table 1.8.2 gives examples of constructed research questions.

TABLE 1.8.2 Structuring a research question

Guiding word(s)	Example research questions	What are you being asked to do? What are cognitive verbs?
what	• What is the effect on the potential difference of the cell if the temperature of the solution is increased? • What is the concentration of the solution at the equivalence point when 0.1 mol dm^{-3} solution of acetic acid is titrated against 25 mL 0.1 mol dm^{-3} NaOH solution?	Identify and describe specific evidence, reasons and examples from a variety of possibilities. *identify, describe*
where	• Where should the copper be placed to optimise the catalysis of the reaction between zinc and hydrochloric acid?	Identify and describe giving reasons for a place or location. *identify, describe*
will	• Will the use of a catalyst affect the rate of the reaction between zinc and hydrochloric acid?	Identify and describe giving reasons for effectiveness. *identify, describe*
how	• How can the rate of the reaction between zinc and hydrochloric acid be measured? • How does particle size affect the rate at which sugar dissolves in water?	Identify and describe in detail a process or mechanism. Give examples using evidence and reasons. *identify, describe*
why	• Why does the pH of pure water change as a function of temperature? • Why does the position of a metal in the periodic table affect its reactivity towards 0.1 mol dm^{-3} HCl?	Explain in detail the causes, reasons, mechanisms and evidence for. *identify, explain*
would	• Would the addition of copper speed up the reaction between zinc and 0.1 mol dm^{-3} hydrochloric acid?	Evaluate. Justify, giving reasons for and against (using evidence, analogies and comparisons). *evaluate, assess, justify*
is/are	• Is the amount of electricity provided by a Daniell cell linearly related to the concentration of the copper (II) sulfate solution?	Evaluate. Justify, giving reasons and evidence. *evaluate, assess, justify*
can	• Is the electrical conductivity of strong and weak acids and bases affected by temperature?	Evaluate and assess. Is it possible? Give reasons, suggest possible alternatives. *evaluate, assess, justify, create*
do/does	• Does surface area or volume affect the rate of diffusion? • Does the strength of the acid affect how much acid is required to neutralise the same volume and concentration of a base?	Evaluate. Justify using reasons and evidence for and against. *evaluate, assess, justify*
should	• To increase the accuracy of a titration calculation should the standard solution be in a conical flask or a burette?	Evaluate advantages and disadvantages, implications and limitations. Make a judgement. *evaluate, assess, justify, create*

Formulating a hypothesis

From your research question, a hypothesis can be developed. A hypothesis is a statement that proposes a relationship between variables, as it is based on some level of understanding. This statement *must* be testable, meaning it must specifically and clearly state a change in variables that can be tested through measurement.

The student experiment does not necessarily require a hypothesis as it may not always be appropriate or beneficial.

A hypothesis, if it is suitable, requires the controlled variables to be more stringent during the experiment, to enable the analysis of raw data that can specifically address the original inquiry of the observation. With more stringent controls, it may be possible for errors and uncertainties to be reduced; also the interpretation of results may be more straightforward (though not always).

i The writing of a hypothesis is an optional inclusion that might support the development of your research question. A hypothesis is not an assessed component of the ISMG, and not every research question will lead to the development of a hypothesis.

Scientists use **literature reviews** and background research to develop an understanding of an observation and then infer a reason for their observation. The inference is then tested using experimentation to determine if it is true (verified or supported) or false (falsified or refuted).

Because the hypothesis proposes a specific relationship between the independent and dependent variables, the hypothesis can either be supported or refuted by the results. To be able to propose a specific relationship the scientist must have some knowledge and understanding of the variables.

To develop a hypothesis, similar steps are undertaken to developing a question (Figure 1.8.6).

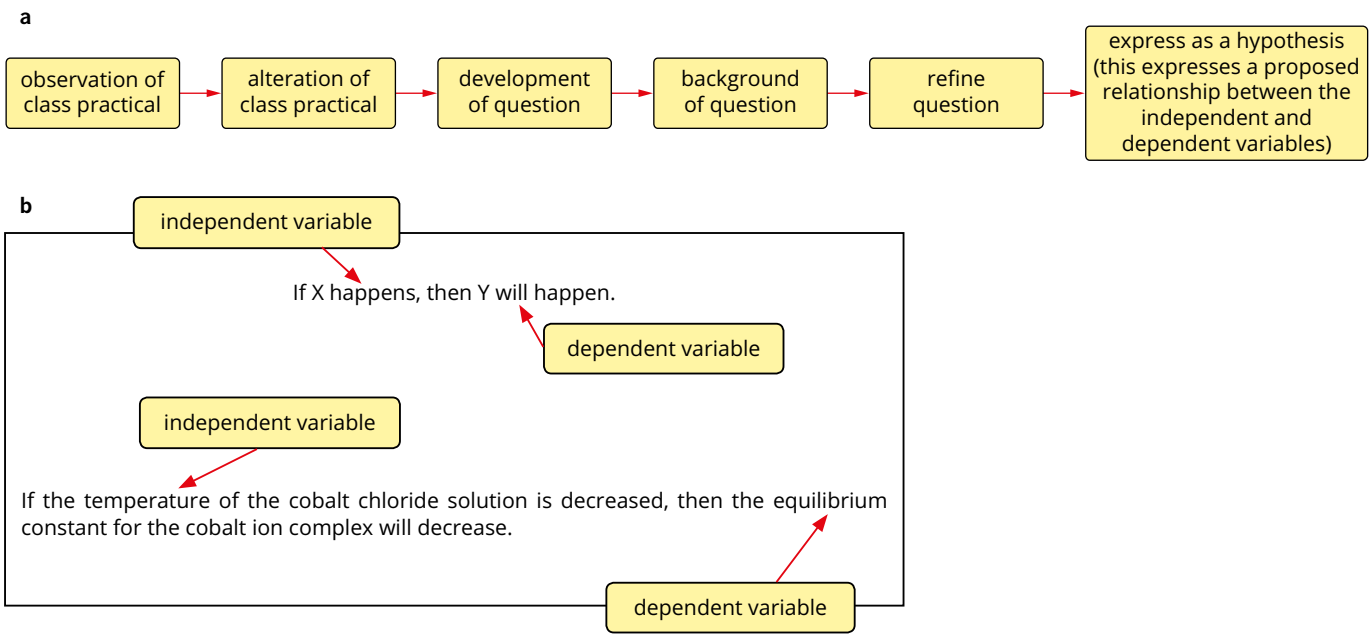


FIGURE 1.8.6 (a) Refining a hypothesis or question. (b) Formulating a hypothesis—write in terms of the dependent and independent variables

The 'if' part of the hypothesis refers to the independent variable—the variable you alter in the experiment. The 'then' part relates to the dependent variable, which is the variable you measure or observe.

A hypothesis does not need to include 'if' and 'then' in its wording. For example, the previous hypothesis could also be worded in the following way:

The equilibrium constant for the equilibrium between cobalt hexahydrate and cobalt tetrahydrate ion complexes will decrease if the temperature of solution is decreased.

A good hypothesis can be tested to be true (verified or supported) or false (falsified or refuted) by investigation.

A well-constructed hypothesis provides guidance and structure to the experiment in the following areas:

- methodology—provides specific limitations and guidance (due to the proposed relationship) directing the planning of the experiment; suggests specific variables to control and measure
- results—offers guidance for analysis and processing of data to determine if the proposed relationship exists; gives direction for the display of results to be specific to the hypothesised relationship between the variables
- evaluation—specifically directs what should be considered for adjustments in the methodology to improve or extend the experiment.

Evaluating your research question

The quality of your research question is vital to the quality of the response that can be written.

Once you have developed your research question, stop to evaluate it before progressing. Follow the prompts in Figure 1.8.7 to refine and improve your research question.

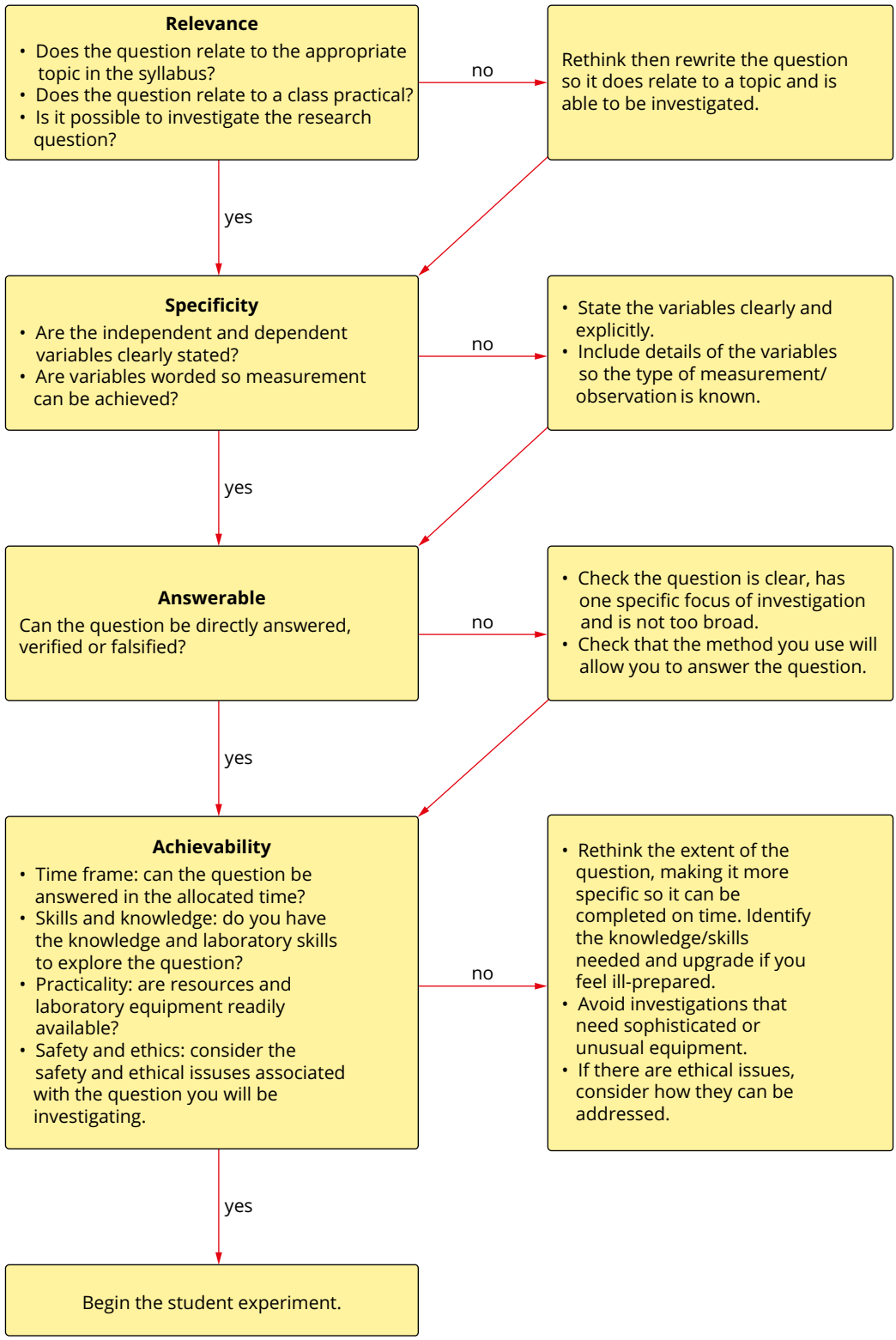


FIGURE 1.8.7 Steps to refine and improve your research question

Examples of research questions and hypotheses

The following examples demonstrate that the student experiment may be expressed as either a hypothesis or a question to be investigated.

Research question: Does the voltage produced by a Daniell cell decrease linearly if the concentration of the zinc electrolyte is decreased from $1.0\,mol\,L^{-1}$ to $1 \times 10^{-6}\,mol\,L^{-1}$?

Hypothesis: If the concentration of the zinc electrolyte in a Daniell cell is decreased then the voltage produced will decrease.

Research question: Does the time taken for the production of 25 mL of hydrogen gas decrease as the temperature of the solution of 50 ml $0.5\,mol\,L^{-1}$ hydrochloric acid and 5 g zinc is increased?

Hypothesis: The rate of reaction increases as the temperature of the reaction mixture increases.

Research question: By burning different masses of ethanol can the accuracy of the calorimetric determination of the molar heat of combustion be improved?

Hypothesis: The accuracy of the molar enthalpy of combustion of ethanol can be increased by performing multiple calorimetry experiments.

DEVELOPING THE RATIONALE

Once you have decided upon an experiment to modify (i.e. refine, extend or redirect) and you have formulated your research question, a rationale needs to be developed. The **rationale** is where you explain the scientific concepts appropriate to your research question.

Research relevant scientific information

The student experiment in the QCAA Chemistry General Senior Syllabus requires you to:

- research what is currently known about the relationship between the dependent and independent variables in your experiment
- develop a methodology that allows sufficient and relevant data to be collected that enables the research question to be answered
- manage the risks and issues associated with the experiment.

The ISMG for the student experiment states that in researching and planning your experiment you are required to demonstrate:

- a rationale for the experiment that demonstrates consideration
- methodological modifications that have been justified
- a methodology that collects data that is pertinent to and adequate to test the research question, with deliberate design.

Furthermore, the syllabus requires background scientific information to be used in a rationale for the experiment to:

- explicitly justify the modifications to the methodology (alterations to the class practical)
- explain how the methodology will enable the research question to be answered through the collection of the data
- inform risk. This relates to identifying how the risks associated with the experiment will be mitigated through personal protective equipment or specific features of the methodology.

The rationale is also expected to inform the interpretation of the evidence (results) and conclusion.

There is a lot of information to record during the student experiment so it is best to keep it all in a single document. Scientists always document their ideas, questions, background research, drafts, revisions and refinements in a single document. This document is known as a **scientific journal**.

Taking notes and recording your thoughts in a scientific journal provides a record of all the information that arose during the process of the scientific method. It is unknown how vital some information will become throughout the process until it is complete and summarised into the scientific report. It will be used in a rationale for the experiment; to explicitly justify the modifications to the methodology (alterations to the class practical); provide a reason for collecting data and to inform risk, ethical and environmental management. It is also expected to inform the interpretation of the evidence (results) and conclusion.

The purpose of researching background scientific information in the scientific method is to develop understanding and knowledge. It must be relevant to the independent and dependent variables in the research question. As the variables become known, this will direct the research. The scientific method specifically requires scientists to demonstrate understanding and knowledge of the direct, and possibly indirect, relationship between the independent and dependent variables and perhaps controlled or measured variables. The background research is essential to achieve all this.

PLANNING AND REFINING METHODOLOGY

This section is a guide to some of the key steps that should be taken when planning and refining an investigation.

Planning experiments

Once you have formulated your research question, defined the variables and developed knowledge and understanding of concepts and relationships, you will need to develop your experiment. You will also need to consider the ethical and safety implications of the experiment.

Create a work schedule that outlines the time frame of your experiment (including all trials and/or samples), being sure to include sufficient time to repeat experiments if necessary. Remember that the whole process should be completed in the main at school and take about 10 hours. Check with your teacher that your protocol and schedule (methodology) are appropriate and that others will be able to repeat your experiment exactly by following the methodology you have written. If you have planned well you will be able to test your methodology and run trials. You need to be able to perform your experiment independently, in the time available in the school laboratory and with minimal support from your teachers and school laboratory staff.

The methodology of your experiment is a specific step-by-step procedure. Though, when written in the final scientific report, it may be written in paragraph form. You must ensure that the methodology is valid, specific, reliable and accurate. All of these factors need to be considered when planning.

Validity

Validity refers to whether an experiment or investigation is in fact testing the set research question or hypothesis. Is the experiment obtaining data that is relevant to the question?

Factors influencing validity include:

- whether your experiment measures what it claims to measure. In other words, your experiment should test your research question
- the certainty that something observed in your experiment was the result of your experimental conditions and not due to some other cause that you did not consider. In other words, whether the independent variable influenced the dependent variable in the way you intended
- the degree to which your findings can be generalised to more broad chemistry phenomena from which your experiment is taken. In other words, how your experiment fits in to the big ideas in chemistry.

To ensure an investigation is valid, it should be designed so that only one variable is being changed at a time. The remaining variables must remain constant so that meaningful conclusions can be drawn about the relationship between variables.

Also, the raw data collected during the experiment must be appropriate to ensure the data is valid. To ensure validity, carefully determine the:

- independent variable
- dependent variable
- controlled and/or measured variables
- appropriate raw data that will be collected (quantitative versus qualitative) and that each will be measured, collected or controlled appropriately.

Data can either be qualitative or quantitative. **Qualitative data** is descriptive and unmeasurable and uses descriptions or adjectives to record observations. **Quantitative data** is empirically measurable and uses instruments to record observations as numbers with units.

Qualitative and quantitative data have further subsets in each category, as shown in Figure 1.8.8.

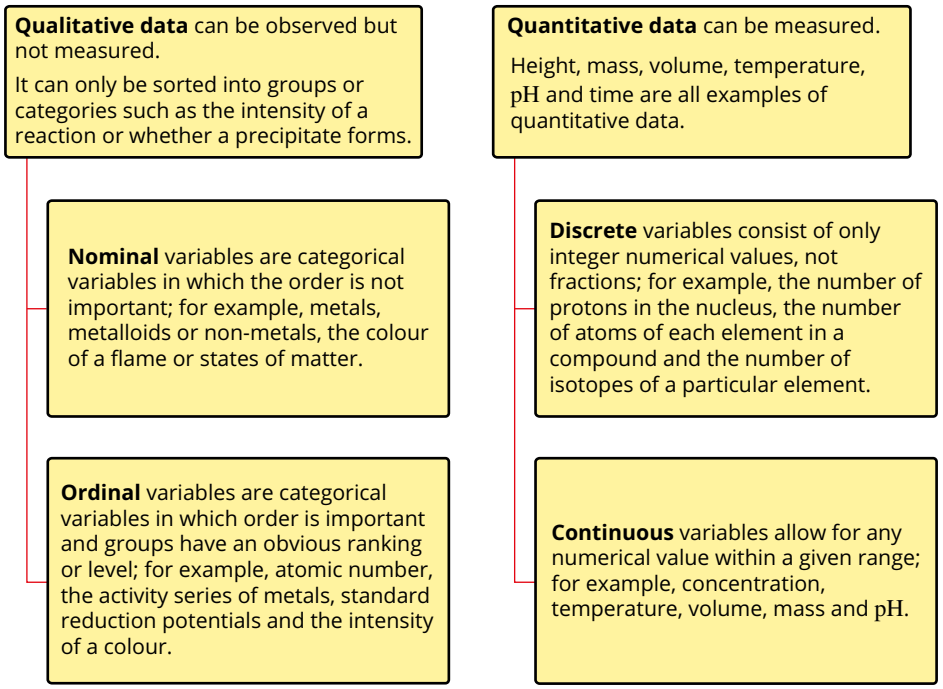


FIGURE 1.8.8 Quantitative and qualitative variables

Measurement of temperature requires an instrument and provides quantitative data (Figure 1.8.9).



FIGURE 1.8.9 (a) Using a thermometer or a wireless temperature sensor will measure temperature empirically and provides quantitative data that can be analysed statistically. Processing empirical data can produce discrete, explicit and comparative analysis. (b) A liquid thermometer for measuring water temperature. (c) Feeling heat radiating from a heater is an example of qualitative data as it is based on personal observation. Qualitative data cannot be statistically analysed.

Depending on the experiment, it may be appropriate to record the qualitative observation (e.g. colour of a solution), or perhaps measure the quantitative results (e.g. mass of a substance).

Controls

Controls are required in an experiment. Controlling as many variables as possible to determine what has influenced the results goes a long way to providing accurate and precise data.

It is difficult—sometimes impossible—to eliminate all **variables** that might affect the outcome of an experiment. Concentration of solution, temperature, mass of reactants, pH and surface area of reactants are examples of such variables. A methodology to overcome this is to set up a second group within the experiment (called a **control group**) that is identical in every way to the first group (the **experimental group**) except for the single experimental (independent) variable that is being tested. This is a controlled experiment. This allows the examination of one variable at a time (the independent variable), which is required to validly test a hypothesis.

Reliability

Reliability (sometimes called repeatability) is the ability to obtain the same results if an experiment is repeated (Figure 1.8.10). The closer the results are to the true value, the more accurate the results will be. Because a single measurement or experimental result could be affected by errors, **replication** of samples within an experiment and **repeat trials** are key components of reliability. To improve reliability you should:

- specify the materials and methods in detail (including precision, see Module 1.5 Uncertainties in measurement and error)
- include replicate samples within each experiment or several observations within an investigation
- take repeat readings of each sample
- run the experiment or trial more than once.

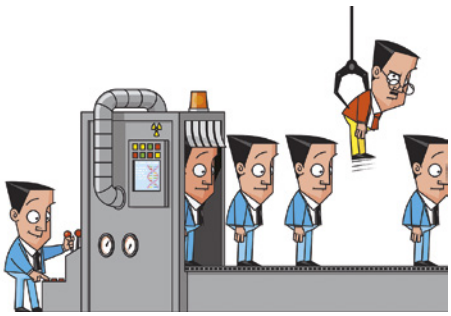


FIGURE 1.8.10 If you can reproduce your results, they are reliable.

Sample size is extremely important in scientific experiments. The sample size affects the:

- representation of the phenomenon
- natural variation, errors and uncertainty
- results by offering more evidence to support the experimental results
- repeatability and therefore reliability.

The greater the sample size, the more reliable the data. Reasons why a measurement or observation could vary include:

- natural variation
- human error
- uncalibrated instruments or instrumental error
- influence from unforeseen variables.

Accuracy and precision are also important in obtaining reliable (repeatable) data.

Sourcing appropriate equipment and materials

You will need to decide on the materials, technology and instrumentation that will be used to carry out your experiment or investigation. It is important to find the right balance between items that are easily accessible and those that will obtain accurate and precise results. When conducting your investigation, the precision of the chosen instrumentation and how this affects the accuracy and validity of the results should be recorded in your journal for the scientific report.

ELECTRONIC DATA ACQUISITION

Data collection has come a long way in the past 20 years. Previously, discrete measurements were recorded from manual tools and human readings were made over short periods of time. In recent times, the ability to connect independent sensors to any device has enabled simple and highly effective electronic data acquisition over extensive periods of time.

Data acquisition can be achieved through sensors, or probes, recording data to a standalone device, computer, tablet or smart phone (Figures 1.8.11 and 1.8.12). The software will generally graph and allow advanced calculations directly without the need for an additional program. This specialised software allows for many analysis functions not found in standard spreadsheets—and follows scientific rather than business standards.



FIGURE 1.8.11 Data acquisition software produces real-time graphs that can be downloaded or printed.

You will use data acquisition in many investigations in your chemistry course. With the many different probes available, there are many applications.

Many smartwatches and smartphone apps include digital sensors and **data loggers** that can be accessed and used for some class practicals and experiments.



FIGURE 1.8.12 Many smartwatches and smartphones have digital sensors and in-built data loggers.

Electronic data acquisition and data logging

Electronic data acquisition takes advantage of highly accurate sensors to collect data directly for processing by a computing device (Figure 1.8.13). There are many sensors, probes and instruments available that can measure a vast variety of phenomena in a single device.

Often one of the measurements is time; the user decides what the other measurement (or variable) is by selecting the type of sensor, or probe, to use. Probes can measure temperature, pH, gas pressure, conductivity, concentration of gases in air, or the amount of pollutants in the environment along with many more phenomena.

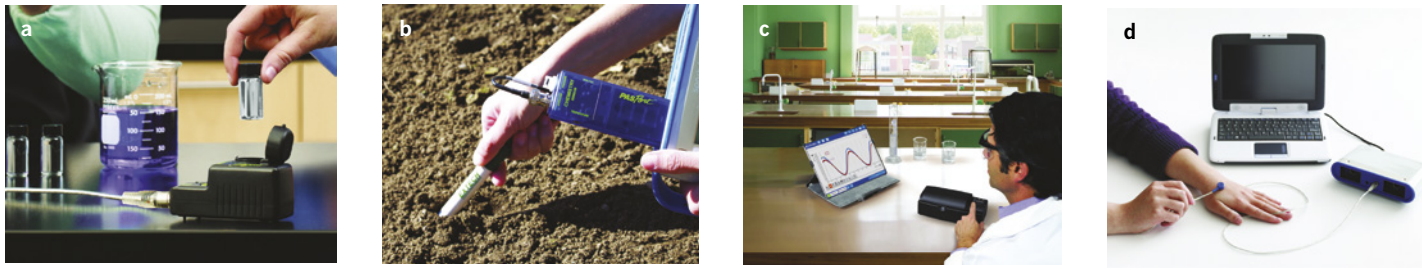


FIGURE 1.8.13 (a) Sensors connected to computing devices such as phones and tablets are readily used in the field or lab to measure the concentration of solutions and other key physical measurements. (b) Many different probes and sensors can attach to a single device, such as those used to measure soil pH. (c) They can be very precise and measure many times per second, such as a polarimeter that measures the concentration of sugar solutions. (d) They are usually easy to use and produce results immediately; for example, providing the temperature of skin upon contact.

Recording is done accurately and can be continuous or manual and the measurements are saved electronically. The saved measurements can then be accessed via a computer or directly from the tablet screen.

The rate at which measurements are recorded is called the sample rate. Data capture rate can vary from 100 000 times per second through to once an hour. The data capture rate selected will depend on what the operator needs. Sometimes, data may need to be captured over many days, weeks, months or even years. In these cases, time and date information are automatically recorded.

Uses of electronic data acquisition

Given the number of different probes available, electronic data acquisition has many uses (Figure 1.8.14). For example, probes can monitor the temperature of ice cream being transported from a factory to the supermarket. They are used to record the speed, engine conditions and brake force of trains, buses and trucks. An engine control unit in a car can record data from parts of the engine and the mechanic can access this data when servicing the car. The control unit records any problems with the car's engine and computer system.



FIGURE 1.8.14 Data acquisition is used throughout many industries, including the automobile industry. This image shows a data logger connected to a steering wheel. The collected data provides informative feedback to manufacturers.

RISK ASSESSMENT

While planning for an investigation in the laboratory or outside in the field, it is important for your safety and the safety of others that you consider the potential risks.

Everything you do involves some risk. **Risk assessments** identify, assess and control hazards. A risk assessment should be performed for any situation, whether in the laboratory or out in the field, that could hurt people, property or animals. Always identify the risks and control them to keep everyone safe.

To identify risks, think about:

- the activity that you will be carrying out
- where in the environment you will be working, e.g. in a laboratory, school grounds, or a natural environment
- how you will use any equipment or chemicals that you will be handling, including sources of heat and electricity
- what clothing you should wear, e.g. lab coat and goggles.

The hierarchy of risk control shown in Figure 1.8.15 is organised from the most effective risk management measures at the top of the pyramid to the least effective at the bottom of the pyramid. The most commonly used risk control measure that addresses the majority of risks is personal protective equipment. The least common but most protective control measure is eliminating the risk from the scientific investigation.

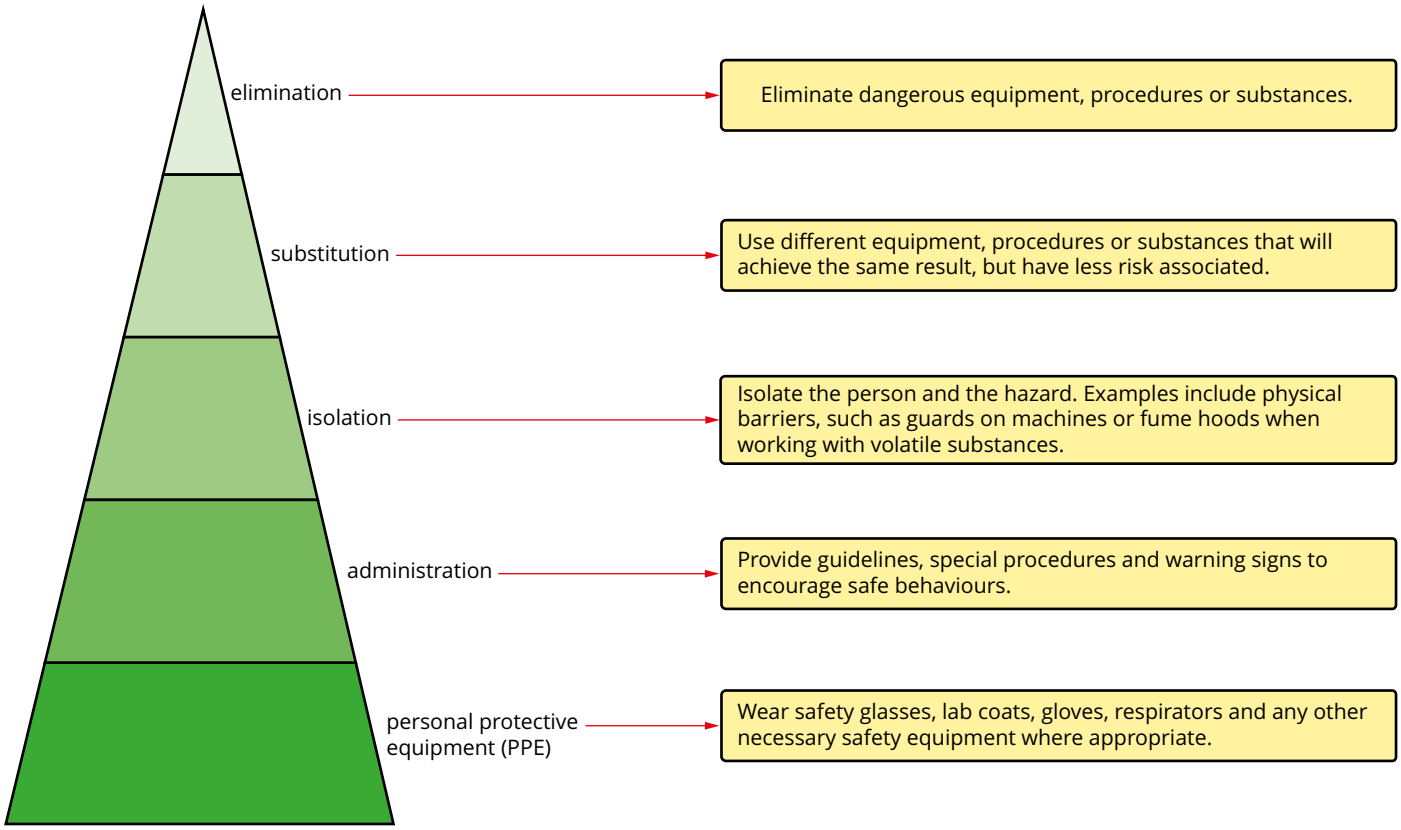


FIGURE 1.8.15 The hierarchy for risk control is shown in this pyramid, marked from bottom to top in order of increasing importance.

Personal protective equipment

Everyone who works in a laboratory wears items that help keep them safe, like those shown in Figure 1.8.16. These items are called **personal protective equipment (PPE)** and include:

- safety glasses
- shoes with covered tops
- disposable gloves
- a disposable apron or a lab coat.



FIGURE 1.8.16 Examples of PPE shown are protective eye wear, lab coats and gloves

Chemical codes

The chemicals used at school or found in a hardware store have a warning symbol on the label. These warnings are called **chemical (HAZCHEM) codes**. Some common pictogram codes and their meanings are shown in Table 1.8.3.

TABLE 1.8.3 Common HAZCHEM codes and their meanings

GHS symbol	Meaning
	Corrosive—can dissolve or eat away at substances, including tissues such as your skin or airways.
	Poison—can cause injury or death if ingested, inhaled or absorbed.
	Irritant—causes discomfort, pain or itchiness.
	Flammable
	Danger—can cause biological harm; for example cancer, allergic reactions, breathing difficulties etc.

Safety data sheets

Each chemical substance has an accompanying document called a **safety data sheet (SDS)**, as shown in Figure 1.8.17. An SDS contains important safety and first aid information about each chemical you commonly use in the laboratory. If the products of a reaction are toxic to the environment, you must pour your waste into a special container—not down the sink.

1. IDENTIFICATION OF THE MATERIAL AND SUPPLIER

Product Name: **HYDROCHLORIC ACID - 20% OR GREATER**

Recommended use of the chemical and restrictions on use: Precursor for generation of chlorine dioxide gas used in water treatment.

Supplier: Ixom Operations Pty Ltd
ABN: 51 600 546 512
Street Address: Level 8, 1 Nicholson Street
Melbourne 3000
Australia

Telephone Number: +61 3 9665 7111
Facsimile: +61 3 9665 7937
Emergency Telephone: **1 800 033 111 (ALL HOURS)**

Please ensure you refer to the limitations of this Safety Data Sheet as set out in the "Other Information" section at the end of this Data Sheet.

2. HAZARDS IDENTIFICATION

Classified as Dangerous Goods by the criteria of the Australian Dangerous Goods Code (ADG Code) for Transport by Road and Rail; DANGEROUS GOODS.

This material is hazardous according to Safe Work Australia; HAZARDOUS SUBSTANCE.

Classification of the substance or mixture:
Corrosive to Metals - Category 1
Skin Corrosion - Sub-category 1B
Eye Damage - Category 1
Specific target organ toxicity (single exposure) - Category 3

SIGNAL WORD: DANGER



Hazard Statement(s):
H290 May be corrosive to metals.
H314 Causes severe skin burns and eye damage.
H335 May cause respiratory irritation.

Precautionary Statement(s):

Prevention:
P234 Keep only in original container.
P260 Do not breathe mist / vapours / spray.
P264 Wash hands thoroughly after handling.
P271 Use only outdoors or in a well-ventilated area.
P280 Wear protective gloves / protective clothing / eye protection / face protection.

FIGURE 1.8.17 Extract from a safety data sheet (SDS) for concentrated hydrochloric acid. The SDS alerts the reader to any potential hazards when using a substance, including appropriate measures to reduce risk of harm.

The SDS provides employers, workers and health and safety representatives with the necessary information to safely manage the risk of hazardous substance exposure.

Ethical considerations

When planning an investigation, you should always identify all possible ethical considerations and evaluate their necessity or find ways to reduce or mitigate them. **Ethics** is a set of moral principles by which your actions can be judged as right or wrong. Every society or group of people has its own principles or rules of conduct. Scientists have to obtain approval from an ethics committee and follow ethical guidelines when conducting research that involves animals or humans.

These are some of the ethical issues that must be considered.

- How can this affect wider society?
- Does one party benefit over another; for example, one individual, a group of individuals or a community?
- Is there a risk of harm (physical or mental) to people involved in the research?
- Does it prevent anyone from gaining their basic needs?
- Will this have consequences for future ethical decisions or issues?
- Does the research cause damage to the environment or other living things?

In reality, school chemistry investigations generally will have minor ethical issues, if any, but these should be considered in your planning.

Refining the methodology

As the planning of the methodology is not linear, refinement will occur several times (due to further background research, refining the research question or as variables become understood). Scientists will employ an experimental methodology that has been refined numerous times over several years.

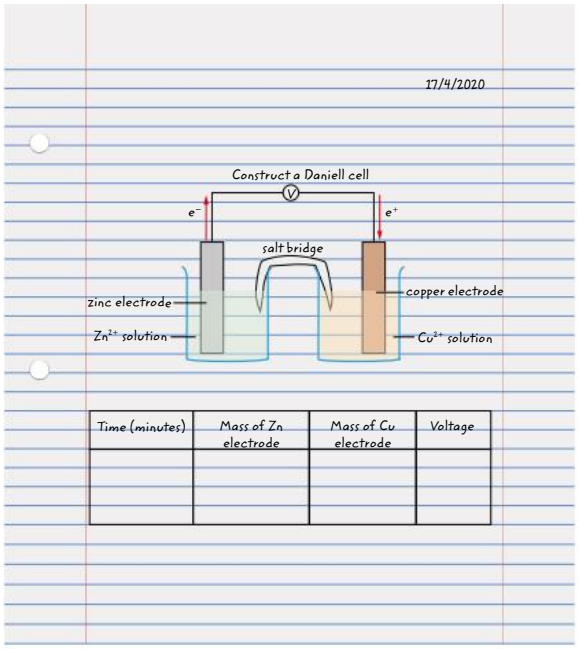
> It is common for experimentation and testing not to go according to plan. This may be due to time constraints, instrumental limitations or resource limitations etc. It is vital that comprehensive background research has been undertaken. Refinements are often made during experimentation to improve validity and reliability. Refinements also reduce error and uncertainty as the experimenter becomes aware of these problems.

Record all refinements in your journal as shown in Figure 1.8.18. The following may help with refining the methodology.

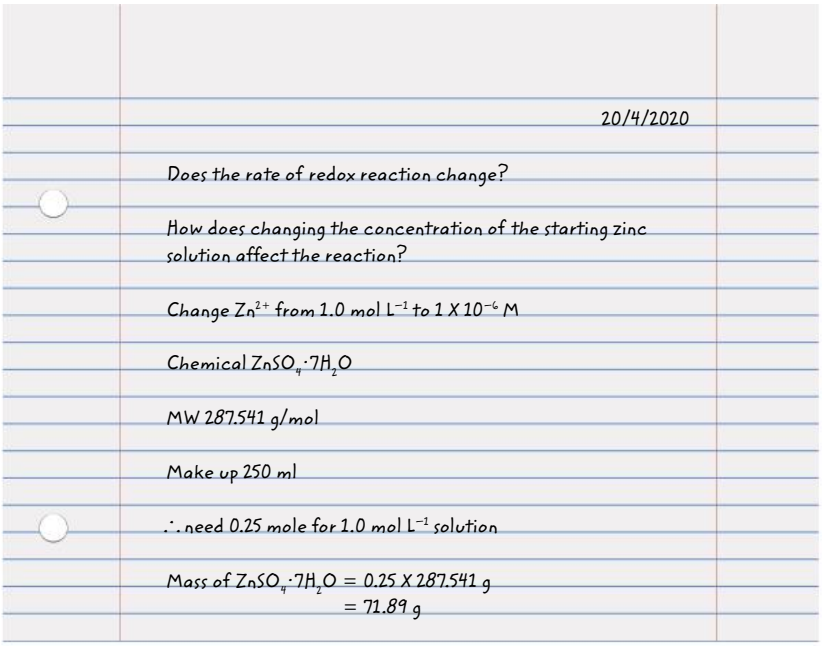
- Record everything.
- Be prepared to make changes and refinements to the plan and methodology.
- Note any difficulties encountered and the ways they were overcome. What were the failures and successes?

Every test carried out can contribute to the understanding of the investigation as a whole, no matter how much of a disaster it may first appear.

a



b



c

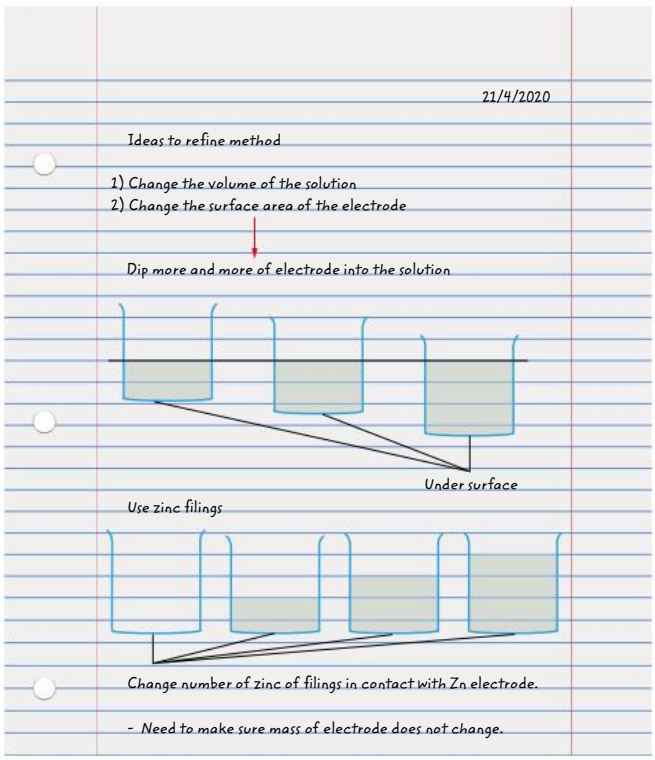


FIGURE 1.8.18 Student journal demonstrating basic developments and refinements in their methodology

If the expected data is not obtained, don't worry. As long as it can be critically and objectively evaluated, the limitations of the investigation can be identified and further investigations proposed, the work is worthwhile. Sometimes a different point of view, such as from a fellow student or a teacher, is all that is needed to find a solution. An evaluation and suggested improvement to the methodology or experiment are required in the scientific report.

1.8 Review

SUMMARY

- An independent variable is a variable that is controlled by the researcher (the variable that is selected and changed).
- A dependent variable is a variable that may change in response to a change in the independent variable and is measured or observed.
- Controlled variables are the variables that are kept constant during the investigation.
- Measured variables are the variables in an open system that cannot be controlled and therefore must be measured.
- Research questions should have the following characteristics:
  - measurable variables (the independent and dependent variables)
  - a guiding word, such as 'who', 'what', 'why' or 'will'
  - be phrased so that a definitive answer can be developed
  - be able to link the guiding word to command verbs (such as 'identify', 'describe', 'compare', 'contrast', 'distinguish', 'analyse', 'evaluate' or 'create') so that a task can be determined.
- A simple way to formulate a hypothesis is to link the independent and dependent variables using the following sentence structure:

  If (independent variable) happens, then (dependent variable) will happen.
- A scientific journal is a document a scientist uses to record all their ideas, questions, background research and literature reviews, methodology drafts and revisions, results and refinements related to an experiment.
- Validity refers to whether an experiment or investigation is in fact testing the set research question or hypothesis.
- Data can either be qualitative or quantitative.
- Qualitative data is descriptive and unmeasurable and uses descriptions or adjectives to record observations.
- Qualitative data can be characterised as either:
  - nominal, when the order of data is not important
  - ordinal, when the ordering of data is important.
- Quantitative data is empirically measurable and uses instruments to record observations.
- Quantitative data can be characterised as either:
  - discrete, when data can only be recorded as particular numerical values
  - continuous, when data is not restricted to particular numerical values, but occurs within a given range.
- Reliability refers to the notion that if the experiment is repeated many times, the results obtained should be consistent.
- Reliability is improved by:
  - replication, having multiple samples within an experiment
  - repeat trials, repeating the experimental test.
- Risk assessments identify, assess and control hazards.
- HAZCHEM pictograms are warning images used to identify hazardous substances.

KEY QUESTIONS

Retrieval

1 **a** State the meaning of the term 'variable'.

b Copy and complete the table below with definitions of the types of variables.

Independent variable	Controlled variables	Dependent variable

Comprehension

2 Explain the difference between quantitative and qualitative data.

Analysis

3 To determine the concentration of an alkaline solution, 25 mL of the unknown solution was measured using a measuring cylinder and placed in a conical flask. The inner surfaces of the flask were rinsed with water. A $1.0\,mol\,L^{-1}$ solution of hydrochloric acid was poured into a burette, using a funnel that was left in the top of the burette.

Five or six drops of phenolphthalein were added to the conical flask and the solution turned pink. The initial reading on the burette was 1.2 mL. The hydrochloric acid solution was run into the unknown solution until it went clear, at which point the burette reading was 34 mL.

Identify as many sources of error as you can. For each source indicate the direction in which the error would have resulted. That is, identify whether the error would have caused the experimentally derived value to be less than or more than the accepted value.

4 A student wanted to determine how the conductivity of acetic acid varied with temperature.

- **a** Determine the independent variable for the experiment.
- **b** Determine the dependent variable for the experiment.
- **c** Identify an appropriate way of measuring quantitatively the electrical conductivity of the acetic acid solution.
- **d** Identify the variables that would need to be controlled in the student's experiment.

5 A student is investigating how the rate of electrolysis of copper sulfate is affected by changing the concentration of copper sulfate by measuring the time taken to produce 25 mL of oxygen gas. Identify a methodology that will enable the collection of sufficient data, including identifying the dependent and independent variables.

1.9 Conducting an experiment

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- determine relevant data that is needed to test a research question
- determine what is considered to be sufficient data to test a research question
- select appropriate equipment to collect relevant and sufficient data.

Now that much is known about the variables involved and the experiment methodology is planned, your experiment can be conducted. Since experiments rarely run according to the precise plan, understanding the variables involved enables changes or refinements to be made to the experiment.

CONDUCTING THE EXPERIMENT

While conducting the experiment, variables must be controlled and conditions maintained to ensure the measured or recorded raw data is valid and reliable. Other scientists or investigators must be able to repeat your results by collecting and measuring raw data under the same conditions. Depending on what your student experiment is testing, there are several aspects of the experiment that should be included in the planning, such as:

- equipment
- instruments
- safety precautions
- time (preparation, testing)
- complexity of testing
- chemical concentrations and volumes
- sequential order of activities to complete testing.

Equipment

Choice of equipment will influence the reliability of the experiment. Therefore, it is important to choose equipment wisely. It needs to provide the required precision but also be something that you are capable of using correctly.

Use the equipment that is best suited to the data that needs to be collected to validate the hypothesis. Determining the units of the data being collected and at what scale will help you to select the correct equipment (Table 1.9.1). Using the correct unit and scale will ensure that measurements are more accurate and precise (with smaller systematic errors).

TABLE 1.9.1 Examples of rudimentary testing versus improved experimental testing

Rudimentary set-up	Improved set-up
estimating the temperature of a liquid by hand 	measuring the temperature using a digital thermometer (sensor) with known precision and uncertainty 
measuring time using a five-minute sand hourglass 	measuring time using a digital timer with known precision and uncertainty 

Instruments

The precision of the instruments used to measure and record data is important. It determines the significant figures when analysing the data, it may affect the accuracy of the experiment and it could provide assistance in producing reliable results. The more precise the instruments, the more accurate the measurements and the more reliable the data is.

When conducting the experiment, it is recommended to use the most precise instruments available. Table 1.9.2 demonstrates the benefits of greater precision instruments through lower uncertainty.

TABLE 1.9.2 The difference in precision between instruments: (a) a glass thermometer with a precision of ±2.5°C; (b) a measuring beaker with a precision of ±5 mL; (c) a digital laser thermometer with a precision of ±0.2°C and (d) a measuring cylinder with a precision of ±0.25 mL

Lower precision instruments	Higher precision instruments
a 	c 
b 	d 

Safety precautions

Always employ safe procedures. The use of common sense during activities is essential. For example, all glass equipment and instruments should be used at the back of the bench so students walking by do not cause an accident. Place a sign on the lab bench warning other students and staff not to touch the equipment.

The school's and teacher's safety and risk assessment guidelines need to be adhered to. Completing the risk assessment for your experiment may require completing a form or completing an online process.

COLLECT SUFFICIENT AND RELEVANT DATA

It is important that the instruments and methodology used will enable you to measure and collect the data. The data must be relevant to the variables in the research question or hypothesis. The collected and measured data must be relevant to the proposed relationship in the research question or hypothesis. Also enough data, enough sampling and appropriate accuracy and precision are required when collecting or measuring data. If this is not achieved, the analysis and interpretation of the data will not be reliable or valid in relation to the research question or hypothesis.

Collection of sufficient data

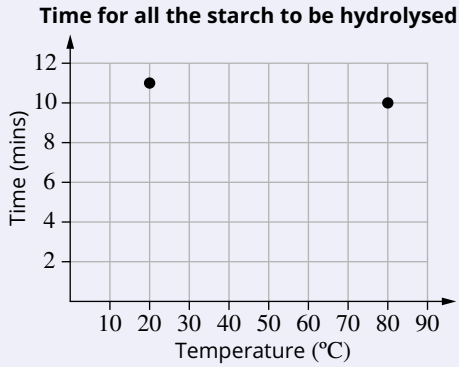
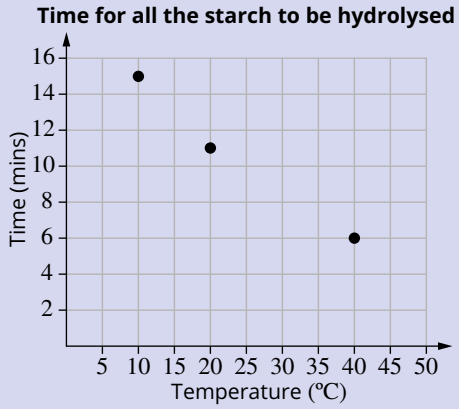
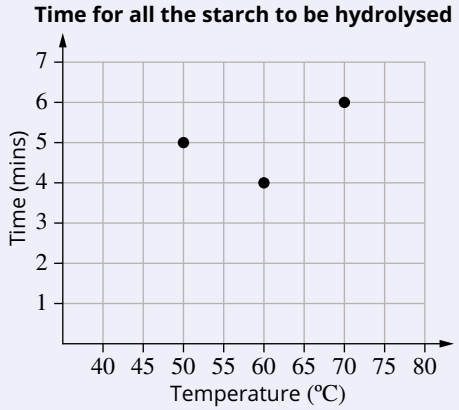
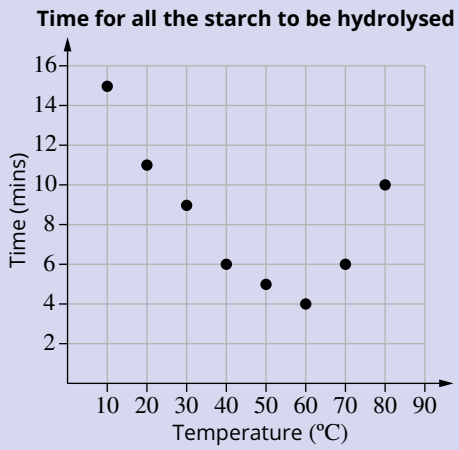
The term 'sufficient' is defined by the QCAA Chemistry General Senior Syllabus as 'enough or adequate for the purpose'.

Enough data needs to be collected to substantiate whether or not a relationship exists between the variables. This includes collecting an appropriate number of replicates and also an appropriate number of individual samples (also known as observational or collection points).

This will impact on the accuracy of the data and the uncertainty within the data collected. This is vital to determine a valid interpretation of the data. In general, a minimum of five data points and three measurements per data point are needed to improve the accuracy of the individual data points.

Table 1.9.3 below outlines examples of sample size and their effect on the results of an experiment.

TABLE 1.9.3 Examples of sample size and their effect on an experiment

Example of analysed data	Effect of sample size on analysis
	A line graph with two sample points: With only two individual sample points, these results suggest an inappropriate relationship between temperature and enzyme activity; that enzyme activity exhibits a slight linear decrease with temperature.
	Line graph with three sample points using an uneven scale: The spread between the chosen individual sample points is inappropriate for this experiment as they should be evenly spread. This example produces results with an incorrect relationship between temperature and enzyme activity, that enzyme activity increases then the rate of enzyme activity increases as temperature increases.
	Line graph showing limited sample points: The chosen number of individual sample points is appropriate. This may be sufficient; however, the next example provides more precision and validity for the relationship.
	Line graph with the appropriate number and distribution of sample points: The number of individual sample points here best demonstrates the relationship between the variables.

Collection of relevant data

The variables to be measured or collected must be directly related to the proposed independent–dependent variable relationship. Additional variables can be measured or collected that are indirectly related to the hypothesised relationship if the background research shows it could be beneficial in the analysis or interpretation of the relationship. If you do not have any background research relating a variable to the research question, then it is not relevant and should not be measured or collected.

1.9 Review

SUMMARY

- The choice of equipment and instruments will influence the reliability of the experiment.
- The precision of equipment and instruments is important for accuracy and reliability.
- The collected and measured data must be relevant to the proposed relationship in the research question.
- Equipment used during an experiment should enable you to collect and measure relevant data.
- Sufficient data must be collected to substantiate whether or not a relationship exists between the variables.

KEY QUESTIONS

Retrieval

1 Define the phrase 'sufficient and relevant' as it relates to the student experiment.

Comprehension

2 Explain the meaning of the term 'sufficient data'.

Analysis

3 In an experiment to determine how the boiling point of a homologous series of alcohols varied with temperature, a student recorded the following data. Assess whether the data collected is sufficient and relevant.

Expt no.	Compound	Trial 1 (°C)	Trial 2 (°C)	Average boiling point (°C)
1	ethanol	78	76	77
2	propan-1-ol	97	107	102
3	propan-2-ol	83	84	83.5
4	hexan-1-ol	157		157

1.10 Results

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- analyse raw data to produce processed data
- interpret data to draw valid conclusions.

All measurements and observations made during the experiment must be recorded in your journal. This constitutes your raw data. Choosing not to record certain measurements or observations renders your experiment invalid, shows bias and is scientifically fraudulent. Unusual and unexpected measurements and observations may be due to valid relationships between variables that are unknown to you. This cannot be determined until the raw data is processed, analysed and interpreted.

The results, after analysis, need to show whether or not a relationship exists between the variables in the research question. To achieve this, variables need to be presented appropriately. Being able to present results appropriately is dependent on appropriate measurement, observation and recordings (e.g. quantitative or qualitative). You need to make sure this is planned before the experiment is conducted.

The raw data needs to be analysed and then represented using tables, graphs, schematics or diagrams. Refer to Module 1.6 for specific guidance on producing quality and appropriate graphs, and Module 1.11 for details on writing a scientific report.

IDENTIFYING ERRORS

Most practical investigations have errors associated with them. As shown in Figure 1.10.1 on page e88, there are many different types of errors that can occur.

ANALYSING

Analysing raw data enables processing in numerous ways to search for relationships between variables, trends or patterns in the data, uncertainties and errors, outliers and results of significance. This will produce processed data.

There are a number of ways to present data, including tables, graphs, flow charts and diagrams. The best way to visually represent the data depends on its nature. More information on these different formats is provided later in this module. In this module, you will learn how to discuss your investigation and draw evidence-based conclusions in relation to your research question.

It is important that when analysing data, it is not selectively processed to demonstrate what you expected or wanted to see. Such bias will result in using analysis tools (for example, statistics) inappropriately or erroneously and will result in invalid conclusions. Quality scientific analysis processes raw data objectively and is open to any result.

The QCAA criterion 'Analysis of evidence' stipulates the characteristics of the top performance level. The interpretation of these characteristics is shown in Figure 1.10.2 on page e92. To be awarded a mark of 5 or 6 for this criterion, you need to show the steps and calculations that you have performed to demonstrate 'correct and relevant processing of data'.

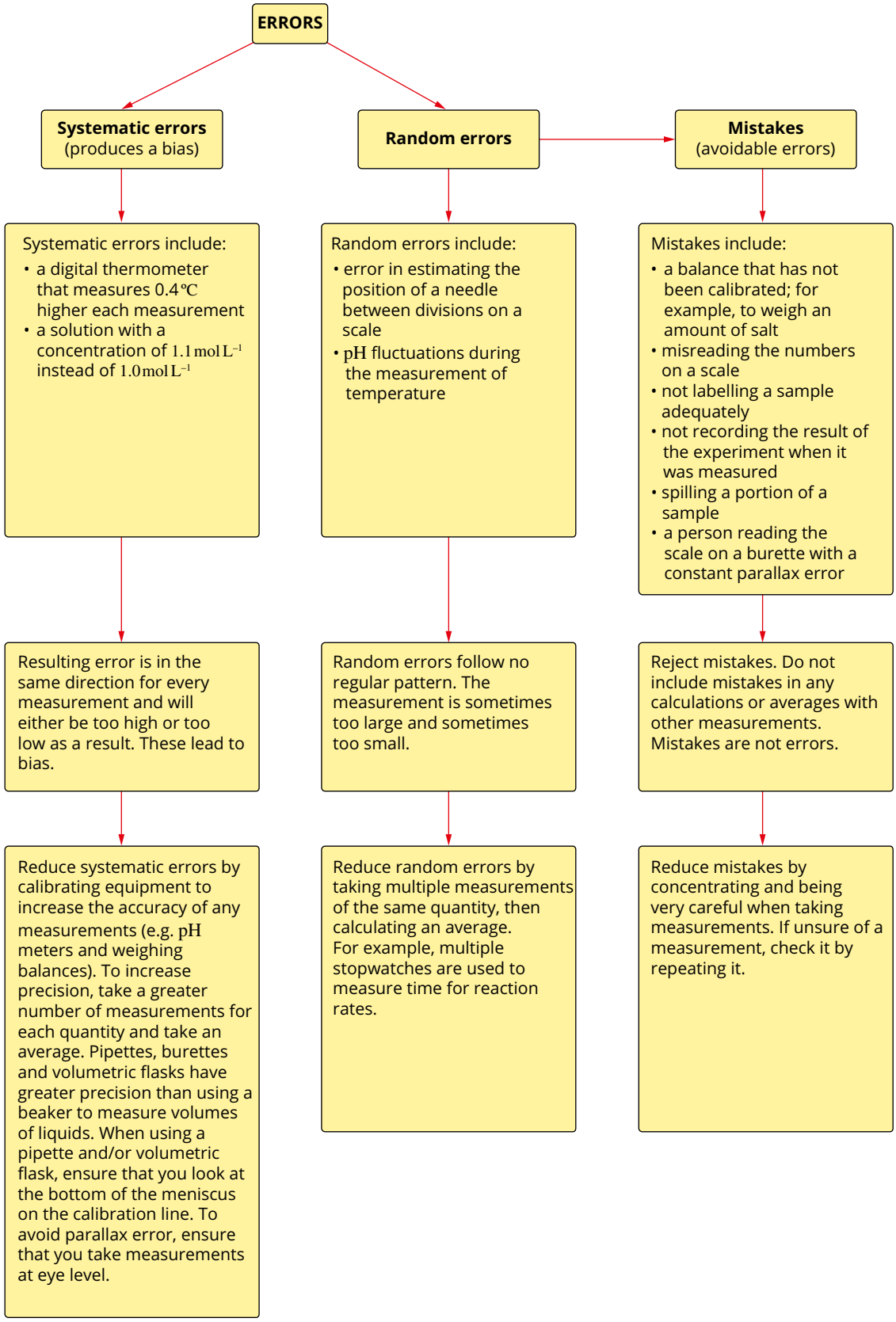


FIGURE 1.10.1 Types of errors that can be made in an experiment

Analysing precision

Understanding uncertainty and precision is vital to any analysis of data. In chemistry, there is always variation in measurements, so if the variation is caused by a systematic or random error, this needs to be determined. Or, in other words, how much of the variation is due to nature and how much is due to instrumentation or recording? (Precision and uncertainty were explained in Module 1.5.)

The precision and uncertainty of the instruments must always be displayed as a range of data next to the results (e.g. measurement ± Δ measurement). If calculations are performed with the results then the appropriate calculations must be done with the uncertainties. When the total uncertainty is known, then it can be established if variation in the data is due to the instrument or the variables being tested.

If the measurements between trials fall within the uncertainty range of the instrument (Table 1.10.1), then the variation in results could simply be due to the instrument. If the differences between the measured results are greater than the uncertainty range, then the variation in the results is not due to the instrument and is due to other variables.

TABLE 1.10.1 Volume of 1.0 mol L^{-1} hydrochloric acid required to neutralise 25 mL of an unknown concentration of sodium hydroxide solution

Trial	Volume of hydrochloric acid used (mL)
titration 1	20.6 ± 0.05
titration 2	20.9 ± 0.05
titration 3	20.1 ± 0.05
titration 4	20.4 ± 0.05
mean	20.5 ± 0.2

Table 1.10.1 shows the volume of 1.0 mol L^{-1} hydrochloric acid required to neutralise 25 mL of an unknown concentration of sodium hydroxide solution, the mean and the absolute uncertainty in the mean. The uncertainty in the mean is calculated using the methods outlined in Module 1.5. There is a notable variation between the measured results. The difference between the volume of hydrochloric acid used between titrations 1 and 2 is just 0.3 mL; however, the difference between titrations 2 and 3 is 0.8 mL. The uncertainty due to the precision in the measurement due to the precision of the instrument is half a division of the scale, so 0.05 mL. Since the difference between the measurements is greater than the uncertainty, these results represent an actual difference in the volumes used.

If the difference in the values is less than the uncertainty in the measurement of the instrument then it cannot be ruled out that the difference is due to the instrument and not some physical reason. Therefore, the result would be interpreted as being the same.

It is important to understand the accuracy and precision of the instruments as it affects the interpretation of your results. There are a few ways to analyse precision:

- instrumental uncertainty—displays the precision of the instrument and explains instrumental variation in the measured results
- range—outlining the difference between the smallest measurement and the greatest
- central tendency (e.g. mean) with instrumental uncertainty—outlining the potential variation in instrumental measurements due to the instrument's design or increments.

Analysing validity and theoretical relationships

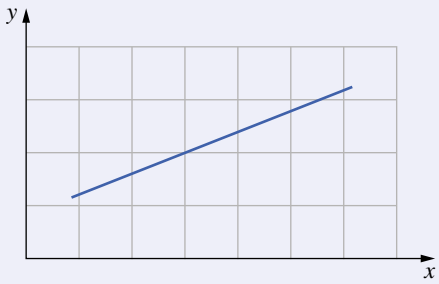
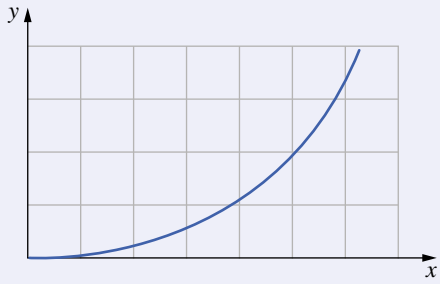
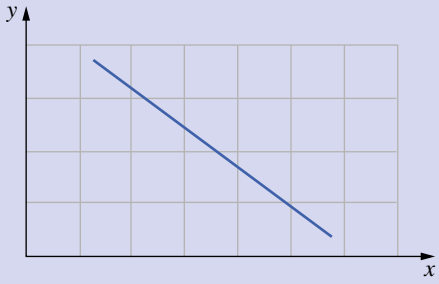
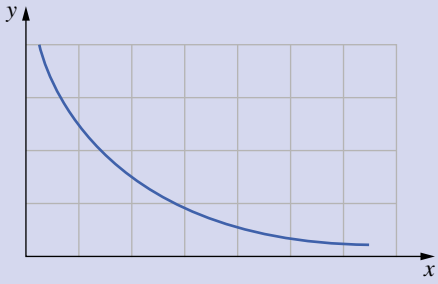
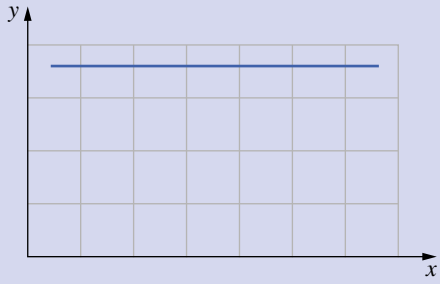
The results and data also need to be processed to look for trends, patterns or differences. Some of the first processes in analysing data are to use statistical calculations to determine the true values, uncertainties, errors and significance of the measurements. Once the quality of the data is understood then the validity in relation to established theoretical concepts can be analysed.

Analysis can also find **anomalies** and outliers in data, which are not valid measurements. Your record of observations may provide a reason for an outlier in your data if one is found. This can then be used to suggest improvements in the methodology to remove such measurements.

Trends in line graphs

Graphs are drawn to show the relationship, or trend, between two variables (Table 1.10.2). Remember that the results may be unexpected. This does not make the investigation a failure. However, the findings must be related to your research question, purpose and method.

TABLE 1.10.2 Graphs showing different trends and relationships between variables

Variables that change in linear or direct proportion to each other produce a straight, sloping trend line. 	Variables that change exponentially in proportion to each other produce a curved trend line. 
When there is an inverse relationship, one variable increases as the other variable decreases. It may be (a) direct or (b) non-linear. **a**  **b** 	When there is no relationship between two variables, one variable will not change even if the other changes. 

INTERPRETING

The final part of your investigation involves summarising your findings in an objective, clear and concise manner for your audience. Consider the message you want to convey when writing your discussion. Statements need to be clear and concise. At the conclusion of your discussion, the audience must understand the context, results and implications of your investigation.

The discussion is the part of your investigation in which you evaluate and explain your methods and results. You should interpret what the results mean. The key sections of the discussion are:

- interpreting and evaluating data
- evaluating the investigative method
- explaining the link between the investigation findings and relevant chemical concepts.

When your results have been processed and analysed, you must apply your scientific understanding and conceptual knowledge to offer explanations of what occurred and why. Your explanation of the results is an interpretation. Interpretations are limited by the methodology employed, the instruments used, the variables controlled and the raw data measured. Interpretations should never provide an explanation beyond the constraints of the experimentation and methodology. Interpretations are not meant to provide answers and comprehensive explanations, only a valid and reliable plausibility based on what was measured. To meet the student experiment word limit, the interpretation of results in your scientific report will need to be concise.

DISCUSSING RELEVANT CHEMICAL CONCEPTS

To make your investigation more meaningful, it should be explained within the right context, meaning the related chemical ideas, concepts, theories and models. Within this context, explain the basis for your hypothesis. For example, if you were studying the impact of temperature on the pH of acetic acid you could include the information in Table 1.10.3 in your discussion.

TABLE 1.10.3 Examples of how to include chemical concepts in your discussion

Key ideas	Example
definitions of key terms	'pH', 'weak acid' and 'equilibrium constant'
relationship between variables	the concentration volume of the acetic acid was controlled in the experiment; the temperature was such that water did not evaporate
chemical principles	Le Châtelier's principle and the relationship between $[H^+]$ and pH including relevant equations
sources of error	reducing random error by repeating measurements and calculating average

Relating your findings to a chemical concept

During the analysis stage of your investigation, you identified trends, patterns and mathematical models of your results. This is the framework needed in which to discuss whether the data supported or refuted the hypothesis. Ask questions such as these.

- Was the hypothesis supported?
- Has the hypothesis been fully answered? If not, explain why and suggest what could be done to either improve or complement the investigation.
- Do the results contradict the hypothesis? If so, why? The explanation must be plausible (reasonable) and must be based on the results and previous evidence.

Providing a theoretical context also enables comparison of the results with existing relevant research and knowledge. After identifying the major findings of your investigation, ask questions such as these.

- How does the data fit with the literature?
- Does the data contradict the literature?
- Do the findings fill a gap in the literature?
- Do the findings lead to further questions?
- Can the findings be extended to another situation?

Be sure to discuss the broader implications of your findings. Implications are the bigger picture. Outlining them for the audience is an important part of the investigation. Ask questions such as these.

- Do the findings contribute to or impact on the existing literature and knowledge of the topic?
- Are there any practical applications for the findings?

EVALUATING

In the discussion, you need to be able to:

- explain your results in relation to chemical ideas, concepts and theories
- discuss whether your data supports or refutes your research question
- discuss any secondary data you have found from journal articles or other reliable sources that is directly connected to the experiment in the interpretation and evaluation of your results and methodology.

Explain if your results support your observations. If they do, you should report that your results are consistent with the findings, otherwise, it is essential that you reflect on the contrasting results and identify or suggest possible explanations as to why the results do not support your observations. This could be due to differences in the measurement technique or other factors such as the controlled or measured variables. It might also help you to identify possible sources of error within your investigation. At this stage, it is important to check your calculations to make sure that you have not made an error.

Ask yourself questions relating to your research question and the literature regarding chemical concepts, as shown in Figure 1.10.2.

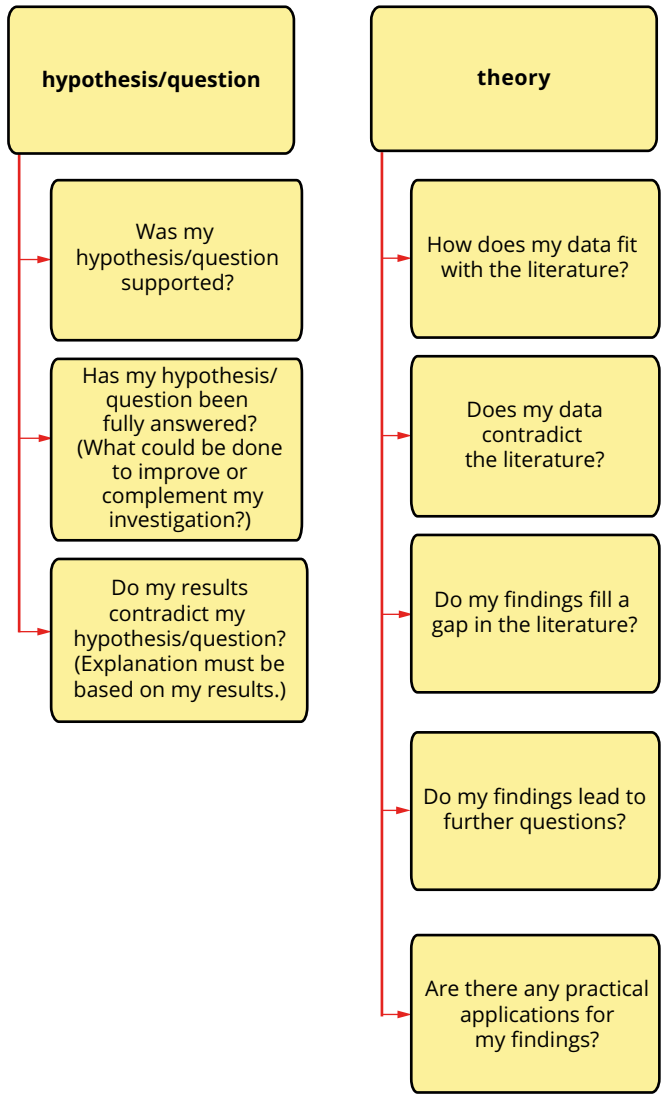


FIGURE 1.10.2 Use these questions to help relate your data to your research question.

Evaluating the method

The interpretation and evaluation criterion requires:

- critical evaluation of experimental processes
- suggested improvements and extensions to the experiment that are logically derived from the analysis of the evidence.

The following points can help your evaluation.

- Evaluate the method. When relevant, compare the chosen method with any other methods that might have been selected, evaluating the advantages and disadvantages of the selected method and the effect on the results.
- Discuss the results. Indicate the range of the data obtained from replicates.
- Explain how the sample size was selected. Larger samples are usually more reliable, but time and resources might have been scarce. Discuss whether the results of the investigation have been limited by the sample size.
- Discuss reliability in terms of the control group. A control group helps determine if a variable that should have been controlled has been overlooked and may explain any unexpected results.
- Discuss any source of systematic or random error and suggest ways of improving the investigation. For instance, the more times an experiment is repeated, the more reliable the results are.
- Identify issues that could affect validity, accuracy, precision and reliability of data.
- State sources of systematic and random errors.
- Identify any bias in any part of the investigation method, including sampling and measurements. Bias is a form of systematic error resulting from the researcher's personal preferences and can include poor definitions, incorrect assumptions, errors in design and methodology. Some biases cannot be eliminated, but should at least be addressed in the discussion.
- Evaluate the degree of accuracy and precision of the measurements for each variable of the hypothesis. Comment on the uncertainties obtained.
- Recommend improvements to the investigation if it is to be repeated.

Once any limitations or problems in the methodology have been identified, recommend improvements on how the investigation could be conducted if repeated. In the evaluation of the experiment ensure you discuss the broader implications of your findings.

DRAWING EVIDENCE-BASED CONCLUSIONS

To meet the top performance level in the ISMG (IA2), you need to insightfully interpret the experimental evidence. This must be demonstrated in your report by including a justified conclusion linked to the research question.

So, the report must analyse your data to link the findings from the experiment back to the research question that has informed your investigation. A conclusion is usually a paragraph that provides a justified and relevant response to your research question. Read the examples of strong and weak conclusions in Table 1.10.4 for the hypothesis and research question shown.

TABLE 1.10.4 Strong and weak conclusions to a research question and hypothesis

	Weak conclusion	Strong conclusion
Research question How does temperature affect the pH of water?	The results show that temperature does affect the pH of water.	Analysis of the results on the effect of an increase in temperature of water from 5°C to 40°C showed an inverse relationship in which the pH of water decreased from 7.4 to 6.8. These results support the current knowledge that an increase in water temperature results in a decrease in its pH.
Hypothesis An increase in the temperature of pond water will result in a decrease in the measured pH of the water sample.	The pH of water decreased as temperature increased.	An increase in temperature from 5°C to 40°C resulted in a decrease in the pH of the water from 7.4 to 6.8.

1.10 Review

SUMMARY

- Raw data includes the measurements and observations made during an experiment.
- Processed data is derived from processing and manipulating raw data.
- Processed data enables trends, patterns and differences to be identified.
- If the measurements between samples or tests fall within the uncertainty range of the instrument, then the variation in results could simply be due to the instrument.
- Interpretations of data attempt to explain the observed results.

KEY QUESTIONS

Retrieval

1 Name two types of data.

2 Define a systematic error.

3 State what a random error is.

4 State the evidence that is required to attain the top performance level in the analysis criterion.

Comprehension

5 Explain the difference between processing data and interpreting data.

6 Explain whether the following are mistakes, systematic errors or random errors.

a a student spills some solution during a titration

b the reported measurements are above and below the true value

c a weighing balance has not been calibrated

Analysis

7 A group of students wanted to test whether the amount of hydrogen gas produced from 0.5 g of zinc was different with 1.0 mol L^{-1} hydrochloric acid or 1.0 mol L^{-1} acetic acid.

Their hypothesis was that the acetic acid would not produce the same amount of hydrogen gas as it was a weak acid.

Their results are shown in the table below.

Trial number	Volume of hydrogen gas from hydrochloric acid (mL)	Volume of hydrogen gas from acetic acid (mL)
1	90 ± 2	86 ± 2
2	85 ± 2	86 ± 2
3	87 ± 2	87 ± 2
4	86 ± 2	88 ± 2
5	84 ± 2	85 ± 2
6	89 ± 2	84 ± 2
mean	87 ± 2	86 ± 2

Determine if the students' hypothesis is correct, based on their results.

1.11 Communicating and writing a scientific report

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- identify and explain the sections of a scientific report
- write a scientific report.

To write a scientific report some general conventions need to be followed. Even though there are many ways to present a report, the report must follow a scientific genre and meet the requirements of the QCAA Chemistry General Senior Syllabus. This module will provide a guide to writing an appropriate scientific report.

> **Your journal should contain all the information required to complete the scientific report. After all, it is a report and reports summarise research and information gathered on a topic. The scientific report does not require much time to complete when reporting from a comprehensive journal.**

SCIENTIFIC WRITING AND LITERACY

The words used by scientists (the agreed scientific language and terms) have specific meanings and may differ from your understanding of the term in everyday language (Table 1.11.1). This allows a common understanding of words across all languages, to convey scientific meaning.

TABLE 1.11.1 A comparison of common and scientific language

Term	Common language meaning	Scientific language meaning	Difference in meaning
sample	a representative part or a single item from a larger whole or group especially when presented for inspection or shown as evidence of quality	the specifically chosen physical representatives of a phenomenon that was tested, measured or observed during experimentation or an investigation	Very similar. The scientific term is specific to a controlled or measured phenomenon. The quality is not known until after analysis, though inspection is carried out through testing. In common language it can be used generically, while in scientific language it is specific to the independent variable.
results	to proceed or arise as a consequence, effect, or conclusion; to have an issue or result	the recorded evidence of the sample during experimentation or observation	Very similar. The scientific term requires measurement or explicit recording of the observed consequence or effect arising from the independent variable.
significance	something that is conveyed as a meaning often obscurely or indirectly; the quality of conveying or implying; the quality of being important	important; of consequence; expressing a meaning; indicative; includes all that is important; sufficiently great or important to be worthy of attention; noteworthy; having a particular meaning; indicative of something	Similar. The scientific term refers to the quality of being important. To establish importance statistical analysis has to have been conducted to achieve the meaning, or indicate sufficient difference, or worth and to indicate a particular meaning.
correlation	the state or relation of being correlated; specifically a relation existing between phenomena or things or between mathematical or statistical variables which tend to vary, be associated, or occur together in a way not expected on the basis of chance alone	a relationship existing between phenomena on the foundation of statistical or processed analysis	Almost identical. The scientific term refers to when data processing or statistics has been applied to the common term. As such the strength of the correlation can be predicted or assumed.

Your report must be written using scientific language and conventions, and should be fluent and concise. Carefully plan all parts of your report, including the introduction, the summary of the altered methodology, the results, the analysis (including the interpretation) and conclusion (including evaluation and suggested improvements). Having a plan helps to achieve fluent and concise writing.

Writing fluently and concisely

The report should be brief and comprehensive, so only use the words required to communicate your information. Writing a concise report avoids repetition and helps remain within the required word count. Use scientific language as it allows you to communicate details and knowledge in fewer words. Table 1.11.2 demonstrates communication of the same concept in a few different ways. Being fluent and concise will significantly influence the word count of the report and the quality of the writing.

TABLE 1.11.2 Communicating concepts in various ways

Concept	Communication	Commentary of communication
A weak acid has a higher pH than an equivalent concentration of strong acid.	A weak acid only partially dissociates into its ions.	This is fluent and concise, but lacks scientific terms or language to convey in-depth understanding.
	In a solution of water, a weak acid does not break up into its constituent ions, including the H^+ ion. The mathematical calculation of pH is done by taking the negative log (base10) of the hydrogen ion concentration, $-\log_{10}[H^+]$. On the other hand, strong acids do dissociate fully and completely into the ions. Therefore, a solution in water of a strong acid has a lower (closer to 1) pH than a weak acid of the same concentration.	This is fluent, but not concise. There is repetition (e.g. 'fully' and 'completely'—these terms have the same meaning). It also uses many words without using scientific terms to provide detail and understanding. This may be useful language in the journal when learning about a topic, but not in the scientific report.
	An aqueous solution of a weak acid is only partially dissociated into its ions. This means that the concentration of hydrogen ions in solution is low. Since the pH of a solution is the $-\log_{10}[H^+]$, the pH of a weak acid is much higher than a strong acid of the same concentration.	This is fluent and concise. In-depth understanding is communicated through scientific terms, which enables much information to be conveyed in fewer words.

Writing in a scientific genre

There are a number of genres or styles of scientific communication. The focus here will be on scientific reports. A report is a document that communicates a summary of information, focusing on the main points of interest. It uses headings, sections, tables and graphs to present information. A scientific report is written to scientific conventions including format and language.

Reporting

Using headings in scientific reports is essential. Table 1.11.3 lists headings that are commonly used in scientific reports and describes the information that would be provided under each heading. Sections can be broken down further into subsections. For example, the method can be broken into subsections like sampling techniques, preparation for experiment, equipment used and methodology. Some subheadings are suitable for more than one section; however, each scientific report will only use each heading and subheading once. It is best to ask your teacher about which headings they prefer and how to align your scientific report and its headings to the syllabus.

TABLE 1.11.3 Scientific report sections, headings and information

Scientific report section title	Common title alternatives	Expected information within the section
title	n/a	• a specific statement that outlines the expected relationship between the independent and dependent variables, or a question asking about the relationship between the independent and dependent variables
abstract	n/a	• summarises the entire experiment/investigation into a single paragraph outlining the main information for each section of the background information, method, results, analysis and conclusion • summary for each section is usually one to three sentences per section, usually less rather than more
introduction	• background information • background research • literature review	• provides the information already known or inferred from previous experimentation and scientific literature specific to the research question • explains the current scientific knowledge about the relationship between the independent and dependent variables and any other variables that may alter the relationship • must also make reference to the original experiment and justify the modification that was made
method • sampling technique • preparation • experiment	procedure	• outlines the exact details for other scientists to repeat the experiment including specific details about instruments, equipment models and precision, techniques employed and all information required for others to repeat the same results • is not common to differentiate the materials (equipment and instruments used) from the procedure that uses them
results • raw data • analysis • statistical analysis • interpretation	processed data analysis	• all the data, observations and results need to be presented to explain the interpretation and conclusion • must show all the required information to answer the research question
conclusion • analysis • interpretation • discussion • evaluation	• interpretation • discussion • evaluation • sources of error • suggestions for improvements/ modifications	• provides an explanation of the results including quality of experimentation (accuracy, precision, validity and reliability of the methodology) and relates the results to current scientific understanding (theory) • the strength of the relationship between the experimental evidence (data, observations or results) is to be stated • no new data is to be included in this section
references	n/a	• a list of all sources used in the scientific report

Scientific writing

Since the report is written for a scientific audience, it is important to ensure that the report uses appropriate scientific language and conventions. This contrasts with writing used in everyday situations.

The scientific report is to be written using paragraphs, with each paragraph explaining only one idea. The first sentence (topic sentence) of the paragraph introduces the topic. Following sentences provide the details of the idea. The final sentence concludes the idea. Each sentence should flow onto the next, slowly building the details of the explanation. The report should be brief and comprehensive, so you should only use the words required to communicate and use language that conveys detailed understanding.

Reports should be written using:

- the past tense—as the experiment was conducted in the past, so the report should be in the past tense
- the third person, passive voice and impersonal verbs—science uses this language convention (Table 1.11.4)
- scientific language—the terms used are specific to concepts, models and theories
- objective, unbiased language—avoid subjective and emotional or persuasive writing (Table 1.11.5)
- concise language—avoid unnecessary repetition and express ideas. Scientific language allows more details, knowledge and understanding to be communicated in fewer words. Use shorter sentences that are less wordy. Table 1.11.6 shows some examples of concise wording.

TABLE 1.11.4 Examples of first-person and third-person narrative

First person	Third person
I put cyclohexene and cyclohexane in two test tubes and then I added 5–6 drops of bromine water.	Cyclohexene and cyclohexane were placed in two test tubes and mixed with 5–6 drops of bromine water.
After I observed the reaction, I found that ...	After the reaction was completed, the results showed ...
The chemistry students in my group and I found ...	The results from this investigation showed ...

TABLE 1.11.5 Examples of unscientific and scientifc writing

Unscientific writing	Scientific writing
Examples of biased and subjective language: • The results are extremely bad/atrocious/ wonderful ... • This is terrible because ... • This produced a disgusting odour ... • Health crisis!	Examples of unbiased and objective language: • The results showed ... • The implications of these results suggest ... • This produced a pungent odour ... • Health issue
Example of exaggeration: • The object weighed a colossal amount, like an elephant.	Example of accurate language: • The object weighed 256 kg.
Examples of everyday or colloquial language: • The bacteria passed away. • The results don't ... • The researchers had a sneaking suspicion ...	Examples of formal language: • The bacteria died. • The results do not ... • The researchers predicted/hypothesised/ theorised ...

TABLE 1.11.6 Examples of verbose and concise writing

Verbose writing	Concise writing
due to the fact that	because
Smith undertook an investigation into ...	Smith investigated ...
It is possible that the cause could be ...	The cause may be ...
end result	result
in the event that	if
shorter in length	shorter

To produce a fluent report, the scientific language must be used without error so that the reader understands the meaning of the information easily. For the report to be concise there should not be any repetition. Being fluent and concise will significantly influence the word count and the quality of writing within the specified word limit.

Presenting scientific ideas

An efficient way of presenting complex data and explaining scientific concepts is through photographs, graphs, tables and scientific models such as flow charts and diagrams. Ensure you include:

- a descriptive title
- labels, captions or descriptions
- numbering; for example, Figure 1, Figure 2 or Table 1, Table 2 etc.
- a source if the work is not your own or is adapted from work that is not your own.

Using tables and graphs

In general, tables provide more detailed data than graphs. However, it is easier to observe trends and patterns in graphs, making them a very useful tool for presenting evidence. Pie charts illustrate percentages well, while bar charts and line graphs illustrate relationships between variables well. More information on tables and graphs can be found in Module 1.6.

Editing your report

Editing your report is an important part of the writing process. After editing your report, save new drafts with a different file name and always back up your files in another location. Pretend you are reading your report for the first time when editing. Once you have completed a draft, it is always good practice to read your work again hours or a day or two after you have completed it. When checking your own work, read the report out aloud.

When editing, look for content that is:

- ambiguous or unclear
- repetitive
- awkwardly phrased
- too lengthy
- not relevant to your research question
- poorly structured
- lacking evidence
- lacking a reference (if it is another researcher's work)
- spelt incorrectly
- grammatically incorrect.

Acknowledging sources

All the quotations, documents, publications and ideas used in your investigation need to be listed in the references and acknowledgements. In order to avoid plagiarism and to ensure creators are properly credited for their work, this must be completed accurately. References and acknowledgements also give credibility to your study and allow the audience to locate information sources should they wish to study it further.

Plagiarism is using other people's work without acknowledging them as the author or creator. To avoid plagiarism, include a reference every time you report the work of others; for example, at the end of a sentence or following a diagram. If you use a direct quotation from a source, enclose it in quotation marks. This will ensure you give credit to the original author and it will enable the reader to find the original source.

Referencing

The sources of your information must be acknowledged using a referencing style that is suitable for the purpose of the investigation. Check the preferred referencing style or convention of your teacher for in-text referencing and a complete **reference list**. APA (American Psychological Association) style is a commonly used referencing style.

The student experiment does not require a bibliography; a reference list is sufficient. A bibliography is a list of all the sources used during the research to develop understanding (including information in the journal) even if the information was not used directly or explicitly in the scientific report. A reference list only lists the sources used and cited (or in-text referenced) in the scientific report.

The sources must be listed at the end of the report in alphabetical order (by the author's last name or organisation name). The referencing needs to give the reader the opportunity of easily locating the source.

Compile your references in a separate document as you conduct the student experiment. This will save you time later.

In-text citations

Each time you write about the findings of other people or organisations, you need to provide an in-text citation and provide full details of the source in a reference list. In the APA style, in-text citations include the first author's last name and date in brackets (author, date).

The following example shows two types of in-text citation and reference list entry.

In-text citations
It was reported that in testing of five pro-oxidant additives added to commonly manufactured polymers, none resulted in significant biodegradation after three years (Selke et al., 2015).
Selke et al. (2015) reported that in testing of five pro-oxidant additives added to commonly manufactured polymers, none resulted in significant biodegradation after three years.
Reference list
Selke, S., Auras, R., Nguyen, T.A., Aguirre, E.C., Cheruvathur, R., & Liu, Y. (2015), Evaluation of biodegradation—promoting additives for plastics. *Environmental Science & Technology*, 49(6), 3769–3777.

ADDRESSING THE SYLLABUS INSTRUMENT-SPECIFIC MARKING GUIDE

It is imperative that your final scientific report addresses all the characteristics in the performance level descriptors of the student experiment instrument-specific marking guide (ISMG). Before you begin the scientific report it would be best to plan the sections and titles and then assign the ISMG characteristics to each section. It would be even better to discuss this with your teacher and develop a plan together.

Word limits can be assigned to each section. Apply a larger word count to the sections requiring explanations such as the introduction, discussion/conclusion and maybe the analysis (depending on the convention chosen). This word allocation will act as a guide, but is flexible.

When you edit your completed report assess whether it includes all the evidence in the four criteria (Research and planning, Analysis of evidence, Interpretation and evaluation, Communication) that make up the instrument-specific marking guide (IA2). These are the words that follow 'demonstrated by …'

1.11 Review

SUMMARY

- A scientific report has the following features.
  - Title: a specific statement that outlines the expected relationship between independent and dependent variables
  - Abstract: a single-paragraph summary of the entire experiment/investigation
  - Introduction: an explanation of the current scientific knowledge about the relationship between the independent and dependent variables and any other variables that may alter the relationship
  - Method: an outline of the exact details of the experiment, including specific details about instruments, equipment models and precision, techniques employed and all information required for others to repeat the same results
  - Results: present the data, observations, discussion and results in the most appropriate way to explain the interpretation and conclusion. The results must show all the required information to answer the research question
  - Conclusion: an explanation of the results, including quality of experimentation. The explanation is related to current scientific understanding. The strength of the relationship between the experimental evidence is stated. Do not put any new data into this section
  - References: a list of all sources used in the scientific report.
- The scientific report must address the requirements of the syllabus.

KEY QUESTIONS

Retrieval

1 Describe what information is included in the following sections of a scientific report.

a method

b conclusion

2 Recall in which section of a scientific report you would find processed data.

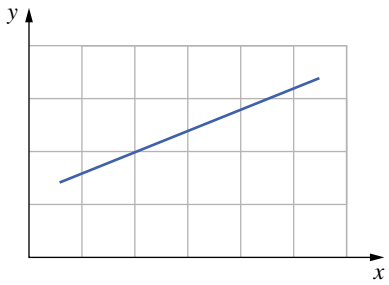
Comprehension

3 Explain the difference between a bibliography and a reference list.

Analysis

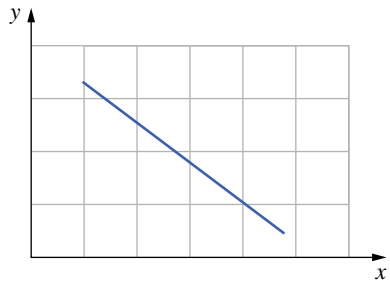
4 Use the graphs below to answer the following questions.

a **Direct or linear proportional relationship**



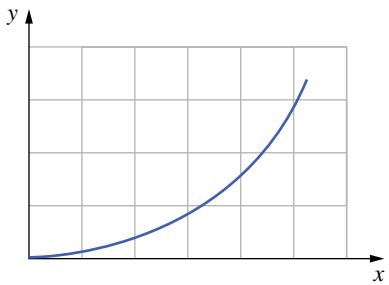
- Variables change at the same rate (graph line is straight, slope is constant).
- Positive relationship—as x increases, y increases.

b **Inverse direct or linear proportional relationship**



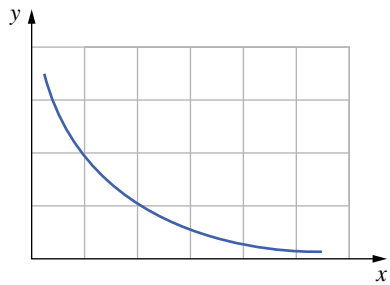
- Variables change at the same rate (graph line is straight, slope is constant).
- Negative relationship—as x increases, y decreases.

c **Exponential relationship**



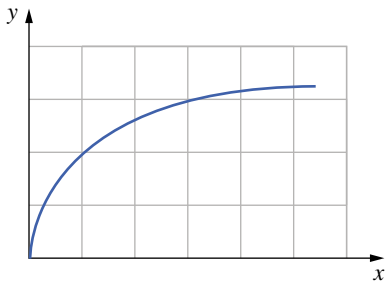
- As x increases, y increases slowly, then more rapidly.

d **Inverse exponential relationship**



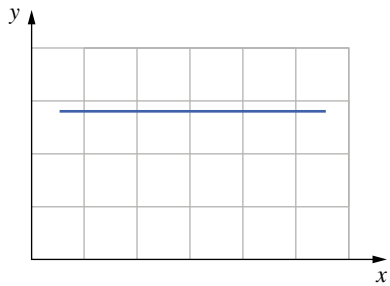
- As x increases, y decreases rapidly, then more slowly, until a minimum y value is reached.

e **Exponential rise, then levels off or plateaus (stops rising)**



- As x increases, y increases rapidly at first, then slows, then finally does not increase at all—y reaches a maximum value.

f **No relationship between *x* and *y***



- As x increases, y remains the same.

a Identify the graph/s that shows that the dependent variable is increasing at a constant rate.

b Identify the graph/s that shows that the dependent variable is decreasing at a decreasing rate.

c Identify the graph/s that describes the following observation.

You are measuring the volume of air in a vertically held syringe. A number of books are placed on top of the syringe and you observe the volume of the air decrease at a decreasing rate.

d Describe the relationship between the dependent variable and the independent variable in graph **f**.

5 Explain what might cause a sample size to be limited in an investigation.

PART C RESEARCH INVESTIGATION (IA3)

The QCAA stipulates that you complete the Research investigation (IA3) in Unit 4.

The research investigation requires you to locate and use information beyond the scope of the knowledge and data you have been given. It requires you to investigate a claim by drawing on secondary evidence from credible scientific sources such as scientific journals, books, government websites, universities, independent research bodies or science and technology manufacturers.

Research conventions are to be used to analyse and interpret the evidence in order to reach a justifiable conclusion about the claim.

The QCAA Chemistry General Senior Syllabus states that you must work individually to develop and investigate your own research question based on a number of possible claims provided by your teacher.

The research investigation constitutes 20% of the total assessment in chemistry.

The research investigation may be presented in:

- written form (e.g. scientific report), 1500–2000 words, or
- multimodal presentation form (e.g. poster presentation), 9–11 minutes.

A summary of the instrument-specific marking guide (ISMG) for the research investigation is provided below. It includes the objectives and marking for this summative internal assessment.

Criteria	Assessment objectives	Demonstrated by	Marks
Research and planning	• apply understanding • perform an investigation	• a considered rationale showing how the research question was developed from the claim • a research question that is specific and relevant • collected sources that are sufficient and relevant	6
Analysis and interpretation	• analyse the evidence sourced during the research • interpret the research evidence	• collection of sufficient and relevant sources • detailed and careful coverage of relevant trends, patterns and relationships • detailed and careful coverage of the limitations of the evidence • justified scientific arguments based on evidence	6
Conclusion and evaluation	• interpret the evidence from the research • evaluate the processes, claims and conclusions within the research	• a conclusion that is justified and addresses the research question • insightful examination of the quality of the evidence • extension of investigation findings that are credible • consideration of possible improvements and extensions to the investigation that are relevant to the claim	6
Communication	• present the research findings, including arguments and conclusions	• scientific language and representations that are concise and fluent • suitable use of genre conventions • appropriate referencing conventions to acknowledge sources.	2
Total			20

The scientific inquiry is not a linear process. Scientists will not necessarily complete these steps in the stated order and some steps may need to be repeated or altered to more accurately address the research question.

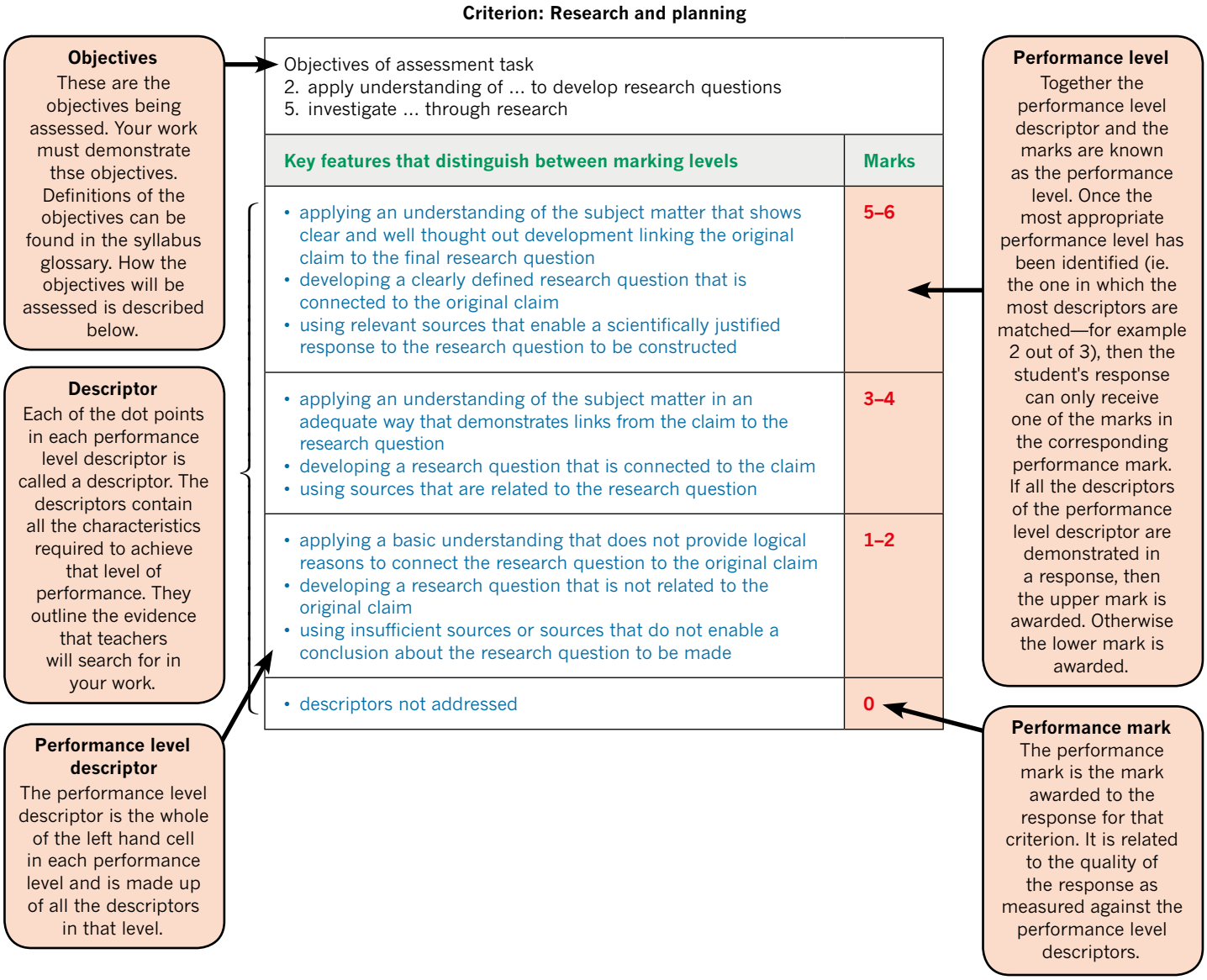
INSTRUMENT-SPECIFIC MARKING GUIDE

Student responses are assessed against an instrument-specific marking guide (ISMG). In developing your research question and planning your response it is important to always have in mind the assessment objectives and in particular the characteristics that are described in the performance level descriptors.

The major features of the ISMG are outlined below.

- Just as with the student experiment, the ISMG is organised into four criteria: research and planning, analysis and interpretation, conclusion and evaluation and communication.
- Criteria are differentiated into performance levels, against which the qualities of the responses are assessed.
- A performance level comprises a mark, which may be a single mark or two-mark range, and a performance level descriptor.
- The performance level descriptor describes the characteristics that are demonstrated by a response at this quality.
- Each dot point is referred to as a descriptor and can be made up of single or multiple characteristics.

A summary of the objectives and marking for the criterion Research and planning of the research investigation is provided below.



The following modules outline the steps that assist the development of the research investigation report.

1.12 Developing the research question from a claim

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- analyse a claim to identify scientific concepts, variables and measurable terms within a claim
- develop a research question from a claim.

The research question should specifically address one of the concepts associated with the claim. Your teacher will provide a number of possible claims. You will develop your own research question based on one of these claims. The research question should clearly state the relevant variables. Secondary evidence should be used to evaluate the claim. All the research and the research investigation should be directly related to the research question. Therefore, the process begins with the claim and understanding the concepts it addresses.

UNDERSTANDING THE CLAIM

The QCAA Chemistry General Senior Syllabus defines a claim as 'an assertion made without any accompanying evidence to support it'.

The assertion or claim can be a sentence, a statement within a sentence, the title of an article, a quote or anything published in any form. Your research question will focus your investigation, necessitating evidence to be gathered so that the claim can be evaluated.

So how is a research question formed from a claim that is not supported by evidence? The claim itself has to be analysed and understood. Within the claim, identify one or more of the following:

- known scientific concepts
- variables
- measurable terms
- ideas related to concepts
- a term that is stated to influence another.

You should record all the information you collect during the investigation in a journal, including the process of developing a research question from a claim. This will be used in your research investigation report to address the ISMG characteristics about developing a research question from a claim. Write down all the elements found in the claim and try to categorise them using the above list. Each element within the claim may suit more than one category. Table 1.12.1 outlines an example of analysing and categorising elements of a claim.

TABLE 1.12.1 Three examples of analysing and classifying elements of a claim

Example 1		
Claim	A battery made of two teaspoons of salt can power an LED bulb for 8 hours.	**Classifying elements of the claim** How much power is generated? • length of time (8 hours) • amount of light needs to be practical (at least 22 W) What is the electrochemical reaction? • the reactants are readily available and cheap • do they generate electricity or store it? Are the products of the reaction safe? • no likelihood of fire • if water is electrolysed what happens to the hydrogen and oxygen produced? • concentration of the solution
Elements in the claim	• How much power is generated? • What is the electrochemical reaction? • Are the products of the reaction safe?	

Example 2		
Claim	Biodiesel is better for the environment than diesel.	**Classifying elements of the claim** Define the term 'better'. • carbon neutral • fewer toxic chemicals released Non-renewable versus renewable resources. • most biodiesel is produced from crops • petrodiesel is derived from oil Energy density of biodiesel is less than that of petrodiesel. • biodiesel and petrodiesel are mixtures of compounds • energy density is related to the compounds in the fuel
Elements in the claim	• Define the term 'better'. • Non-renewable versus renewable resources. • Energy density of biodiesel is less than that of petrodiesel.	

Example 3		
Claim	A car powered by a hydrogen fuel cell can travel 800 km on a single tank of fuel.	**Classifying elements of the claim** Hydrogen fuel cell • how does it work? • efficiency of energy conversion • storage capacity Environmental benefits • fewer pollutants released • products are non-toxic and safe Safe storage and production of hydrogen • how much hydrogen would be required for all vehicles for a year? • in the event of an accident is the car likely to explode? • how will the hydrogen be stored in the car?
Elements in the claim	• hydrogen fuel cell • environmental benefits • safe storage and production of hydrogen	

Separating the claim into elements, such as related terms and concepts, enables you to formulate variables, measurable items and questions.

FORMING A QUESTION

A research question needs to be formed from the claim, as the variables stated in the claim may not be measurable or directly observable and therefore they may not be scientific.

After **extrapolating** and expanding the claim further into possible scientific elements, each of these elements can be used to form a question (Table 1.12.2). It is best to formulate a number of questions related to the claim and write them all down in your journal. Each question must specify a dependent variable and enable a response that will evaluate the validity or the reliability of the claim.

This necessitates forming questions and using the elements of the claim in the phrasing of the research question. To complete this task you will need to have an understanding of the dependent and independent variables related to the claim and the relationship between the variables. The claim must identify the dependent variable. The claim may also specify the independent variable.

Some guidelines to help form a question include:

- finding the dependent variable in the claim or refining it by rephrasing it into something measurable
- choosing an element of the claim to become the independent variable or identifying it in the material.
- phrasing a question to ask if the independent variable will influence, cause or correlate with the dependent variable
- writing a few different questions. Usually the questions improve as you write more, which allows the formulation of a more developed research question

Read through Table 1.12.2 to see examples of questions formed from the elements of the claims that are refined.

TABLE 1.12.2 Three examples of questions formulated from a claim

Example 1	
claim	A battery composed of two teaspoons of salt can power an LED for eight hours.
elements of a claim	• How much power is generated? • What is the electrochemical reaction? • Are the products of the reaction safe?
formulated questions	Is a salt water battery capable of providing power for use in homes? What is the power output and capacity of the seawater cell?

Example 2	
claim	Biodiesel is better for the environment than diesel.
elements of a claim	• define the term 'better' • non-renewable versus renewable resources • energy density of biodiesel is less than petrodiesel
formulated questions	Could biodiesel replace petrodiesel as a fuel for Australian vehicles? Is biodiesel less polluting than petrodiesel?

Example 3	
claim	A hydrogen fuel cell car can travel 800 km on a single tank of fuel.
elements of a claim	• hydrogen fuel cell • environmental benefits • safe storage and production of hydrogen
formulated questions	How much hydrogen is required to drive a car 800 km? Can Australia produce enough hydrogen to meet current demand for fuel?

Refining the research question

It is possible that one of the questions you write in your journal, from the elements in the claim, will become your research question. As you conduct research into the concepts of the independent and dependent variables, new information will refine the question.

The process of developing a research question is often cyclical, as shown in Figure 1.12.1.

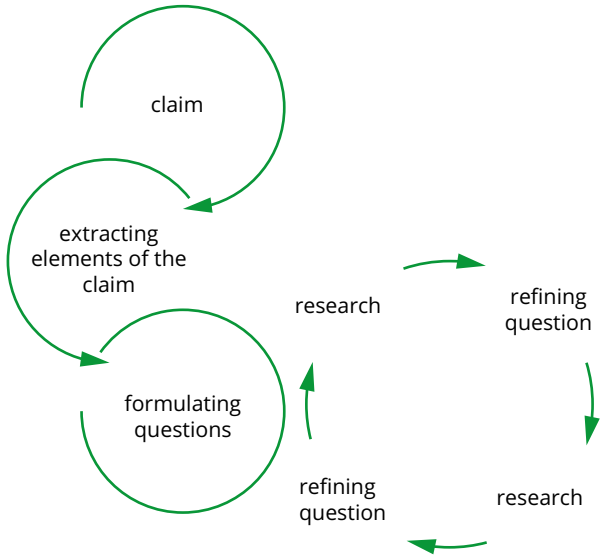


FIGURE 1.12.1 A chart of a common process for developing a research question. This cycle can be repeated as many times as necessary until you are satisfied with the research question.

It is important to record your development of conceptual understanding and the knowledge you gain about the relationships between variables. The research investigation requires evidence of the development from the claim to the research question, as stated in the ISMG.

The research question and the development of the research question from the claim using research, scientific concepts, knowledge and understanding is related to the ISMG dot points after the term 'demonstrated by'.

During the research, continue to record your findings in your journal and make note of any ideas that may arise related to the questions. As your knowledge and understanding about the variables is developed, refine the question to be more specific.

The goal is to develop the research question to a point at which exact data or evidence can be found regarding the variables in the question. Hence it will develop into a research question when evidence from research can answer the question. Table 1.12.3 demonstrates how a formulated question can be transformed into a developed research question.

TABLE 1.12.3 Development of the original questions formulated into research questions

Example 1		
claim	A battery composed of two teaspoons of salt can power an LED for eight hours.	
formulated question	Is a salt water battery capable of providing power for use in homes?	What is the power output and capacity of the seawater cell?
refined research question	Can a salt water battery power a 22 W LED light for eight hours?	How much energy can a salt water battery produce?

Example 2		
claim	Biodiesel is better for the environment than diesel.	
formulated question	Could biodiesel replace petrodiesel as a fuel for Australian vehicles?	Is biodiesel less polluting than petrodiesel?
refined research question	How much soybean is required to produce sufficient biodiesel to replace all the petroleum-based fuel in Australia?	Are the greenhouse gas emissions from a biodiesel car travelling 15 000 km lower than an equivalent car fuelled with petrodiesel?

Example 3		
claim	A hydrogen fuel cell car can travel 800 km on a single tank of fuel.	
formulated question	How much hydrogen is required to drive a car 800 km?	Can Australia produce enough hydrogen to meet current demand for fuel?
refined research question	What is the volume of hydrogen required to power a hydrogen fuel cell car for 800 km?	Are current production methods able to produce sufficient hydrogen to fuel all vehicles in Australia?

In your research investigation report, your journal will be used to write the considered rationale for the research question, displaying its clear development from the claim. This will be achieved by using the research in your journal to outline its step-by-step development, justifying the steps using scientific concepts, knowledge and understanding, as shown in Figure 1.12.1.

The QCAA Chemistry General Senior Syllabus defines 'specific' as *clearly defined or identified; precise and clear in making statements or issuing instructions; explicit* and 'relevant' as *bearing upon or connected with the matter in hand; to purpose; applicable and pertinent; having a direct bearing on*.

Therefore, a specific research question must explicitly identify the dependent and independent variables. The research question must be connected to the considered rationale and the topic of study.

1.12 Review

SUMMARY

- A claim is an assertion made without any accompanying evidence to support it.
- Research questions can be developed from claims by identifying the underlying scientific concepts and variables of a claim.
- The number and nature of the sources selected will depend on the specific nature of the claim but need to be sufficient to be able to address the claim within the assessment conditions.

KEY QUESTIONS

Retrieval

1 Define a claim.

2 State what a research question should explicitly identify.

Comprehension

3 Explain why the research question is refined during the research investigation process.

4 Explain the relationship between research and understanding, and the research question that is relevant to the ISMG.

Analysis

5 Propose a question for each of the following claims.

a Biofuels are a realistic alternative to traditional petroleum-derived fuel.

b The chemicals in cosmetics are killing you.

c The addition of sodium carbonate to soaps can improve their effectiveness.

1.13 Finding and choosing suitable resources

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- distinguish between primary and secondary sources
- locate a range of primary and secondary sources
- determine the validity and reliability of a source.

When gathering scientific evidence for the research investigation, source it from reputable publications including:

- scientific journals—research papers and scientific reviews
- scientific articles written by organisations who apply scientific research to their industry
- commercial articles such as science magazines, newspapers and also websites.

The research investigation must include a reference list of sufficient and relevant sources. The QCAA Chemistry General Senior Syllabus defines 'sufficient' as *enough or adequate for the purpose* and 'relevant' as *bearing upon or connected with the matter in hand; to the purpose; pertinent; applicable and pertinent; has direct bearing on.* Figure 1.13.1 points out the features of sources deemed sufficient and relevant.

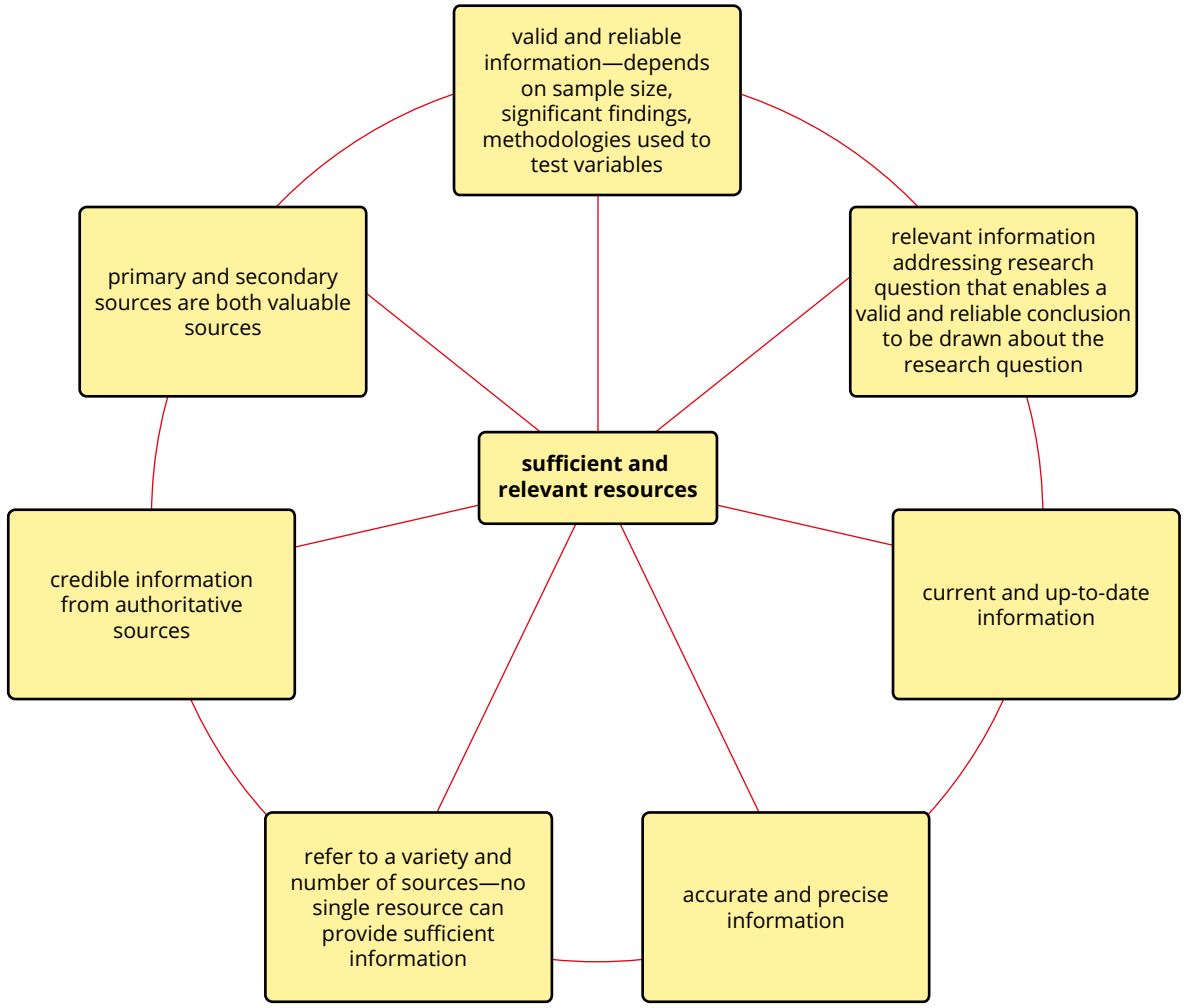


FIGURE 1.13.1 Features of sources suitable for the research investigation

SOURCING INFORMATION

Consider whether the information you use is from a primary or secondary source.

Primary and secondary sources

Table 1.13.1 summarises the characteristics of primary and secondary sources. Sometimes the same information may be contained within a primary and a secondary source, depending on when and by whom it was written. For example, a scientist's journal article on a clinical trial of treatments for teenage obesity is a **primary source**, while a general magazine article about teenage obesity, written by a journalist and referring to the scientific study, is a **secondary source**.

TABLE 1.13.1 Summary of primary and secondary sources

	Primary sources	Secondary sources
characteristics	• first-hand records of events or experiences • written at the time the event happened • original documents	• interpretations of primary sources written by people who did not see or experience the event • use information from original documents but rework it
examples	• results of experiments • scientific journal/magazine articles • reports of scientific discoveries • photographs, specimens, maps and artefacts • interviews with experts • websites (if they meet the criteria above)	• textbooks • biographies • newspaper articles • magazine articles • radio and television documentaries • websites that interpret the scientific work of others • podcasts

A primary source is written by the observer or witness of an event or the scientist who conducted the research. The information has only been processed by the original observer, therefore it is the least biased of all available sources of information. However, even primary sources may be biased, as the observer or researcher had to make choices related to the observation, control of variables, use of instruments and choices for processing data.

Secondary sources of information are not eyewitness accounts but interpretations of events by other people. As second-hand information, accuracy and reliability may be reduced and events may be interpreted through the writer's perception and bias. You should aim to use a wide range of data sources when using secondary data, to cross-check for accuracy, reliability and validity of information.

When searching for information and evidence, follow these guidelines.

- Determine if it is a primary or secondary resource.
- Confirm that it is valid.
  - Check that it contains information that is specifically related to the claim.
  - Check the evidence and information is pertinent to the variables in the research question.
- Assess its reliability.
  - Is it current/recent information?
  - Is it up-to-date in its understanding of relationships?
  - Is the evidence equivalent to other sources?
  - Check credibility—consider who the author is, their qualifications and expertise.
  - Evaluate the methodology, including what variables were controlled or measured.

Articles in scientific journals

Peer-reviewed scientific journals are excellent sources of information. Journals are a collection of scientific reports written by scientists who conducted the research. The reports and articles found in scientific journals are published primary sources, meaning they are the results of the experiments (Figure 1.13.2).

Open Journal of Polymer Chemistry, 2015, 5, 34-40
Published Online August 2015 in SciRes. http://www.scirp.org/journal/ojpchem
http://dx.doi.org/10.4236/ojpchem.2015.53004

Scientific Research Publishing

A Review of Vegetable Oil-Based Polymers: Synthesis and Applications

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Abstract

The reviewed work addressed the shift in focus from conventional polymers to bio-based and renewable polymers. The environmental attributes of the renewable polymers make them preferred choice of matrix. The properties of the matrices from renewable origin could compete in high end applications. The composition of the fatty acids in plant seed oil was discussed and the determination of the level of unsaturation used the iodine value. This review also extensively discussed the values of various fatty acid components present in the oils. Areas of application of the thermosetting polymers obtained from plant seed oils were also discussed.

Keywords

Polymer, Fatty Acid, Renewable, Bio-Based, Iodine Value

1. Introduction

Health-related issues, stringent environmental protection policies, search for cost-effective and alternative materials, and the quest for renewability, sustainability, and high-performance materials for technical applications have led to intense research in the production of renewable thermosetting polymers from plant seed oils and shift in focus from the petrochemical based polymers. Bio-based polymers are gaining overwhelming interest and recognition worldwide due to the health, safety, and environmental concerns associated with the conventional synthetic polymers. These bio-based polymers are renewable, biodegradable, and environmentally-friendly. The examples of the bio-based polymers are thermosetting polymers from plant seeds such as soybean oil, sun flower oil, cashew nut oil and linseed oil rapeseed oil. There are also the thermoplastic counterparts such as poly-lactic acid PLA from maize/corn, poly-hydroxy buterate poly-capro lactone and so on.

How to cite this paper: Adekunle, K.F. (2015) A Review of Vegetable Oil-Based Polymers: Synthesis and Applications. *Open Journal of Polymer Chemistry*, **5**, 34-40. http://dx.doi.org/10.4236/ojpchem.2015.53004

FIGURE 1.13.2 An extract of a research report in a scientific journal.

Access to scientific journals can be difficult as many journals require you to purchase a subscription or membership, though some are free. Figure 1.13.3 provides ideas for accessing scientific journals.

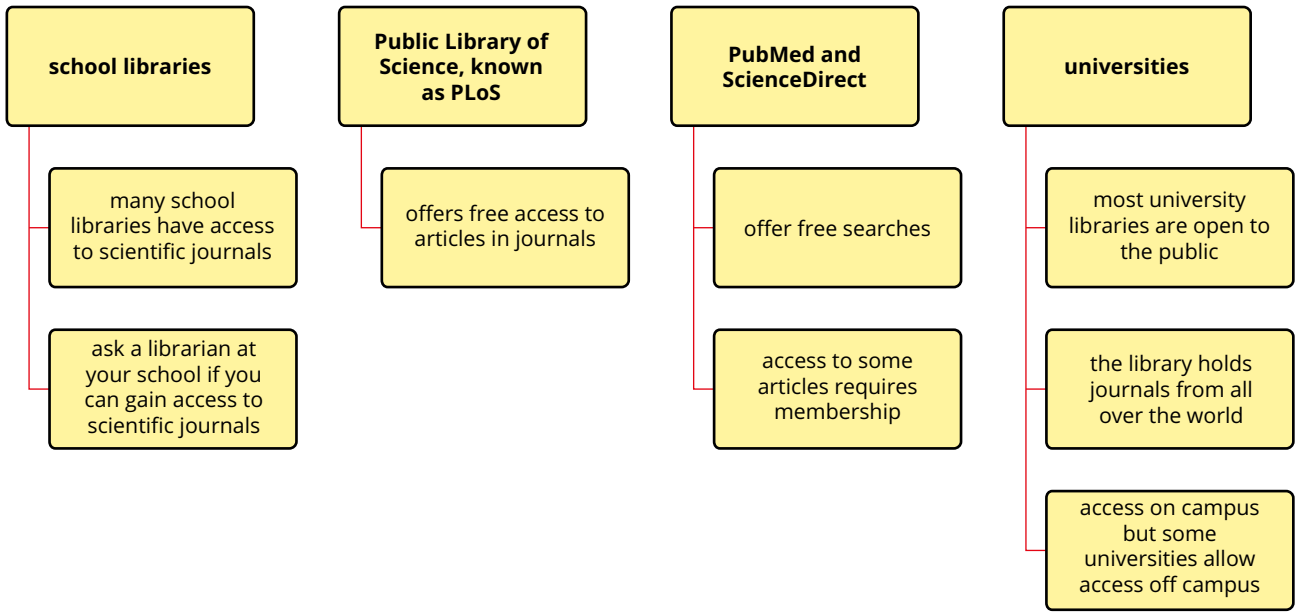


FIGURE 1.13.3 Suggestions and information on accessing scientific journal articles

Scientific articles are excellent sources of information, but also have their drawbacks as sources for the research investigation. Table 1.13.2 outlines some advantages and disadvantages of sourcing and using articles in scientific journals for the research investigation.

TABLE 1.13.2 Advantages and disadvantages of scientific articles

Advantages	Disadvantages
• written by experts • authoritative information (peer-reviewed) • most current information • logical, organised layout • content is relevant to the topic • contains an abstract that summarises all information in the article (if you don't find the information in the abstract, the article is not relevant) • primary source	• information is complex and challenging to understand • complex language and advanced processing and analysis of data • requires a high level of scientific literacy to understand • may be time consuming to read and analyse • well-established concepts do not have recent published articles • may be difficult to locate

Books and physical publications

Secondary sources such as good science magazines and books are valuable sources of secondary information.

The first source you should use is your textbook. The language and concepts are presented specifically for secondary school students. In addition, the textbook addresses the syllabus objectives. Non-fiction books and magazines will probably be commonly used resources for the research investigation. Common commercial science magazines you might find in your school library include *The Helix*, *Cosmos*, *Scientific American* and *New Scientist* (Figure 1.13.4). Table 1.13.3 outlines some advantages and disadvantages of non-fiction books as sources for your research.



FIGURE 1.13.4 A science magazine you might find in your school library

TABLE 1.13.3 Advantages and disadvantages of book resources

Advantages	Disadvantages
• may be written by experts • potentially authoritative information • logical, organised layout • content is relevant to the topic • contain table of contents and index to help find relevant information • easily located in libraries • written in language that is understandable	• may not have been published recently • usable by only one person at a time • may have more bias than primary sources

Searching online

Online sources include online scientific organisations such as CSIRO, NCBI, AIMS, Bioscience (Oxford Academic) and other university publications and press. Many government and privately funded science organisations publish material, along with not-for-profit scientific organisations. Websites may direct you to magazines and scientific journals, such as those described above, the news, podcasts, blogs and videos (institutional, company and personal).

Information located on the internet requires very careful scrutiny. The openness and ease of publishing on the internet means information may not be valid and reliable. Table 1.13.4 outlines some advantages and disadvantages of locating and using information online.

When searching for relevant information, you need appropriate search terms to enter into a search engine. These tips can help your search.

- Break your search statement into concepts and key words.
- Find synonyms, other related terms and concepts that apply to the topic.
- Create concepts of 1–3 words to enter into the search engine.
- Try different combinations of terms.
- Do not settle for the first sites on the list or your first attempt—look beyond the first page of results.
- Look through the results for sites from science organisations and research institutions (e.g. CSIRO, WEHI, NIH; .gov, .org), universities (.edu) and science journals and magazines.

TABLE 1.13.4 Advantages and disadvantages of internet resources

Advantages	Disadvantages
• quick and easy to access • allows access to hard-to-find information • access to the whole world; millions of websites • information is potentially more up-to-date • may be interactive and use animations to enhance understanding	• may not be reliable, valid or credible • can easily side-track with non-relevant information • a lot of 'junk' sites and potentially more biased material • need to discern search engine results to find most useful sites • cannot always tell how up-to-date information is • can be hard to tell who has responsibility for authorship • information may not be well ordered

Overview of resources

Your textbook should be your first source of reliable information. Other information should be consistent with this. Articles published in journals and magazines often present findings of new research, which may or may not be confirmed later, so be careful not to treat such sources of information as established fact. Scientific journals are peer-reviewed (critically reviewed by other specialist scientists), which gives them more credibility than other sources.

SKILLBUILDER 1.13.1

Evaluating sources for validity and reliability

Determining the validity and reliability of a source can be a challenging task. For some sources, it is easy to find details about the author, evidence and concurrency, while others only contain content and do not offer any other details. Another difficulty is when learning about a new topic or concept, we are all novice learners so it can be challenging to tell if a source is valid or not.

Table 1.13.5 outlines an example of evaluating a resource step-by-step for an article related to the synthesis and applications of vegetable-based polymers.

TABLE 1.13.5 Evaluation of a resource

Source evaluated: *A Review of Vegetable Oil-Based Polymers: Synthesis and Applications*			
Criteria		**Decision**	**Support/justification**
primary or secondary	Is this an eyewitness account or a second-hand source?	secondary	• review of current status of polymer research in the field • results, findings and implications from other research published in article
validity	Does it contain information that is specifically related to the topic?	yes	• outlines information directly related to the synthesis and use of biologically sourced polymers
	Is the evidence and information pertinent to the variables in the research question?	yes	• information is specific to the composition of fatty acids present in different oils
reliability	Is it current/recent information?	yes	• published August 2015
	Is it up-to-date in its understanding of relationships?	yes	• information outlined about the possible applications and research being undertaken with the different fatty acid is current (up to start 2015)
	Is the evidence equivalent to other sources?	yes	• the article is a review so presents the work from different articles
	Check credibility—consider who the author is, their qualifications and expertise.	yes	• author Kayode F. Adekunle is based in two research organisations • *Open Journal of Polymer Chemistry* is a reputable peer-reviewed journal • the article has been cited several times in other research work
	Try to find the sample size.	N/A	
	Try to establish what variables were controlled or measured.	N/A	

A judgement could be made about the credibility of this source, such as:

The information and evidence was published by experts in a peer-reviewed journal article that is concurrent and with variables of experimentation known and directly related to the claim and research question. Though as the results are new, it is yet to be seen if they are substantiated, therefore affecting the reliability of the evidence. This resource is both valid and reliable.

1.13 Review

SUMMARY

- Scientific evidence for the research investigation can be sourced from numerous publications including scientific journals, scientific articles and commercial articles.
- A primary source is written by the observer/witness of an event, or the scientist who conducted the research.
- A secondary source is a document that refers to or analyses a primary source.
- It is important that all sources are evaluated for their credibility, validity and reliability.

KEY QUESTIONS

Retrieval

1 Define the following.
- **a** a primary source
- **b** a secondary source

Comprehension

2 Determine whether each of the following is a primary or a secondary source.
- **a** a newspaper article about climate change
- **b** an experiment to investigate chemical changes when mixing combinations of chemicals
- **c** an interview with a forensic scientist about using science to track criminals
- **d** a website with information about the concentration of atmospheric pollutants emitted from a vehicle

Analysis

3 Determine whether each of the following is a primary or a secondary source.
- **a** an interview with a polymer scientist about using biodegradable polymers for plastic shopping bags
- **b** a website with information about the equilibrium conditions for the contact process
- **c** an experiment to investigate the effect of temperature on the electrolysis of copper sulfate solution
- **d** a newspaper article about the environmental and economic impact of green chemistry

4 You are learning about the use of fuel cells and are searching for information about fuel cells in space craft. From the list below, determine the best resource to use. Explain your answer.
- **A** the book *Fuel Cells and their Applications*, published in 2006
- **B** the article 'Batteries and Fuel Cells in Space' by G. Halpert, published by the Electrochemical Society in 1999
- **C** the website www.nasa.gov/topics/technology/hydrogen/hydrogen_2009.html, accessed on 30 October 2015

1.14 Research: taking and organising notes

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- use your scientific journal to take and organise notes and to refine experimental procedures
- paraphrase information found in primary and secondary sources.

As previously mentioned, a journal should be kept to record all the ideas, research and developments of your research investigation. Once all the investigative work is complete, the information in your scientific journal should form the basis of your response. There is no need to produce new work as it is already completed in the journal.

Scientists organise their journal notes with the following general features:

- a date for each journal entry
- journal entries include:
  - ideas, observations, proposals and questions
  - background information for ideas, observations, proposals and questions
  - refinements
  - personal explanations of information, concepts, ideas, observations, proposals and questions (this often includes diagrams)
  - results, data and evidence
- a record of the origin of information (recording sources).

RECORDING DATE OF JOURNAL ENTRIES

Always place the date at the beginning of your work. This is done by professionals worldwide to catalogue and file information. When trying to find previous work completed, most people search their memory as to when they completed the work. If you always date your work and research, it will become a simple yet effective filing system.

RECORDING JOURNAL ENTRIES

Each journal entry should follow a cataloguing system; most typically this is the date and a title. A reference point or cataloguing system helps you to find information when you are searching for it later.

Ideas, observations, proposals and questions

You may be surprised how often simple ideas, observations, proposals and questions influence, direct and help your research days or weeks later.

Your ideas, observations, proposals and questions could be related to:

- the variables or concepts involved in your investigation
- new terms you were exposed to and do not understand
- data or evidence you do not currently understand but know to be important to a part of your investigation
- statistics about significance in the analysis of some information
- ideas and proposals about possible future research and questions.

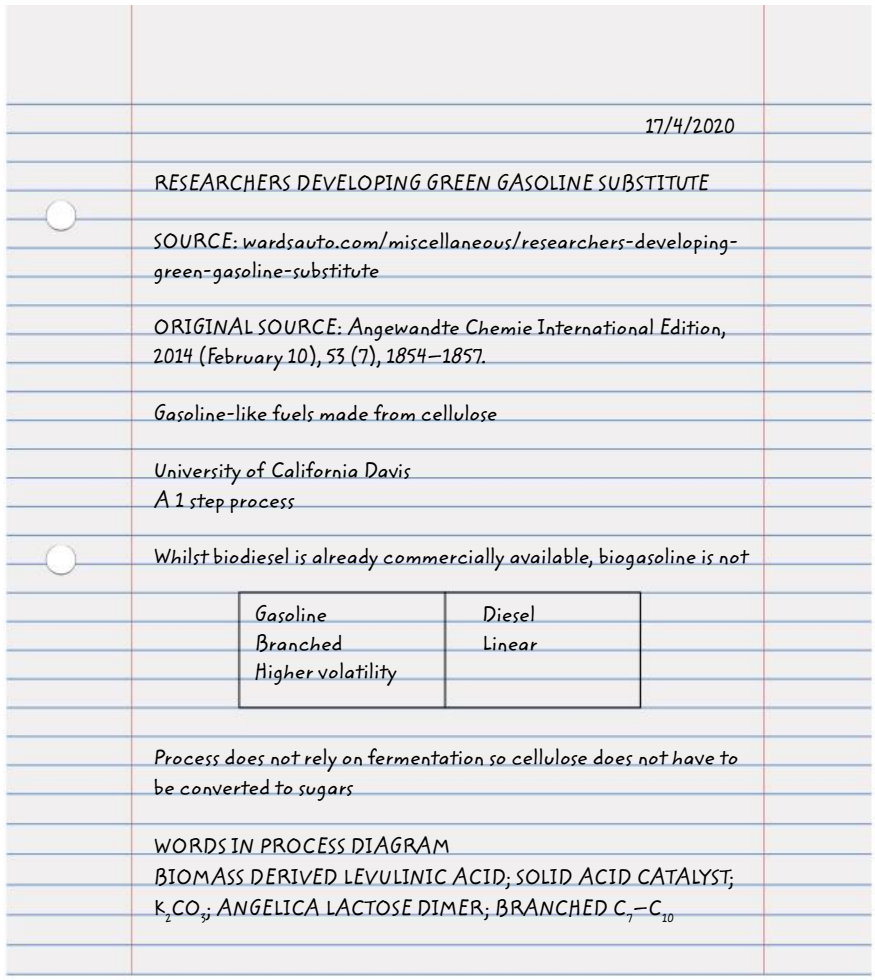
Journal entries usually record the date and a title for the entry. These titles are often related to the researcher's own work and objectives rather than the title of the source. The title of the source is recorded when the origin is recorded.

Record all of these in your journal. The value and benefit they may offer later could include:

- saving you time by:
  - not researching the same idea twice
  - helping you to link ideas from one day or week to the next when you return to your work
  - suggesting guidance and pathways for research and queries that are related
- providing links between concepts in the future that are currently unknown
- providing answers (or partial answers) to future issues, conceptual blocks and questions
- developing understanding of unrelated concepts that become pertinent later.

The content of your journal will not be in a logical conceptual order. This is because you are researching unfamiliar knowledge and you won't know how it all fits together until your research is complete.

Before you add an entry to your journal, make sure you have recorded the date and provided your own title for the entry. As you take notes from different sources, always record the source information; for example, the title, web address, author name and page number. Figure 1.14.1 is an example of a journal entry.


17/4/2020

RESEARCHERS DEVELOPING GREEN GASOLINE SUBSTITUTE

SOURCE: wardsauto.com/miscellaneous/researchers-developing-green-gasoline-substitute

ORIGINAL SOURCE: Angewandte Chemie International Edition, 2014 (February 10), 53 (7), 1854–1857.

Gasoline-like fuels made from cellulose

University of California Davis
A 1 step process

Whilst biodiesel is already commercially available, biogasoline is not

Gasoline	Diesel
Branched	Linear
Higher volatility	

Process does not rely on fermentation so cellulose does not have to be converted to sugars

WORDS IN PROCESS DIAGRAM
BIOMASS DERIVED LEVULINIC ACID; SOLID ACID CATALYST; K_2CO_3; ANGELICA LACTOSE DIMER; BRANCHED C_7–C_{10}

FIGURE 1.14.1 A journal entry with the journal entry date and title. There may be a number of journal entries on any given date, each with their own title. Also, the same titles will appear on different entry dates as research continues on that topic.

Background information

Information taken from a source should be rewritten or summarised in your own words in the journal. Avoid copying information verbatim so you are not tempted to plagiarise when you write up the research investigation.

It can be difficult sometimes to reword sources into your own words, especially if it is already expressed well and concisely. Before you write and record the research information, read the material and grasp its understanding. Without referring back to the source, write notes in your journal, in your own words. Use multiple sources and a dictionary as references for information. In your journal, your notes should be detailed with extended explanations that you will fully comprehend when you refer back to them at a future date. See the worked example below for a few examples of rewording information.

Worked example 1.14.1

REWORDING INFORMATION FROM SOURCES

A resource states that:

'Proteins are formed when 2-amino acids undergo condensation polymerisation.'

Reword this information into your own words.

Thinking	Working
You can swap the order of information, i.e. the process (2-amino acids undergo condensation polymerisation) with the product formed (proteins).	The condensation reaction between 2-amino acids results in the formation of proteins.
You can change numerous words such as adjectives, verbs, adverbs and nouns.	The synthesis of proteins occurs through the condensation reaction between 2-amino acids.
You can elaborate on the information to explicitly outline explanations.	The elimination of water in the condensation reaction between the amino functional group of one 2-amino acid and the carboxylic acid functional group of another 2-amino acid forms a peptide group. This peptide group has an amino group at one end and a carboxylic acid group at the other and so is capable of polymerising. Proteins are polypeptide chains that contain more than 50 amino acids.

➤ Try yourself 1.14.1

REWORDING INFORMATION FROM SOURCES

A resource states that:

'The increased intermolecular forces mean that organic compounds containing functional groups have higher boiling points than alkanes of similar molar masses.'

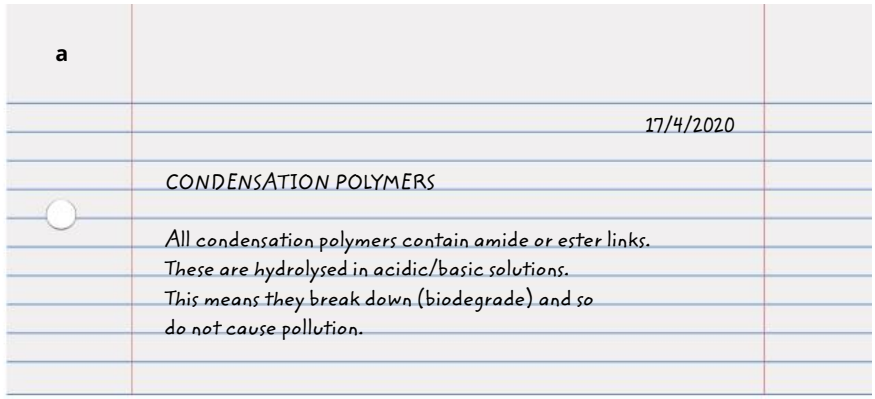
Reword this information into your own words.

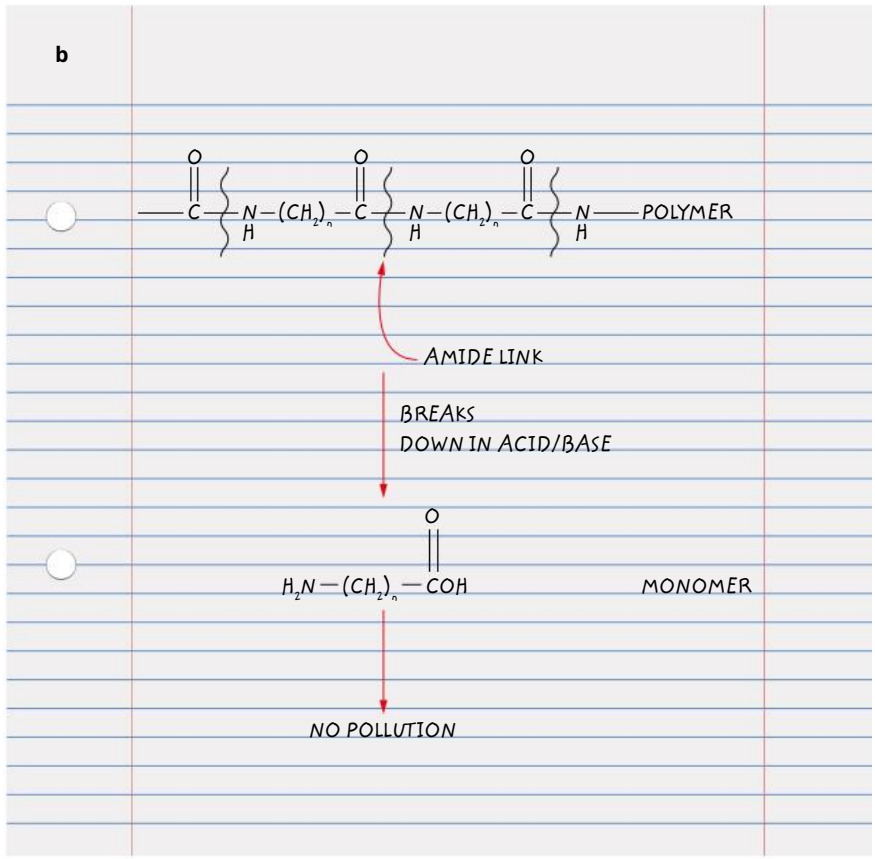
When making journal entries it is important for your understanding and analysis of statistical method (e.g. R^2 value, **confidence interval** or standard deviation) that you express information in your own words. You will most likely have to conduct further research to understand the statistics, their meaning and the author's interpretation of the results as you will come across new statistical calculations you have not seen previously.

Personal explanations and interpretations

Your journal is a valuable tool that is personal to you. As such, it should be written and displayed in formats that you understand and that make meaning of information to produce the research investigation report. It can include writing, drawings and schematics (e.g. flow charts).

Sometimes, one form of recording information provides more details than others. Details are not limited to just facts, they can be the order of events, their location or their physical orientation. Therefore use a variety of ways to record or present the information to encapsulate more comprehensive details. The same information can be represented in a few different ways, as shown in Figure 1.14.2.

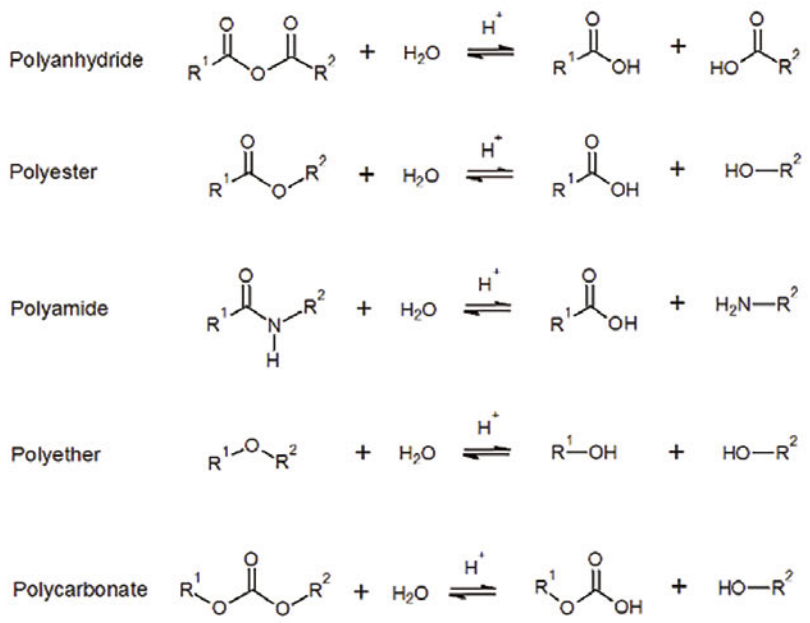




c

HYDROLYSIS OF CONDENSATION POLYMERS

Hydrolysis is the cleavage of bonds in functional groups by reaction with water. This reaction occurs mainly in polymers that take up a lot of moisture and that have water-sensitive groups in the polymer backbone. Some synthetic polymers that degrade when exposed to moisture include polyesters, polyanhydrides, polyamides, polyethers, and polycarbonates. The rate of hydrolytic degradation can vary from hours to years depending on the type of functional group, backbone structure, morphology and pH. Polymers that readily degrade in the presence of water include polyanhydrides, aliphatic polyesters with short midblocks like polylactic acid and certain poly(amino acids) like poly(glutamic acid). Assuming similar midblocks, the rate of hydrolysis decreases in the order anhydride > ester >> amide >>> ether.



SUMMARY

HYDROLYSIS

is the cleavage of bonds in functional groups in the polymer backbone by reaction with water.

Many synthetic polymers with water-sensitive groups in the backbone as well as most natural polymers undergo hydrolytic bond cleavage to form water soluble fragments. The process is known as polymer erosion.

Polymers that contain ester and amide groups generally undergo bulk erosion whereas more hydrolytical stable (less water soluble) polymers like polycarbonates and polyethers tend to erode by surface erosion.

For bulk eroding polymers, the erosion rate increases over time due to the formation of pores, greater chain mobility of lower MW

FIGURE 1.14.2 Different ways of recording information about the same topic in a journal. (a) Sample page from a student journal summary about condensation polymers. (b) Sample page from a student journal explaining condensation polymers in a flow chart. (c) Sample page from a chemical database explaining hydrolysis of condensation polymers.

Results, data and evidence

When you read scientific results, data or evidence in a resource, it is important to record the values in your journal. Figure 1.14.3 shows examples of research evidence and how they can be reinterpreted for a journal entry. Along with the results, data or evidence includes:

- specific details and your own interpretation of significant values
- trends or patterns
- the comparison or difference between one set of values and another
- the statistics used to establish significance and also the author's interpretation.

a

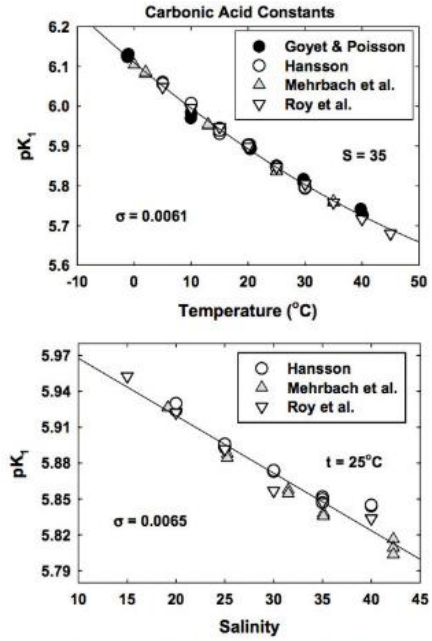


Fig. 1. Values of pK_1 of various workers for carbonic acid (Mehrbach et al., 1973; Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993) as a function of temperature ($S = 35$) and salinity (25°C). Goyet and Poisson (1989) did not make any measurements at 25°C so these results are not shown as a function of salinity. The smooth curve is calculated from Eq. (5).

b

17/4/2020

How carbonic acid equilibrium changes as a function of temperature and salt

SOURCE Millero et al. Deep Sea Research 49, (2002), 1705–17

$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$ (1)

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

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

The $pK_1 = -\log K_1$

So a non linear decrease in pK_1 observed with temperature shows that as temperature increases the Eq (1) shifts to the right.

Same effect for salinity (except linear decrease)

FIGURE 1.14.3 Examples of interpretations of research evidence. (a) Original evidence using graphs from a source located from research. (b) Student's interpretation and journal recording of the evidence.

RECORDING THE ORIGIN OF INFORMATION

As you conduct your investigation and research, it is important to write down the source of the information. This will enable you to return to the source later to continue researching, collect further information or recheck details. You will also be required to produce a reference list in the report and it will save time if you have already recorded the source of the information.

Table 1.14.1 summarises the information you need to record about the sources you use.

TABLE 1.14.1 Recording source material

Books	Online resources
• author/s • title • date of publication • publisher • place of publication • page number/s	• author/s or name of organisation • title • date website was written or updated • date website was accessed • website address (URL)

1.14 Review

SUMMARY

- There is no single method for taking and organising notes.
- A scientific journal enables scientists to record and organise their notes.
- Scientists continually revise and refine their experiments based on previous experimentation and results.

KEY QUESTIONS

Retrieval

1 State how you would record information from a source in your journal.

Comprehension

2 Explain the benefit of keeping a scientific journal.

Analysis

3 Apply your skill of paraphrasing and rewrite the following texts in your own words.

a In the recent past, silver nanoparticles (AgNPs) have received enormous attention from researchers due to their extraordinary defence against a wide range of microorganisms and also due to the appearance of drug resistance against commonly used antibiotics. The exceptional characteristics of AgNPs have made them applicable in various fields like biomedical, drug delivery, water treatment and agriculture.

b The major physical and chemical parameters that affect the synthesis of AgNPs are reaction temperature, metal ion concentration, extract contents, pH of the reaction mixture, duration of reaction and agitation. Parameters like metal ion concentration, extract composition and reaction period largely affect the size, shape and morphology of the AgNPs. Most of the authors have reported suitability of basic medium for AgNPs synthesis due to better stability of the synthesised nanoparticles in basic medium. Some other advantages reported under basic pH conditions are rapid growth rate, good yield and mono dispersity, and enhanced reduction process. Small and uniform sized nanoparticles were synthesised by increasing pH of the reaction mixture.

c Water electrolysis has long been known to produce hydrogen. However, for membrane electrolysers, used water must be pure. We show here that wastewater electrolysis gives the same performance or even better performance, because it contains bacteria that produce hydrogen.

1.15 Writing a report for the research investigation

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- write a report for your research investigation
- write a literature review for your research investigation.

There are several genres that can be used to create a report on your research investigation. As a written report, the genres include a literature review, empirical essay and annotated bibliography. The report must be 1500–2000 words long. Alternatively, a poster can be used as part of a multimodal presentation of 9–11 minutes in length. This is not an exclusive list. Even though there are many ways to present your report, it must follow a scientific genre and meet the requirements of the QCAA Chemistry General Senior Syllabus.

Writing a research investigation report requires scientific communication and will need to follow scientific genre conventions. An explanation of these requirements has been provided in Module 1.11. A report will communicate information in a logical sequence (introduction, body and conclusion) and may contain subheadings. Many of the characteristics of the student experiment are closely related to the research investigation. The focus of the student experiment is on interpreting data collected during a scientific investigation, while the focus of the research investigation is to explore a claim.

Characteristics of the genres for presenting the research investigation are summarised in Table 1.15.1. This module will focus on the literature review.

TABLE 1.15.1 Summary of features of presentation genres for the research investigation

Science presentation genre	Brief description	Features
literature review	• a report that evaluates information found in a publication that is related to the selected topic • gives a theoretical base for the claim (question) and analyses and interprets information/data related to the claim • objective is to point out the strengths and weaknesses of the claim	• an abstract • an introduction to the topic that provides context • discussion of information/data • analysis of information/data • evaluation of information/data • a conclusion related back to the claim • paragraphs set out in a logical development of ideas • subheadings
empirical essay		• includes all the features of the literature review
annotated bibliography	• notes, comments and explanations about article/s • evaluation of a claim after investigating how other sources treat the claim	• citation • introduction to the citation • aims, research methods, scope • discussion of usefulness to your research topic • limitations • conclusions • explanation; how the citation contributes to your topic or fits in with your research
poster	• presents ideas concisely and clearly • accompanied by an oral presentation • ideas are elaborated upon in the oral presentation	• includes all the features of the literature review • visual, oral and text presentation • uses colour, font, dot points, subheadings and images to effectively deliver information

LITERATURE REVIEW

A literature review usually includes an introduction, a body and a conclusion. It critically analyses information and convinces the reader of the significance or importance of the topic being investigated. This is achieved through the presentation of information in a logical sequence in which the author guides the reader through the material to understand its significance. The research question provides the foundational direction and guidance of the literature review.

Elements of a literature review

Not all qualities and elements of a full literature review will be appropriate for your research investigation report. Your literature review will be limited to the word count and ISMG descriptors specified in the syllabus. Depending on your research question and the topic being investigated, choose to cover some of the following elements of a literature review.

- Determine the current understanding of your topic in the scientific community.
- Provide an overview of key concepts relevant to your research question.
- Identify important relationships between variables (specific to variables that influence the independent or dependent variables stated in your research question).
- Identify the strengths and weaknesses of evidence in the information used for the above points.
- Identify any gaps in the research.
- Identify any conflicting evidence.

One of the key qualities of a literature review is that it is a critical analysis of the evidence to communicate a true understanding of the 'big picture' about a topic. It does not just summarise information. Science is more about models, theories, laws and principles and these are continually developing. The purpose of your literature review is to critically analyse evidence, identify any strengths and weaknesses, as well as the gaps and conflicts, to convince the reader about the conceptual relationships.

Qualities of a good literature review include:

- critical analysis of the evidence—establish what it means and account for the statistical processing of data used (be sure to analyse the methodologies, samples, results and data processing and analysis)
- effective discrimination between relevant and irrelevant sources and content—use only the former in your literature review
- logical organisation of the structure of the review to inform and convince the reader—plan the introduction, body and conclusion.

There are no hard and fast rules about what constitutes a sufficient number of sources to consult for your research investigation. The term 'sufficient' is defined by the QCAA Chemistry General Senior Syllabus as 'enough or adequate for the purpose'. The purpose of the research investigation is to evaluate a claim; therefore, if the number of sources enables a justified conclusion to be drawn about your research question and explores both sides of the argument, then the number of sources is sufficient.

A thorough analysis requires attention to every detail and therefore your literature review should include analysis and synthesis from different sources. It should identify patterns, trends and relationships that are related to your investigation. Also, it should be explicitly connected to your research question as well as clarifying where the sources agree and disagree.

Your literature review should discuss the limitations of the research as this may have a bearing on the extent to which information (primary or secondary) is valid to the research question. It is important to analyse data and its limitations objectively, rather than selecting data that supports one claim. Such bias will result in producing an inappropriate and erroneous conclusion. Quality scientific analysis is open to any result.

Justified scientific arguments are those that are supported by sound reasons and evidence. Therefore, you must apply your scientific understanding and conceptual knowledge to the evidence that you have examined. The following points should be examined and discussed.

- State whether a pattern, trend or relationship was observed between the independent and dependent variables.
- Describe what kind of pattern it was and specify under what conditions it was observed.
- Note and explain any deviations in the data or information.
- Identify any limitations in the data or information researched. Why and how do these limitations affect the validity of the research question or conclusion?

An analysis of information may also include an evaluation of the methodology used by authors to obtain their data or information.

Conclusion and evaluation

Your literature review should include a discussion that evaluates the reliability and validity of evidence. Is the data from measured samples or from estimated models? Did the studies occur under different conditions or categorise the independent variables differently so comparison was impossible?

It is important to discuss the limitations of each source. You can do this by:

- evaluating the method of evidence collection
- identifying issues that could affect the validity, accuracy, precision and reliability of evidence
- stating sources of systematic and random errors
- recommending improvements to the evidence to improve validity.

Your literature review must recommend improvements to your investigation that address the limitations and gaps in knowledge that have been identified during your investigation. The suggestions presented must be connected to the claim and allow further investigation.

Communication

Once a plan for the literature review or your preferred presentation mode has been developed, word limits can be assigned to each section (Figure 1.15.1). The notes in your research journal will give you a good idea of which sections will require more words for explanations than others. Distribute the total word count across all sections you plan to include in the report.

The word limit guide is not binding. As you complete your literature review you can alter the distribution of the word count if you feel it is necessary. However, make sure the limit outlined in the syllabus is never exceeded.

Planning your research investigation report will help address the syllabus ISMG.

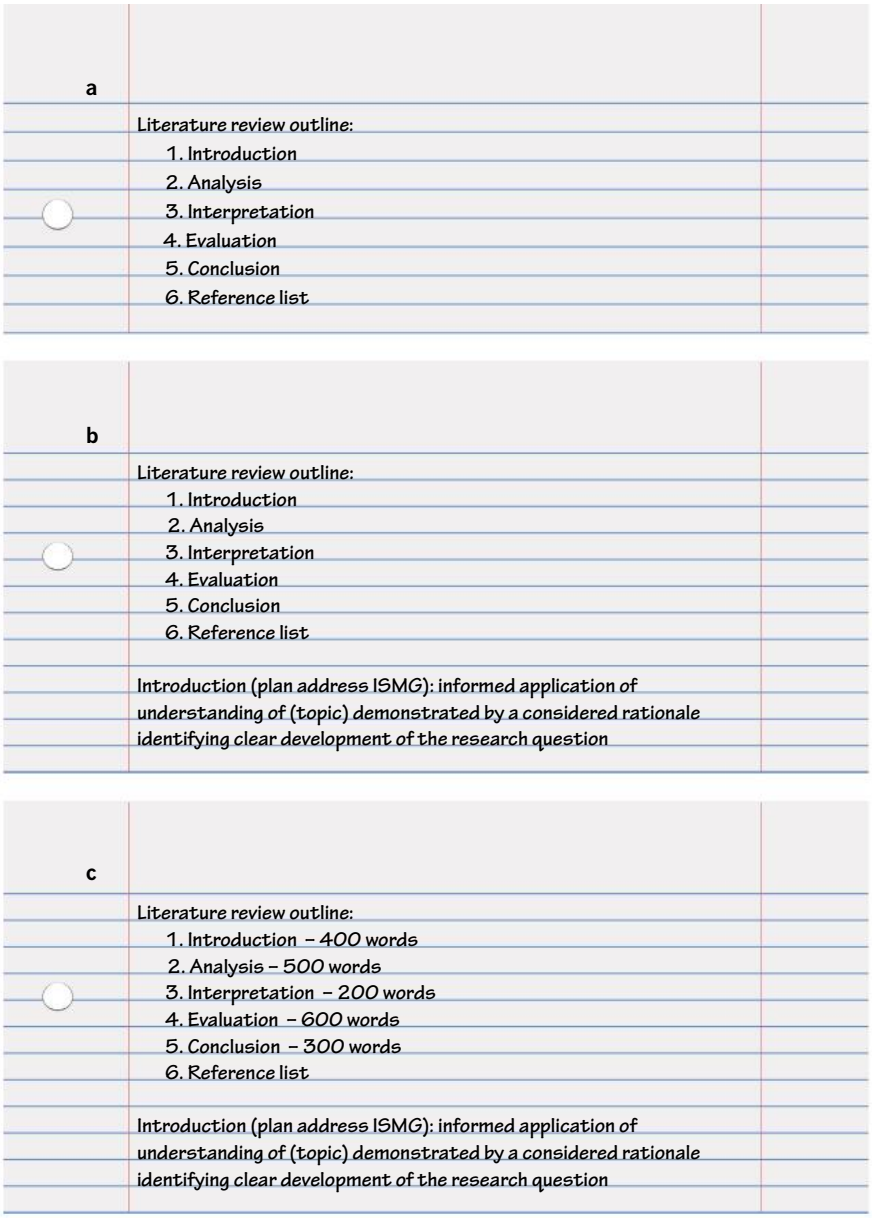


FIGURE 1.15.1 Planning the report: (a) a planned outline of the research investigation report to ensure the syllabus ISMG is addressed; (b) ISMG descriptors assigned to the sections in the planned outline; (c) the word count guide planned

Structure of a written report

Although the use of headings in scientific reports is essential to guide and direct scientists to particular information, there is no single correct convention for headings. A typical structure includes an introduction, body, conclusion and reference list.

Edit your report after you have completed it. Editing is an important part of the writing process. After editing your report, save new drafts with a different file name and always back up your files in another location. Pretend you are reading your report for the first time and try to hear what you have actually written, not what you intended to write. Reading you report out aloud to yourself will help you read it more critically.

When editing, look for content that is:

- ambiguous or unclear
- repetitive
- awkwardly phrased
- too lengthy
- not relevant to your research question
- poorly structured
- lacking evidence
- lacking a reference (if it is another researcher's work)
- incorrectly spelt
- grammatically incorrect.

1.15 Review

SUMMARY

- There are several genres that can be used to report a research investigation, such as a literature review, empirical essay, poster presentation and annotated bibliography.
- A literature review critically analyses information and convinces the reader of the significance or importance of the topic being investigated.

KEY QUESTIONS

Retrieval

1 Describe the structure of a research investigation report.

Comprehension

2 Explain the purpose of the research investigation report.

Analysis

3 Determine how you would achieve an analysis of the methodologies, samples and results in a research investigation report.

PART D EXAMINATION (EA)

The examination is set externally by QCAA and covers both Units 3 and 4 of the syllabus. The examination accounts for 50% of the total assessment in chemistry. The examination is delivered by two papers.

The QCAA defines an examination as a supervised test that assesses the application of a range of cognitions to one or more provided items such as questions, scenarios and/or problems. Students complete their responses individually, under supervision and in a set time.

The assessment objectives are to:

- describe and explain
- apply understanding
- analyse evidence and identify trends, patterns, relationships, limitations and uncertainties in data
- interpret evidence, analyse and draw evidence-based conclusions.

The following table outlines key information about each exam paper. Look at the table carefully and make yourself familiar with the unique features of each paper.

Examination	Papers 1 and 2
Types of items	• multiple choice • single-words • sentences • paragraphs • calculating using algorithms • interpreting using graphs, tables or diagrams • responding to unseen data and/or stimulus
Syllabus coverage	• Units 3 and 4
Assessment objectives	• describe and explain • apply understanding • analyse evidence • interpret evidence and draw conclusions
Conditions	• perusal (reading) time: 10 minutes • writing time: 90 minutes
Equipment	• QCAA approved graphics calculator permitted • seen formula and data booklet provided
Marks	constitutes 50% of total assessment

Engage in positive 'self-talk'.

Careful and thorough preparation for the examination may help reduce some of the anxiety and stress you may experience in the lead-up to this assessment. Many students feel that their performance in the examination, as in all assessments, is what will define them and determine their future career paths.

Remember, no matter how you feel about your performance, there is nothing you can do to change it. If you have not achieved the score that will gain you entrance into the course for your preferred career path, consider your options. Investigate different pathways to move towards your goal. Consider different courses. Seek advice from teachers and especially your careers teacher. Sometimes the path to achieve a career goal is less direct.

It is very common and easy for students to become 'consumed' by the demands and pressures of their final year of school. But remember, there is life beyond Year 12!

This guide provides you with practical suggestions and support to prepare for the examination. The guide takes a year-long approach to your preparation that includes:

- consolidating learning—effective learning routines and strategies for use throughout the year
- revising and practising—study practices and strategies for the weeks leading up to the examination
- sitting the exam—strategies and hints for tackling the examination
- after the exam—some considerations.

1.16 Examination preparation

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- prepare yourself to successfully complete the Examination (EA).

As you work through the course material throughout the year, it is vital that you take detailed notes from classwork and homework. These notes will be the foundation of your revision and summary notes, so they should:

- cover all aspects of the syllabus
- focus on key concepts
- give greater emphasis to larger topics than minor ones
- include examples and applications
- include definitions of key terms
- include questions and answers (that have been checked)
- be legible!

CONSOLIDATING LEARNING

Begin study early. It is easy to procrastinate and then find yourself rushing to revise and study at the last minute. Just-in-time is not a recipe for success. Learning is more effective if it is spread over a long period instead of a last-minute cram.

Learning requires discipline over the duration of the course. Repetitive and frequent revision of the course material helps to reinforce and deepen understanding and helps embed learning in your long-term memory. Studying and revising can be overwhelming. Revise manageable chunks by dividing your work into smaller sections or topics.

Time management is important.
Use your study time effectively.
Use your leisure time effectively.

During the year, get into the habit of revising completed sections of the course. The revision may be done, for example, at the end of a week, a topic, a chapter or at intervals that best suit you. Revise work from earlier in the year on a regular basis. Ask your teacher for copies of any past exams you have done and use the answer/marking scheme to help you revise. It is easy to forget information if you don't keep reminding yourself.

There are a number of revision strategies you might use. Identify your own study strengths—what works best for you—then make effective use of these strengths.

Following are some effective learning routines and strategies for use throughout the year.

1 Your teacher is a chemistry expert. He or she is an excellent resource and should be the first person you consult for support and help. Seek help during class if you are struggling to understand concepts. If you encounter problems out of class time, it is a good idea to write down areas that you are struggling with and consult your teacher at a later time. Remember to pinpoint specific concepts or questions. Ask your teacher to re-explain concepts and ask for more material and/or questions for practice.

2 Make your own flash cards. Dedicate each card to a particular idea that could include:
   - definitions—key term on one side with the definition on the back
   - diagrams—diagram on one side with a brief explanation on back
   - equations and formulas—formula on one side with worked example on back
   - graphs—graph on one side with summary of results on back
   - questions—question on one side and the answer on the back.

Use the cards to test yourself. Ask friends or family to test you. Periodically reading the cards reinforces learning and entrenches concepts in long-term memory (Figure 1.16.1). Flash cards are an excellent tool for subject matter that must be remembered.

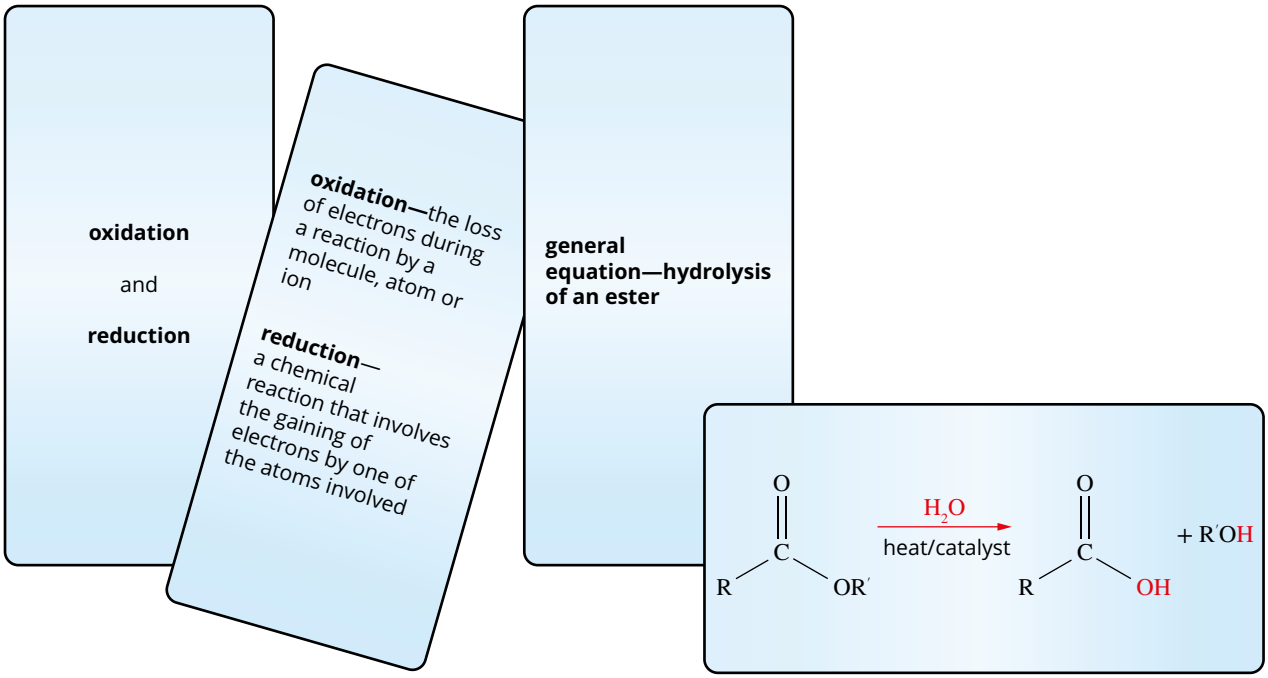


FIGURE 1.16.1 Flash cards are an excellent tool for remembering and testing yourself on factual material.

3 Trigger words. Write down the key words associated with a topic or theme. Trigger words are useful in helping to generate other related words and ideas. This approach is helpful in preparing everything from quick drafts to questions and concept maps to summarising whole topics.

4 Diagrams are useful memory triggers—draw first, explain second!

5 Test yourself. Complete as many questions as possible to test your learning. Handwrite (not type) your answers. Writing is more valuable practice than just thinking about your answer. Writing is a good way to memorise material. Remember, you will need to be able to write for 90 minutes in the allocated writing time in the exam and your writing must remain legible.

6 Summary notes. Consider your preferred learning style and take advantage of it to make revision notes. Summaries help you identify essential concepts and reinforce learning. Keep in mind that any study notes you make are most effective when they are:

- clear
- to the point
- uncluttered.

Some techniques you may apply to create useful summaries include:

- highlighting or underlining important points as you read your notes or text
- creating headings or appropriate structures under which to organise dot points
- using diagrams to summarise concepts
- creating tables to make comparisons (e.g. causes/effects, for/against)
- creating summary sheets
- using boxes, circles and colour to highlight points on your summary sheets
- using mnemonic devices to remember key points; for example, Oil Rig: Oxidation is loss; Reduction is gain (of electrons)

- compiling a glossary of new terms. Use your own words, not those lifted straight from the textbook. Your own words cement your understanding and help you remember new terms
- employing scatterplots, mind maps or concept maps to organise key information (Figure 1.16.2).

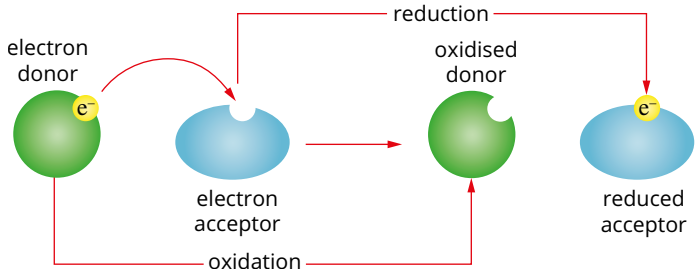


FIGURE 1.16.2 Creating visual representations in the form of concept maps is an effective revision and study tool.

7 Use chapter and module openers and module review summaries as a checklist for the key ideas in a chapter.
   - Tick those with which you feel confident.
   - Highlight those you need to revisit.
   - Reread relevant sections of text.
   - Rewrite notes, definitions or equations that you need to consolidate.

8 Form a study group with friends. The group can meet face-to-face or online. Discuss and explain key points to each other. If you are struggling with a difficult concept, try to teach it to a friend. You cannot explain something to another person until you have it clear in your own mind. Teaching and explaining to someone else makes it clearer to you.

9 Complete lots of practice questions. Write down your answers so that you get practice expressing yourself. Verbalising or thinking the answer is not the same and your responses may not always come out in writing how you intend unless you have plenty of practice.

10 Familiarise yourself with the data booklet. In the exam, you have access to the data booklet. Make sure that you use the data booklet throughout the year, as needed, to become familiar with when and how to use it. Print yourself a copy and keep it on hand. You will use it more in some topics than others.

REVISING AND PRACTISING

In the months and weeks leading up to the exam, most if not all of the course will have been taught. Your focus should now shift to studying in preparation for the exam. You will be at an advantage if you have taken comprehensive notes throughout the year, made revision summaries, completed practice questions and generally made every effort to advance your understanding and skills.

Prepare a study timetable

Allocate time to study all the subject matter. The timetable may include daily study time for all your subjects and may specify sections of each subject to be covered. While you may not stick strictly to the timetable, it is a guide to fitting everything in and allocating equal time to different subjects.

Prepare summary notes

You should have been making summary notes of subject matter throughout the year. It is now time to consolidate your learning across Units 3 and 4. Remember that different topics link with each other and it is only when a whole topic or unit is completed that these links become apparent. The summary notes you have prepared can be collated and will serve as a summary of Units 3 and 4.

- List all the topics and subtopics in the syllabus, including the subject matter statements. The opening pages of each chapter in your student book will guide you. You might choose to prepare a separate table for each topic and use it to write your revision notes. The sample shown in Figure 1.16.3 allows for key points, formulas and key terms and definitions for each topic. While this layout may suit some students, it may not suit you. Adjust the labels and organisation to best suit you. For example, you may choose to include a column for worked examples and/or sample questions.

Unit 3 Equilibrium, acids and redox reactions			
Topic 2 Oxidation and reduction			
	Key points	Formulas	Key terms and definitions
redox reactions			
electrochemical cells			
galvanic cells			
standard electrode potential			
electrolytic cells			

FIGURE 1.16.3 A summary of revision notes in table form

- Skim through your student book and class notes. Identify key sections and terms. These can be added to your revision table, for later elaboration.
- Reread your class notes carefully for a section of work. Once you feel you understand and remember them, put the notes aside. Without referring back to the notes, start filling in the revision table. You may need to keep referring back to your notes. Each rereading of the notes will reinforce your learning.
- Handwrite your revision table. The exam must be handwritten so it is a good idea to handwrite your notes as preparation.
- Refer to additional resources if you do not understand anything. This might mean checking the student book, asking your teacher, researching online or discussing with classmates. You can keep track of problem areas by writing questions in the margin of the revision table, highlighting parts of the revision notes you do not fully understand, or keeping a separate queries sheet.
- Use abbreviations and symbols, but remember that only standard symbols and abbreviations may be used in the chemistry exam. In order to save time and space on the revision table, you can develop your own abbreviations.
- Dot-point notes, visuals, tables and graphs are all useful ways of summarising information. Use these in your revision table as appropriate. It is often easier to bring to mind information in these forms than to visualise a large block of text. If you are a visual learner, it may be helpful to colour code your notes to emphasise different concepts. Rewriting notes, whether in note or visual form, helps you remember them.
- Learn the subject matter. In preparing the revision table, you read and reread the subject matter, so your understanding continually improves. Practise rewriting the revision table without referring to the original one. Try making a summary of the revision table so that you focus on the essential concepts. Discuss concepts with classmates to clarify your understanding. Give the revision table to a family member and ask them to test you. These are some of the strategies that can be used to reinforce your learning.

- 'Traffic light' your work. Create a list of the subject matter for Units 3 and 4. Highlight in green the concepts you are very familiar with and for which you can answer medium to difficult questions. Highlight in orange the concepts that you understand but can only answer easy and some medium-level questions. Highlight in red the concepts for which you can only answer basic questions and need help from your teacher or peers.

Practise, practise, practise!

Remember the saying 'practise makes perfect' and complete as many test and exam papers as possible. Sitting an exam requires skill and the more practise you have in advance, the more prepared you will be. Take practise exams in the time limit allocated. Handwrite your answers to get practise at working quickly, writing your ideas legibly and expressing yourself clearly. Exam paper practise will show you what you know, but more importantly, what you do not know and need to revise.

SITTING THE EXAM

Be prepared. Do not cram the night before the exam, but rather reread your revision table to refresh the subject matter. Put new batteries in your calculator! Double-check the date, time and place of the exam. Turn up to the exam with plenty of time to spare. Running late will only create stress before you even get into the exam room. Remain calm and focused as you enter the exam room. At this stage it is too late to worry about your application through the year or your exam preparation.

There are some strategies to keep in mind in the exam that will improve your chances of doing well. Remember, you can only be asked about information that is included in this course. The exam is your opportunity to showcase your knowledge of this subject.

Perusal or reading time

Every exam allocates time for you to look over the exam paper. You are not permitted to pick up pens or pencils at all during this time, not even to write your identification on the answer booklet. Use this time wisely as it is valuable for you to get an overview of the paper.

- Check through the entire paper quickly.
- Carefully read the instructions and reread them.
- Plan how much time you will allocate to different sections of the paper.
- Decide what order you will complete the questions in, i.e. do the easy questions first so you have more time to complete the harder ones.
- Start reading questions and answering them mentally.
- If a question is difficult, do not dwell on it. Move on to the next question. Sometimes another question can give clues to ones that appear difficult.
- Carefully read each question. In your head, translate into your own words what you are required to do.
- Consider the marks allocated to each question. Plan to spend more time on questions that award more marks.

Writing time

Commence writing as soon as you are permitted. Keep in mind the following strategies.

Read questions carefully

If you find it helpful, underline key words in the question. This can be a useful strategy in identifying the focus of the question and giving direction about what is required in your answer. For questions with parts, read the whole question before starting to write your answer. Sometimes the information in one part of a question will provide a hint for another part.

Interpret questions carefully

Look for key verbs like 'explain', 'compare' and 'determine' that tell you what you are expected to do. The questions in your student book and activity book have been written using key verbs from the syllabus so you should be familiar with the style of questioning and will have had practice at interpreting questions. Make sure your answers address all parts of the question. Use scientific terms and give your answers to the correct number of significant figures and with a unit.

Show your working

Show all the steps you took to reach your solution on questions involving calculations. While there may be an error in one part of the calculation, you may still score some marks for correct method. Remember to always include the correct units in answers. Remember to correctly label all graphs (x and y axes, title, units). If you do work that you think is incorrect, simply draw a single diagonal line through the response and write your answer again. If you are using the additional pages provided at the back of the exam paper, do not forget to direct the assessor to the page and indicate on your response which question it refers to.

Working with data

- When a question includes data presented in a graph, read the labels and units on the axes and understand the relationship shown by the graph. The title of the graph will assist with this.
- Use a ruler for reading graphical data accurately.
- When looking at tables, read the headings of rows and columns carefully so you can understand the content of the table. They usually contain symbols and units of the data.
- Refer to the data booklet where appropriate.
- You should include the proper units for each number where appropriate. If you keep track of units as you perform your calculations, it can help ensure that you express answers in terms of the proper units. Depending on the exam question, it is often possible to lose points if the units are wrong or are missing from the answer.

Answer all questions

An unanswered question cannot possibly earn you any marks. It is better to make an intelligent guess that might earn some marks than not answer at all. When you have completed an answer, reread the question. Check that you have addressed the question. An answer that includes correct information but does not answer the question will not earn any marks. Many free-response questions are divided into parts a, b, c and d, with each part calling for a different response. Credit for each part is awarded independently, so you should attempt to solve each part. For example, you may receive no credit for your answer to part a, but still receive full credit for part b, c or d. If the answer to a later part of a question depends on the answer to an earlier part, you may still be able to receive full credit for the later part, even if your earlier answer is wrong.

Answer questions simply and concisely

Sometimes the answer to a question is simply a one-word answer or a numerical reading from a graph. Providing extra information in your answer is unnecessary and can lead to irrelevant or even contradictory information. It is also an inefficient use of exam time. Where possible, use standard phrases that neatly encapsulate meanings rather than wordy explanations. Provide only one answer to each question, never try for an each-way bet!

Don't give extra information

Providing extra information in your answer is unnecessary and can lead to irrelevant or even contradictory an information; it is also an inefficient use of time.

Answer the question being asked

Provide accurate information that addresses the question to attract a score.

Example:

Question: Using Le Châtelier's principle, explain why decreasing the temperature of an equilibrium with an exothermic forward reaction increases the amount of product formed.

Answer 1: Le Châtelier's principle is used to predict changes to the position of an equilibrium. ***No score.***

Answer 2: Le Châtelier's principle states that an equilibrium shifts to oppose the change. So, if the temperature is decreased the equilibrium will shift to favour the direction that generates heat (increases the temperature). That is the exothermic reaction. So if the exothermic reaction is the forward direction then this will increase the concentration of products formed. ***Scores!***

A one-word answer will not be enough if the question asks for an explanation.

Example:

Question: Evaluate the following statement: Alcohols have higher boiling points than an alkane of similar molar mass.

Answer 1: It is correct. ***No score.***

Answer 2: It is correct. The boiling point of a compound is related to the strength of the intermolecular bonds between neighbouring molecules. Because the electronegativity of the oxygen atom is much less than the electronegativity of a hydrogen atom, alcohols contain a very polar OH group. This functional group is capable of forming hydrogen bonds with an OH group in a neighbouring alcohol molecule. Because the electronegativities of C and H are very similiar, there is almost no charge separation in the C–H bond. Therefore, alkanes can only have temporary dipoles and so only form weak Van der Waals forces. Since hydrogen bonds are much stronger than Van der Waals bonds, more energy is required to separate the molecules. Therefore, alcohols have higher boiling points than alkanes of a similar molar mass. ***Scores!***

Answer with clarity

There should be no room for interpretation, so be clear about what you mean to say!

Examples:

Answer 1: Increase in reaction could mean increase in rate of reaction. ***Not clear.***

Answer 2: Increase in reaction could mean increase in vigour of the reaction. ***Clear!***

- Use the number of lines provided in the answer booklet as a guide to how much to write.
- Use the number of marks allocated to a question or part of a question as a guide to how detailed your answer should be. Consider whether you can add more details, clearer explanations, or make corrections to answers.
- Pay attention to your spelling.
- Never leave blanks!

Easier questions

Easier questions should be completed first.

Multiple choice questions

Multiple choice questions are designed to make you select between very similar items. Read all options carefully. If you're unsure, start by eliminating answers you know to be incorrect. Make your final choice from the possible answers that remain. Answer every multiple choice question, even if all you can do is guess. You should answer each multiple choice question before you move on to the next one. You can mark a question to come back to later if you have time but you should still fill an answer before you move on. You should allow just over a minute for each question. If the question takes longer than that, take a guess and move on.

Some exams will require you to complete a separate answer sheet for the multiple choice questions. If your exam does, make sure that you mark your answers on this sheet, not only on the question paper. If you make an error, erase it carefully before writing a new answer.

Difficult questions

If you find a question particularly difficult, skip it. Come back to it later if you have time. You should never use the 'scattershot' or 'laundry list' approach, i.e. writing answers with as many equations or terms as you can, hoping that the correct one will be among them. For questions that ask for two or three examples or equations, only the first two or three examples will be scored.

Mental blocks

Sometimes in conditions when you are under pressure, your mind can go blank. The information is there but temporarily not available to you. Take a few deep, slow breaths. Go back to the question. Try to visualise your notes on the revision table you created. If this does not work, move onto another question and return to this question later.

Recheck your answers

If you have time, return to questions that you are unsure of. There is no need to check all answers if you run out of time. Reread each question when you have finished answering it. This will help you to be sure that you have addressed every part of the question, and that you have not made an error that could change the meaning of your response.

Never leave the exam early

Exams are generally designed to take the full writing time allocated to them. If you finish early, recheck for anything you may have missed. Check for blank pages and both sides of the page to make sure you haven't missed anything! Count the number of questions you have answered against the number listed on the front of the exam paper.

Do not leave a question blank, have a guess! No marks will be deducted for an incorrect answer but you may pick up marks for a partial response. Also, if you're unsure of a multiple choice answer, try to eliminate one or more of the options then have a guess. You may be lucky!

Ignore students who leave the exam early. Just because they leave early does not mean they performed well. It often indicates they did not study enough and do not know the subject matter.

Remember:

- You can only be asked about information that is included in this course!
- The exam is your opportunity to showcase your knowledge of this subject.

AFTER THE EXAM

Once you have left the exam room, avoid talking to other students about the exam. Everyone has an opinion on their own personal performance. Listening to others can be unsettling. Whether you feel you performed well or are disappointed with your performance, it is now beyond your control. Remain calm. It is one exam result, in one subject, in one year of your life. No matter what happens, there are plenty of career pathways to pursue.

UNIT 3

Equilibrium, acids and redox reactions



TOPIC 1 Chemical equilibrium systems

TOPIC 2 Oxidation and reduction

Unit 3 objectives

Students will:

- describe and explain chemical equilibrium systems and oxidation and reduction
- apply understanding of chemical equilibrium systems and oxidation and reduction
- analyse evidence about chemical equilibrium systems and oxidation and reduction
- interpret evidence about chemical equilibrium systems and oxidation and reduction
- investigate phenomena associated with chemical equilibrium systems and oxidation and reduction
- evaluate processes, claims and conclusions about chemical equilibrium systems and oxidation and reduction
- communicate understandings, findings, arguments and conclusions about chemical equilibrium systems and oxidation and reduction.

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CHAPTER

02 Chemical equilibrium

In this chapter, you will investigate the ideas of reversibility and irreversibility of chemical systems. This study of reversible reactions will introduce the concept of chemical equilibrium.

Various factors can change the position of a chemical equilibrium. Le Châtelier's principle enables scientists to understand the effects of changes in concentrations in solutions, pressures of gases and temperature on an equilibrium.

The fact that many reactions do not proceed to completion is of vital importance in nature, including the metabolic processes that occur within the human body and other reactions in the biosphere. It also has serious consequences on the efficiency of many chemical manufacturing industries. You will learn how reaction conditions affect the relative quantities of reactants and products in an equilibrium system.

You will also learn how to write a mathematical relationship, known as an equilibrium law expression, for an equilibrium reaction. This law can be used to calculate the concentrations of reactants and products when a reaction is at equilibrium.

WS 3.1.1

Syllabus subject matter

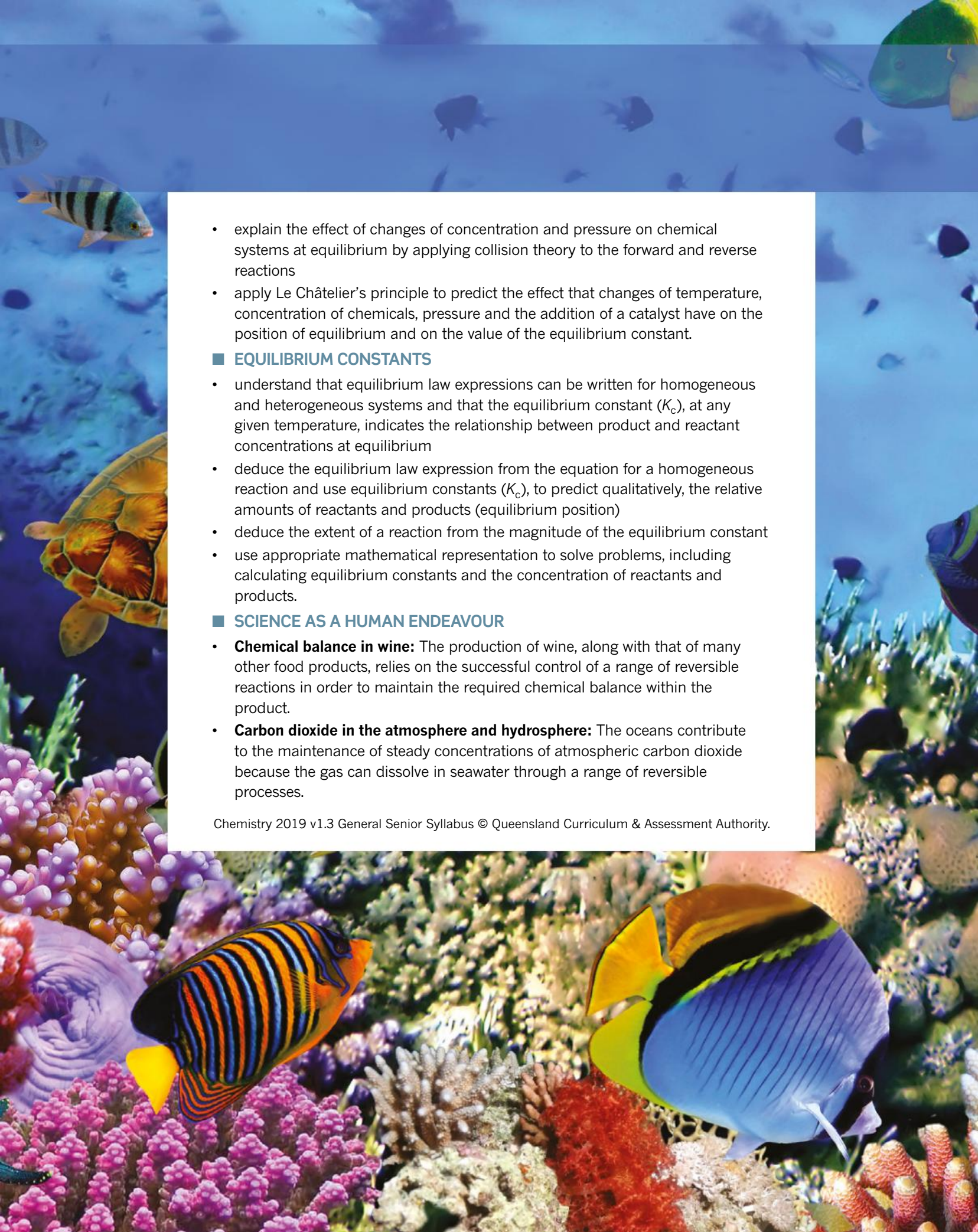
Topic 1 • Chemical equilibrium systems

CHEMICAL EQUILIBRIUM

- recognise that chemical systems may be open (allowing matter and energy to be exchanged with the surroundings) or closed (allow energy, but not matter, to be exchanged with the surroundings)
- understand that physical changes are usually reversible, whereas only some chemical reactions are reversible
- appreciate that observable changes in chemical reactions and physical changes can be described and explained at an atomic and molecular level
- symbolise equilibrium equations by using $\rightleftharpoons$ in balanced chemical equations
- understand that, over time, physical changes and reversible chemical reactions reach a state of dynamic equilibrium in a closed system, with the relative concentrations of products and reactants defining the position of equilibrium
- explain the reversibility of chemical reactions by considering the activation energies of the forward and reverse reactions
- analyse experimental data, including constructing and using appropriate graphical representations of relative changes in the concentration of reactants and products against time, to identify the position of equilibrium.

FACTORS THAT AFFECT EQUILIBRIUM

- explain and predict the effect of temperature change on chemical systems at equilibrium by considering the enthalpy change for the forward and reverse reactions



- explain the effect of changes of concentration and pressure on chemical systems at equilibrium by applying collision theory to the forward and reverse reactions
- apply Le Châtelier's principle to predict the effect that 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.

EQUILIBRIUM CONSTANTS

- understand that equilibrium law expressions can be written for homogeneous and heterogeneous systems and that the equilibrium constant (K_c), at any given temperature, indicates the relationship between product and reactant concentrations at equilibrium
- deduce the equilibrium law expression from the equation for a homogeneous reaction and use equilibrium constants (K_c), to predict qualitatively, the relative amounts of reactants and products (equilibrium position)
- deduce the extent of a reaction from the magnitude of the equilibrium constant
- use appropriate mathematical representation to solve problems, including calculating equilibrium constants and the concentration of reactants and products.

SCIENCE AS A HUMAN ENDEAVOUR

- **Chemical balance in wine:** 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.
- **Carbon dioxide in the atmosphere and hydrosphere:** The oceans contribute to the maintenance of steady concentrations of atmospheric carbon dioxide because the gas can dissolve in seawater through a range of reversible processes.

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Revision

In Units 1 and 2 you covered the content that forms the background required to successfully complete this chapter. To assist you in understanding the content of this chapter, the following key concepts are revisited in summary:

- energy changes in chemical reactions
- rates of reaction.

Reviewing this content should not be factored in as part of the notional hours for Chapter 2.

ENERGY CHANGES IN CHEMICAL REACTIONS

All substances have **chemical energy**. The chemical energy of a substance is the sum of its potential energy and kinetic energy. These energies result from such things as attractions between electrons and protons in atoms, repulsions between nuclei, repulsions between electrons, movement of electrons, and vibrations of and rotations around bonds. The chemical energy of a substance is also called its **enthalpy**, and is given the symbol H.

During a chemical reaction, the atoms in the reactants are rearranged into products with different chemical energies. The reaction can be **exothermic** or **endothermic** depending upon the relative energies of the reactants and products. The energy released or absorbed during a chemical reaction is called the **heat of reaction** (symbol ΔH). For exothermic reactions $\Delta H < 0$, and for endothermic reactions $\Delta H > 0$.

The energy required to break the bonds of reactants so that a reaction can proceed is called the **activation energy**.

Thermochemical equations

Thermochemical equations show the energy released or absorbed during a chemical reaction, symbol ΔH. Energy is usually measured in joules (J) or kilojoules (kJ) and the ΔH value has the units $J\,mol^{-1}$ or $kJ\,mol^{-1}$. This means that the energy shown by the ΔH value corresponds to the mole quantities specified by the coefficients in the equation. Remember:

- when the coefficients of an equation change, the ΔH value changes by the same factor
- when the equation is reversed, the sign of the ΔH value is reversed
- states of matter must be shown in thermochemical equations because changes of state involve enthalpy changes.

RATES OF REACTION

The rate of a chemical reaction can be determined by measuring the change in concentration of the reactants or products with time. As the reaction conditions change, the rate of reaction will change.

There are five main ways in which reaction rate can be increased: increasing the concentration of solutions, increasing the pressure of gases, increasing the surface area of a solid reactant, increasing the temperature, and using a **catalyst**.

Collision theory

For a chemical reaction to occur, the particles involved must collide with each other with sufficient energy to overcome the activation energy 'barrier' to the reaction. This way of visualising reactions is known as **collision theory**.

Only 'successful' collisions, where the energy of collision is greater than the activation energy, allow a chemical reaction to progress. So, the rate of a chemical reaction is also dependent on the proportion of collisions that are successful.

According to collision theory, for a reaction to occur the reactant particles must collide with each other, and have an energy that is equal to, or greater than, the activation energy so that collisions break or weaken the bonds within the reactants and allow products to form.

2.1 Dynamic equilibrium



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- distinguish between open and closed systems
- appreciate why some reactions are described as reversible
- understand how reversible reactions in a closed system reach a dynamic equilibrium
- recognise that the extent of reaction can be different for different equilibria.

In this module, you will learn that some reactions can occur in both the forward and reverse directions. These reactions are called 'reversible reactions'.

Reversible chemical systems are encountered in many everyday situations, including chemical manufacturing processes, the reactions of ions within individual cells in your body and the reactions carbon dioxide undergoes in the environment.

This module also describes how some reversible reactions can reach a point where they appear to 'stop'. At this point, the concentrations of the reactants and products remain constant, even though there are still reactants remaining.

The fact that many reactions do not proceed to completion has important consequences for the production of chemicals by industry. The presence of large amounts of unreacted starting materials in reaction mixtures is wasteful and costly. The profitability of an industry depends on the yield—the extent of conversion of reactants into products.



FIGURE 2.1.1 A queue of constant length can be likened to a reaction that appears to have stopped. People leave the queue at one end at the same rate as others join it at the other end.

Although these reactions appear to stop, they actually continue to proceed. If you could see what was occurring at the atomic scale, you would notice that as rapidly as the reactants are forming products, the products are re-forming reactants. This situation can be likened to the queue shown in Figure 2.1.1. Although the length of the queue may seem constant, people at the front are continually leaving the queue and others are joining it at the back at the same rate.

OPEN AND CLOSED SYSTEMS

In Units 1 and 2, you learnt that a chemical reaction can be regarded as a **system**, with everything else around it (the rest of the universe) being the surroundings. In an endothermic reaction, the system absorbs energy from the surroundings, whereas in an exothermic reaction, energy is released to the surroundings.

Figure 2.1.2 illustrates how you can distinguish between the two different types of systems:

- **open systems**
- **closed systems**.

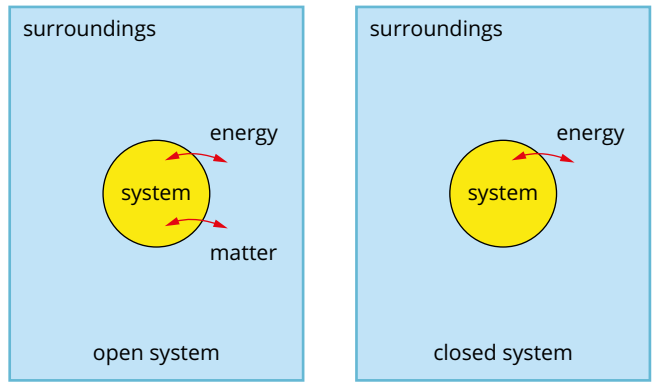


FIGURE 2.1.2 Open systems exchange energy and matter with the surroundings. Closed systems exchange only energy with the surroundings.

In a closed system, only energy can be exchanged with the surroundings.

The most common situation in everyday life is an open system. In an open system, matter and energy can be exchanged with the surroundings. In contrast, a closed system exchanges only energy with the surroundings.

Some examples of open and closed systems are illustrated in Figure 2.1.3.

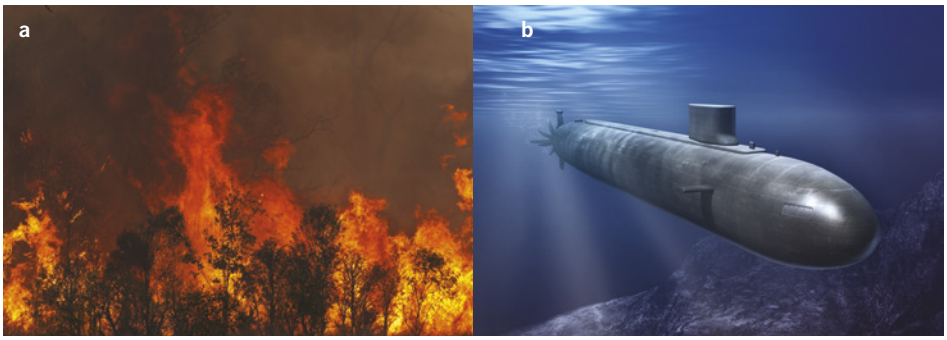


FIGURE 2.1.3 Everyday examples of open and closed systems. (a) A bushfire burning through a forest in south-west Queensland. This is an example of an open system. Carbon dioxide and water vapour produced by the burning trees are released into the atmosphere. (b) A nuclear submarine in operation under water—the carefully monitored environment of the submarine can be regarded as a closed system.

IRREVERSIBLE AND REVERSIBLE SYSTEMS

You may have thought, as a younger student, that when chemical reactions occur the reactants form products and these products cannot be converted back to the reactants. Such reactions, which occur only in one direction, are called non-reversible or **irreversible reactions**.

Baking a cake, like the one shown in Figure 2.1.4, involves several irreversible reactions. The reactions are complex, and include reactions that change the chemical structures of the protein in flour and egg, as well as reactions between protein and sugars.



FIGURE 2.1.4 Baking a cake involves a series of irreversible chemical reactions.

Combustion reactions such as the burning of methane are also irreversible:

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

Once a fuel has burnt, the products, carbon dioxide and water, do not react with each other under normal conditions.

As you will see, other reactions are **reversible reactions** where the products, once formed, can react together to re-form the reactants.

Reversibility of physical and chemical changes

Four examples of systems that are reversible are:

- evaporation and condensation of water
- a saturated sugar solution
- oxygen transport in the blood
- synthesis of ammonia.

These examples are described below.

Evaporation and condensation of water



You are familiar with the idea that a physical change, such as a state change, can be reversed. The evaporation of water from lakes and rivers leading to cloud formation and eventually rain is an example of a physical change. Water can cycle between the different phases of solid, liquid and gas because each process is reversible.

The evaporation of water can be expressed by the equation:

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

The condensation of water can be expressed by the equation:

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

Equilibrium is not achieved in an open system.

Equilibrium is achieved in a closed system when the rates of the forward and reverse reactions are equal.

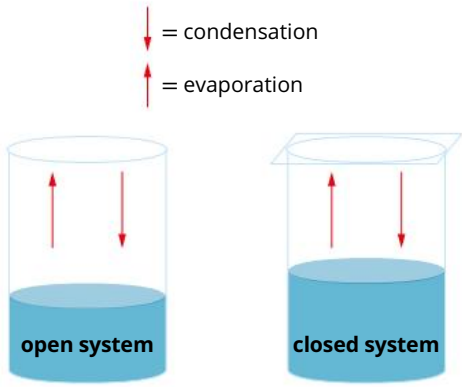


FIGURE 2.1.5 A physical change—the evaporation and condensation of water—in open and closed systems. In the open system, all the water eventually evaporates.

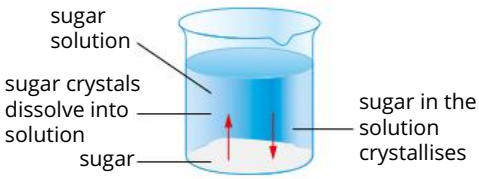


FIGURE 2.1.6 A representation of the processes occurring in a saturated sugar solution

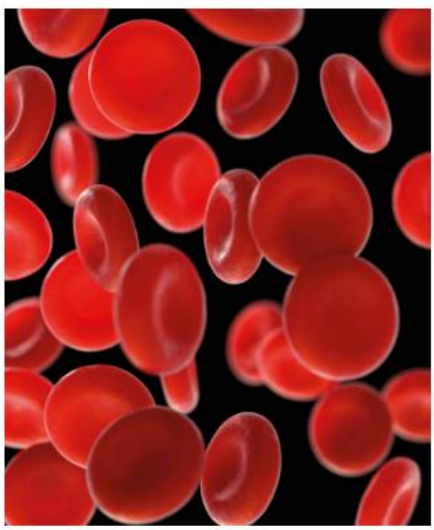


FIGURE 2.1.7 Blood cells contain a red pigment, haemoglobin, that transports oxygen from the lungs to other cells in the body.

In chemistry, a double arrow (⇌) is used when writing a chemical equation to show a reversible process. In this way, you can show the phase changes associated with water using the following equation:

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

As you can see in the diagram of water in two glasses in Figure 2.1.5, these changes of state can occur in either open or closed systems. In a closed system, the water vapour cannot escape. In general, reversible reactions in a closed system eventually reach a situation where the rates of the forward and reverse reactions are equal. At this point there will appear to be no further change to the observer. The system is described as having reached a state of **equilibrium**.

However, in an open system, although water can evaporate and condense, the rate of each process is not equal. Gaseous water molecules are escaping into the atmosphere, so the rate of the reverse reaction (condensation) does not become equal to the rate of the forward reaction. Equilibrium is not achieved in an open system.

Saturated sugar solutions

A **saturated solution** contains the maximum amount of solute dissolved in the solution. Consider a saturated solution of sugar in contact with undissolved sugar crystals at a constant temperature, as shown in Figure 2.1.6.

Even though it appears to an observer that nothing is happening, on a molecular level the molecules are constantly in motion and exchanging between the phases. The sugar molecules ($C_{12}H_{22}O_{11}$) are dissolving at the same rate as they are crystallising and the mass of sugar crystals present is constant. The process is reversible and at equilibrium. It can be represented by the equation:

$$C_{12}H_{22}O_{11}(s) \rightleftharpoons C_{12}H_{22}O_{11}(aq)$$

While there is no lid on the beaker, this system can still be regarded as a closed system. No gas is involved, so there is no loss of the reactant or product molecules to the surroundings.

Haemoglobin and oxygen gas

Haemoglobin is a large protein molecule that is the pigment in red blood cells, as shown in Figure 2.1.7. It is responsible for the transport of oxygen from your lungs to the cells in the body. When you inhale, oxygen from the air combines with haemoglobin in the small blood vessels in the lining of the lungs to form oxyhaemoglobin:

$$\text{haemoglobin} + \text{oxygen} \rightarrow \text{oxyhaemoglobin}$$

The reaction between haemoglobin and oxygen gas is a reversible chemical reaction. The oxyhaemoglobin is transported through the blood system to other cells in the body where oxygen is released:

$$\text{oxyhaemoglobin} \rightarrow \text{haemoglobin} + \text{oxygen}$$

The oxygen is used by cells for respiration, to provide energy for the body.

The reaction can therefore be written as:

$$\text{haemoglobin} + \text{oxygen} \rightleftharpoons \text{oxyhaemoglobin}$$

Although this can be regarded as an open system overall, an equilibrium is established in the blood as it flows through the body. During this period it may be thought of as a closed system because there is no loss of reactants or products to the surroundings.

Synthesis of ammonia

The production of ammonia from nitrogen gas and hydrogen gas is known as the Haber process. (This process will be covered in more detail in Module 12.4.) The main reaction in the Haber process is reversible and can be represented by the equation:

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

Suppose you mix 1 mole of nitrogen gas and 3 moles of hydrogen gas in a sealed container. From the equation, you might expect that 2 moles of ammonia would eventually be formed. However, no matter how long you wait, the reaction seems to 'stop' when much less than 2 moles of ammonia is present, as shown in Figure 2.1.8.

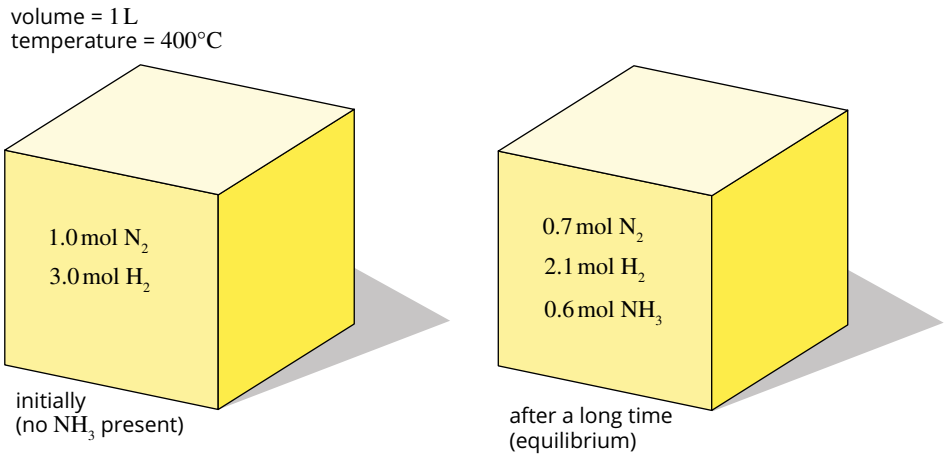


FIGURE 2.1.8 When 1 mole of nitrogen and 3 moles of hydrogen are mixed, the reaction to form ammonia appears to stop before all the reactants are consumed.

The reaction vessel in this process creates a closed system from which the reactants and products cannot escape. Once some products are formed, as a result of collisions between reactant particles, then the collisions between product particles can result in the reactants being re-formed. The reaction eventually reaches a situation where the rate of the forward reaction and the rate of the reverse reaction are equal and an equilibrium is formed.

As for our earlier examples, when a reaction reaches equilibrium there appears to be no further change to the observer and the reaction appears to have 'stopped'. At equilibrium, there still may be significant amounts of reactants in the system.

Explaining reversibility

The reason why reversible reactions can occur can be understood by referring to **energy profile diagrams**, which represent the energy changes that occur during chemical reactions.

When particles collide, the energy associated with collisions can break bonds in the reacting particles, allowing them to rearrange to form new products. The energy required to break or weaken the bonds of the reactants in order for the reaction to occur is known as the activation energy of the reaction.

You can see from the energy profile diagram shown in Figure 2.1.9 that, once products form, if these product particles collide with enough energy to break their bonds (equal to the activation energy of the reverse reaction), then it is possible to re-form the original reactants.

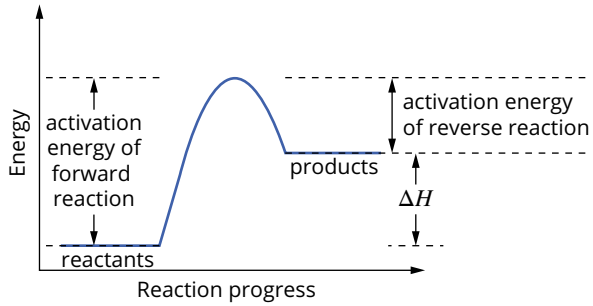


FIGURE 2.1.9 An energy profile diagram for an endothermic reaction showing the activation energy required for both the forward reaction (formation of products) and reverse reaction (re-formation of reactants).

Note that if the forward reaction is endothermic, the reverse reaction will be exothermic, and vice versa.

EXPLAINING EQUILIBRIUM

Because the reaction between nitrogen and hydrogen to form ammonia is a reversible reaction, it is best written using an equilibrium arrow:

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

Equilibrium arrows indicate that the reaction can occur in both the forward and reverse directions. These arrows should not be used where the reaction can only proceed one way.

The idea that processes can be reversed can be used to understand why this reaction reaches equilibrium. When nitrogen gas and hydrogen gas are added to a sealed container at a constant temperature, a sequence of events occurs that can be illustrated by a plot of reaction rate versus time like the one shown in Figure 2.1.10.

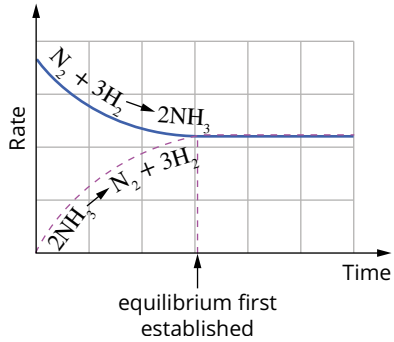


FIGURE 2.1.10 The variation of the rates of the forward and reverse reactions with time when nitrogen and hydrogen are mixed.

If you consider the graph in Figure 2.1.10, you can understand the following:

- Nitrogen and hydrogen gas molecules collide with each other and form ammonia. As the forward reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, proceeds, the concentrations of nitrogen and hydrogen decrease, so the frequency of collisions between molecules decreases and the rate of the production of ammonia decreases.
- At the same time as ammonia is being formed, some ammonia molecules collide and decompose to re-form nitrogen and hydrogen: $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$.
- Eventually the forward and reverse reactions proceed at the same rate. When this situation is reached, ammonia is formed at exactly the same rate as it is breaking down. The concentrations of ammonia, nitrogen and hydrogen then remain constant. To an observer, the reaction now appears to have stopped with no observable change.

In a closed system at constant pressure and temperature, no further change will take place. The reaction has reached a point of balance—an equilibrium.

The concentration versus time graph in Figure 2.1.11 shows the changes in concentrations of the chemicals with time. Equilibrium is established when there is no longer any change in any of the concentrations.

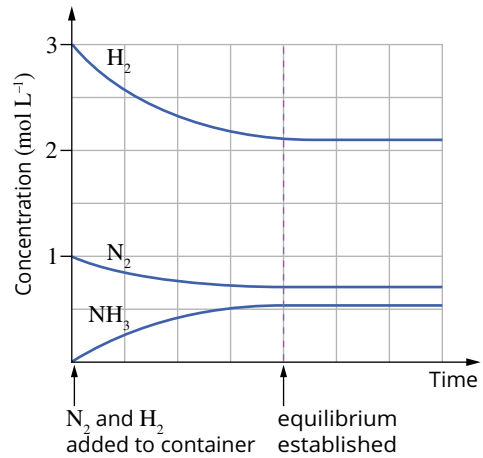


FIGURE 2.1.11 Changes in the concentrations of N_2, H_2 and NH_3 as a mixture of nitrogen and hydrogen gas reacts. As indicated by the coefficients of the equation for the reaction, for every mole of N_2 that reacts, three times as much H_2 reacts and twice as much NH_3 is produced.

When considering graphs involving equilibrium systems, always check if the data is presented as a plot of concentration versus time, or as a plot of reaction rate versus time.

Dynamic state of equilibrium

Chemical equilibrium can be described as being in a dynamic state because the forward and reverse reactions have not ceased. Instead, they occur simultaneously at the same rate.

During **dynamic equilibrium**:

- the reaction is 'incomplete' and *all* of the substances (that is, the reactants and products) are present in the equilibrium mixture
- at the molecular level, bonds are constantly being broken and new bonds are being formed as the reactants and products continue to be converted from one to another.

The decomposition of dinitrogen tetroxide (N_2O_4) to nitrogen dioxide (NO_2) is an example of a reversible reaction that reaches a dynamic equilibrium. The progression of this reaction from pure N_2O_4 to the equilibrium mixture containing both N_2O_4 and NO_2 can be monitored through the changing colour of the gases in the reaction vessel. N_2O_4 is colourless and NO_2 is dark brown.

The reaction occurs according to the following equation:

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

Figure 2.1.12 illustrates the observations made of a reaction vessel that is injected with some pure N_2O_4. As the forward reaction proceeds, the formation of a dark brown gas is observed. The depth of colour increases until equilibrium is reached, at which point there is no further change in the colour.

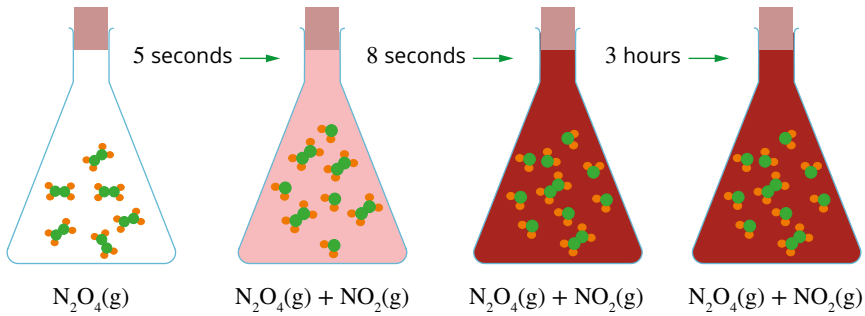


FIGURE 2.1.12 The decomposition of dinitrogen tetroxide produces the brown gas nitrogen dioxide. As the concentration of nitrogen dioxide increases, the colour deepens until equilibrium is reached. At equilibrium (after 8 seconds), there is no further change in colour regardless of how long the reaction is allowed to proceed.

Dynamic equilibrium is reached by reversible physical or chemical reactions taking place in a closed system.

EXTENT OF REACTION

You have seen that reactions are reversible, but do all reactions proceed to the same extent before they reach equilibrium? This can be answered with a simple experiment.

As you will see in Module 3.2, both hydrogen chloride (HCl) and ethanoic acid (CH_3COOH) react with water to form ions, according to the equations:

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

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

Solutions of both chemicals conduct electricity because they contain mobile ions. The relative conductivity of the solutions is proportional to the number of free ions in the solution. By measuring the electrical conductivity of solutions of the same concentration, you can compare how much each compound ionises in water.

Figure 2.1.13 shows the results obtained from such an experiment. You can see that the solution formed when hydrogen chloride dissolves in water (called hydrochloric acid) is a much better conductor than the ethanoic acid solution. Both solutions were formed by adding the same number of moles of acid to identical volumes of water.

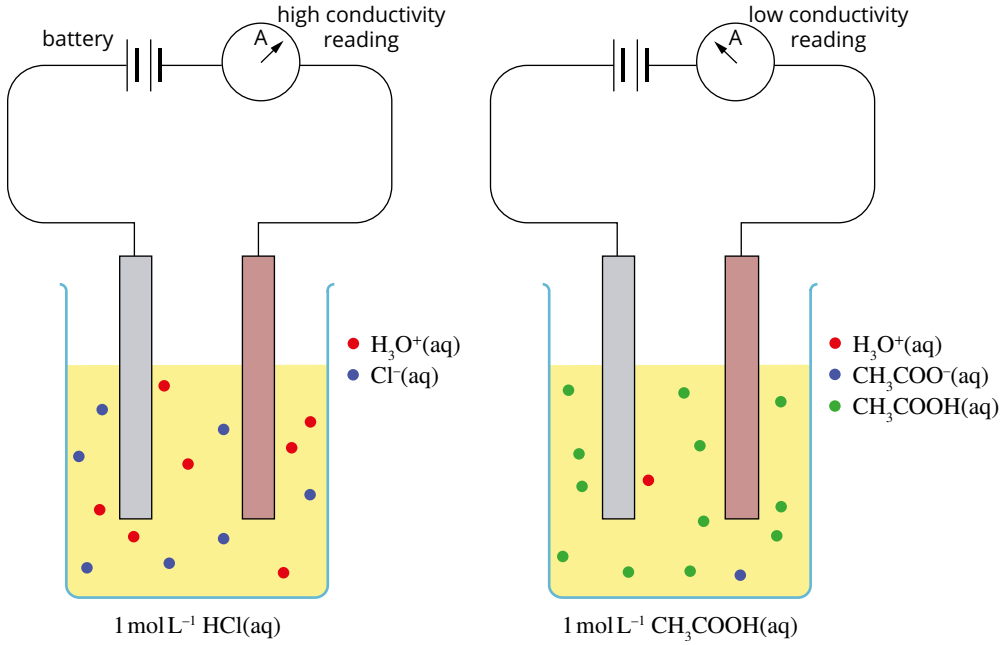


FIGURE 2.1.13 This experiment compares the electrical conductivity of 1 mol L^{-1} solutions of hydrochloric acid and ethanoic acid.

As you will remember from Unit 2, ethanoic acid is a weak acid and will therefore only partially ionise in an aqueous solution. Hydrochloric acid is a strong acid that almost completely ionises in aqueous solution. The concept of equilibrium allows us to better explain the idea of strong and weak acids by looking at the extent of the ionisation reaction (see Module 3.2).

The difference in conductivity observed in the experiment arises because these reactions occur to remarkably different extents. At equilibrium in a 1 mol L^{-1} solution, at 25°C, almost all the HCl molecules are ionised, whereas only approximately 1% of the CH_3COOH molecules are ionised.

We can conclude that different reactions proceed to different extents. The ratios of reactants to products are different for different equilibrium systems.

It is important to note that the **extent of reaction** describes how much product is formed when the system reaches equilibrium. However, the **rate of reaction** is a measure of the change in concentration of the reactants and products with time and is not directly related to the extent of reaction. The rates of reversible reactions range from very slow to very fast and determine how long the reaction takes to reach equilibrium.

The extent of a reaction does not give any information about how fast a reaction will proceed. It only indicates how much product is formed once the system is at equilibrium.

2.1 Review

SUMMARY

- In a closed system, only energy, not matter, is exchanged with the surroundings.
- In an open system, both matter and energy are exchanged between the system and the surroundings.
- A reversible reaction is a reaction in which the products can react together to be converted back to the reactants.
- An irreversible reaction is a reaction in which the products cannot react together to be converted back to the reactants.
- A double arrow (⇌) is used when writing a chemical equation to show a reversible process.
- Reversible reactions can reach a point where the rate of the forward reaction and the rate of the reverse reaction are equal. At this point, a dynamic equilibrium has been achieved.
- Equilibrium can be achieved in closed systems but not in open systems.
- Different reactions proceed to different extents.
- The relative ratio of reactants to products when equilibrium is reached is different for different reactions.
- The extent of reaction indicates how much product is formed at equilibrium, whereas the rate of reaction is a measure of the change in the concentrations of the reactants and products with time.

KEY QUESTIONS

Retrieval

1 Select the correct response in the statements about chemical equilibria.

a An **open/closed** system occurs when both matter and energy are exchanged between the system and the surroundings.

b Chemical equilibria can occur in **open/closed** systems.

c In some circumstances, a reversible reaction can form a **dynamic/static** equilibrium.

d The extent of reaction for chemical equilibria is **constant/different** for different equilibria.

2 Indicate whether each of the following statements about the extent of reaction is true or false.

a The extent of reaction indicates the rate of the reaction, and indicates the time taken to reach equilibrium.

b The extent of reaction is the point when there are equal amounts of reactants and products.

c The extent of reaction indicates how far the reaction has proceeded in the forward direction when equilibrium is achieved.

d The extent of reaction indicates the rate of reaction and is the point when the rate of the forward reaction is equal to the rate of the reverse reaction.

Comprehension

3 Hydrogen gas is mixed with iodine gas in a sealed container. A reaction occurs according to the equation:

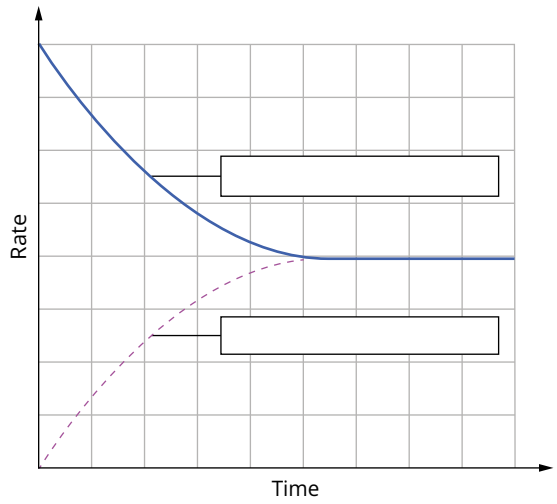
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Refer to the rate–time graph for this system shown below. Determine and label the following items on the graph.

a The forward reaction with the appropriate chemical equation.

b The reverse reaction with the appropriate chemical equation.

c The point when equilibrium is first established.



continued over page

2.1 Review *continued*

4 Summarise dynamic equilibrium using the correct words to fill in the blanks below.
In a _____ system, as the concentrations of the reactants decreases, the rate of the forward reaction also _____. The collisions between these reactant molecules occur _____ frequently. Once some product starts to form, the _____ reaction occurs and the frequency of collisions between product molecules _____. At equilibrium, the rates of the forward and reverse reactions are _____ and the concentrations of all species do not change.

Analysis

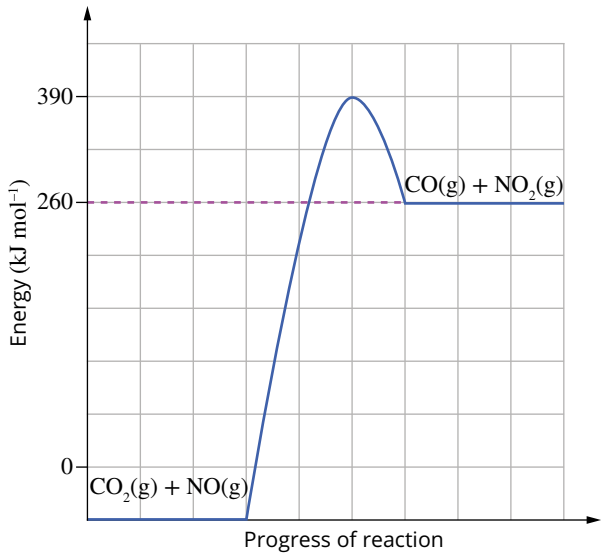
5 Classify the following systems as open or closed and explain your reasoning.
- **a** a car engine in operation
- **b** a can of soup
- **c** a tree

6 Determine which of the following systems are at equilibrium and explain your answer.
- **A** A salt crystal slowly dissolving in a beaker of water.
- **B** A saturated sugar solution with sugar remaining on the bottom of the cup.
- **C** An open bottle of perfume.
- **D** The combustion of a log of wood in a campfire.
- **E** An open bottle of sparkling mineral water.
- **F** An unopened bottle of sparkling mineral water.

7 The graph below shows the energy profile diagram for the reaction:

$$CO_2(g) + NO(g) \rightarrow CO(g) + NO_2(g)$$

Determine the activation energy for the reverse reaction in $kJ\,mol^{-1}$.

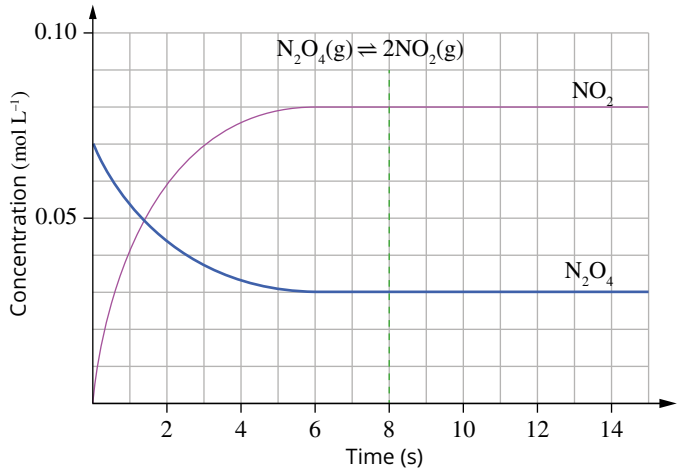


8 Consider the following equilibrium.

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

- **a** Explain what is meant by the 'dynamic nature' of equilibrium and why wet clothes in a closed laundry bag do not dry.
- **b** When the bag in part **a** is opened, the clothes begin to dry. Assess whether this is because of an equilibrium process. Explain your answer.

9 The graph below shows the concentration versus time plot for the decomposition of dinitrogen tetroxide: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 100°C in a 1 L reaction vessel. N_2O_4 is a colourless gas and NO_2 is brown. Use the graph to determine the answer to the following questions.



- **a** State the initial concentration of N_2O_4 in the flask.
- **b** State the initial concentration of NO_2 in the flask.
- **c** Identify the concentration of N_2O_4 at equilibrium.
- **d** Identify the concentration of NO_2 at equilibrium.
- **e** Calculate the number of moles of N_2O_4 that decompose during the reaction.
- **f** State what the horizontal regions of the graph indicate.
- **g** Identify how long it takes for equilibrium to be reached.
- **h** Describe what a student studying this reaction will observe as the reaction proceeds.

2.2 Factors that affect equilibrium

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- explain the effect of adding extra reactant or product on a chemical equilibrium using collision theory and reaction rates
- predict the effect of adding extra reactant or product by the application of Le Châtelier's principle.



In this module, you will learn about some of the effects of changes on chemical systems at equilibrium.

Your understanding of the underlying principles of chemical equilibrium will enable you to predict the impact of changes when a reactant or product is added or removed from an equilibrium system, as seen in the system described in Figure 2.2.1. In this example, the addition of excess Cl^- ions causes a net forward reaction and the solution turns blue as more $CoCl_4^{2-}$ is formed. The addition of excess water causes a net reverse reaction and the solution returns to the original pink colour as more $[Co(H_2O)_6]^{2+}$ is formed.

You have seen in Module 2.1 that different reactions proceed to different extents. As a consequence, the relative amounts of reactants and products differ from one reaction to another at equilibrium. The relative amounts of reactants and products at equilibrium is called the **position of equilibrium**.

The relative amounts of substances present in equilibrium mixtures depend upon reaction conditions. For any equilibrium system, the position of equilibrium may be changed by:

- adding or removing a reactant or product
- changing the pressure by changing the volume of the sealed container (for equilibria involving gases)
- dilution (for equilibria in solution)
- changing the temperature.

Careful control of the reaction conditions allows chemists to maximise the equilibrium yield of a desired product by moving the position of equilibrium 'to the right' (and therefore increasing the amount of products formed).



FIGURE 2.2.1 The effect of changes on the equilibrium: $Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$

LE CHÂTELIER'S PRINCIPLE

The effect of a change in conditions on an equilibrium system is summarised in a useful generalisation called **Le Châtelier's principle**. The principle is named after Henri Le Châtelier (Figure 2.2.2), a French chemist and engineer.

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

When a change occurs to an equilibrium system so that it is momentarily no longer at equilibrium, the system shifts to partially counteract the effect of the change. The system will establish a new equilibrium.

As a result, the position of equilibrium will change. There may be an increase in the amount of either products or reactants, depending on the nature of the change. By understanding Le Châtelier's principle, you can predict the effect of a change to an equilibrium system.

You will now consider the effect of different changes on equilibrium systems.

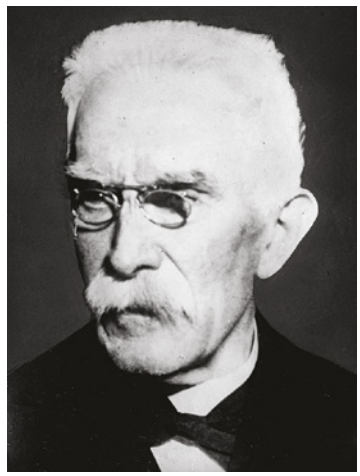


FIGURE 2.2.2 Henri Le Châtelier (1850–1936)

Adding more reactant or product

A sealed reaction vessel of nitrogen and hydrogen gases at a particular temperature will establish an equilibrium according to the equation:

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

At equilibrium, the rates of the forward and reverse reactions are equal. The concentrations of the three gases are constant. If more nitrogen gas were added to the container without changing the volume or temperature, the mixture would momentarily not be in equilibrium. The system would then adjust to form a new equilibrium with different concentrations and partial pressures of N_2, H_2 and NH_3.

You can predict the change in the position of the equilibrium by using Le Châtelier's principle. The underlying basis for this prediction can be understood by applying the principles of collision theory and the rates of reactions.

Predicting the effect of a change using Le Châtelier's principle

The effect of adding the N_2 gas to the equilibrium may be predicted simply by applying Le Châtelier's principle. According to Le Châtelier's principle, if N_2 is added to an equilibrium system, the system will shift to decrease the concentration of the added N_2, so a net forward reaction will occur.

It is important to note that, even though the concentration of N_2 gas decreases as the system moves to establish the new equilibrium, its final concentration is still higher than in the original equilibrium. Le Châtelier's principle states that the change is partially opposed. The system does not return to the initial equilibrium position following the change in conditions.

Explaining the effect of a change using collision theory and reaction rates

Instead of using Le Châtelier's principle, you can apply your knowledge of collision theory and reaction rates to understand the reasons for the effect of adding the extra N_2 gas. Because the concentration of N_2 molecules has increased, the rate of the forward reaction initially becomes greater than the rate of the reverse reaction. Then, as the concentration of N_2 and H_2 decreases and the concentration of NH_3 increases, the rate of the forward reaction rate decreases and the rate of the reverse reaction increases until they become equal again. A new equilibrium is formed.

The rate–time graph in Figure 2.2.3 shows the effect on the rate of the forward and reverse reactions as the composition of the mixture adjusts to form a new equilibrium.

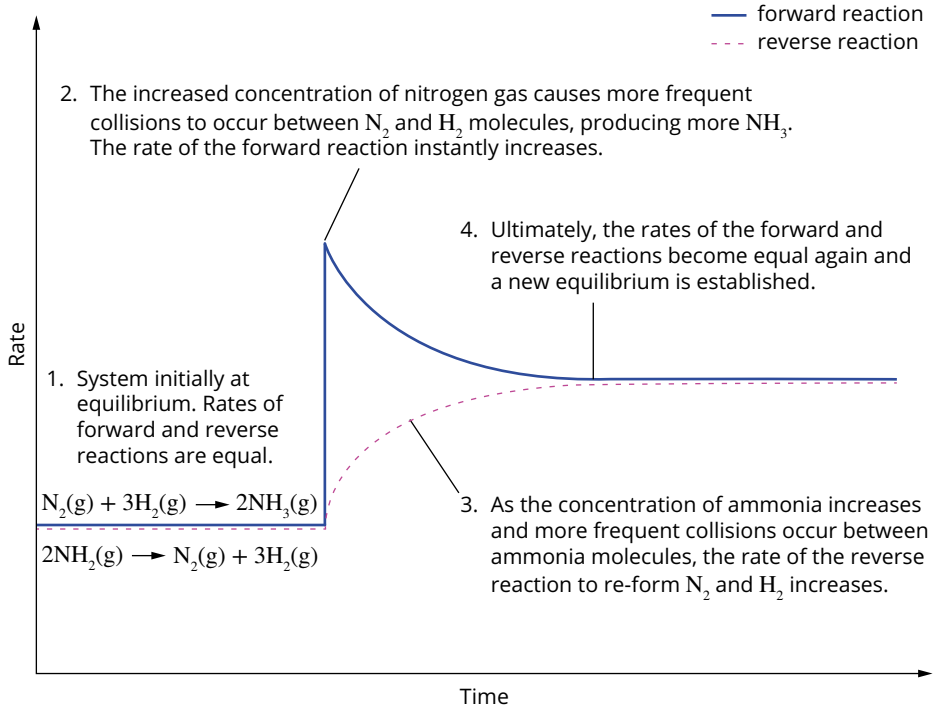


FIGURE 2.2.3 This rate–time graph shows the events that occur as a mixture of nitrogen, hydrogen and ammonia gas returns to equilibrium after the addition of extra nitrogen gas.

Once the system has re-established equilibrium, the rates of the forward and reverse reactions will again be equal. Overall though, a net forward reaction has occurred with an increase in the concentration of ammonia at equilibrium. The equilibrium position is said to have shifted 'to the right'.

The changes occurring to the system can also be shown on a concentration–time graph. Figure 2.2.4 illustrates the effect on the system when N_2 gas is added as described.

If you follow the same reasoning as for N_2, you can see that adding extra amounts of the other reactant, H_2, to the system will also increase the concentration

> **Collision theory** is used to explain the different rates of chemical reactions. It states that for a reaction to occur, the reactant particles must collide. The more successful collisions that occur within a specified time period, the faster is the reaction rate.

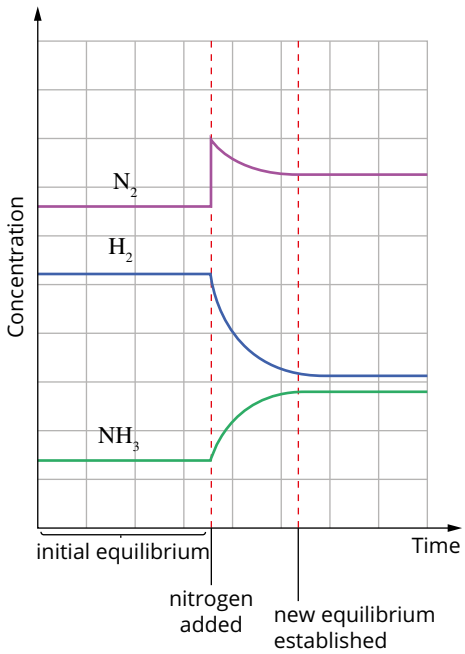


FIGURE 2.2.4 A representation of changes in concentrations that occur when additional nitrogen gas is added to the equilibrium: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

of ammonia produced. However, the addition of more product, NH_3, would result in a net reverse reaction and the equilibrium position shifting to the left, reducing the overall concentration of ammonia as seen in Figure 2.2.5.

While you can apply your knowledge of collision theory and reaction rates to determine the overall effect of changes on an equilibrium as was done above, applying Le Châtelier's principle is a simpler way of predicting these effects.

Table 2.2.1 summarises how an equilibrium system acts to oppose the addition or removal of reactants and products.

TABLE 2.2.1 The general effects of a change to a system at equilibrium as predicted by Le Châtelier's principle

Change to equilibrium	Effect
adding a reactant	formation of more products—a net forward reaction; equilibrium position shifts to the right
adding a product	formation of more reactants—a net reverse reaction; equilibrium position shifts to the left
removing a product	formation of more products—a net forward reaction; equilibrium position shifts to the right

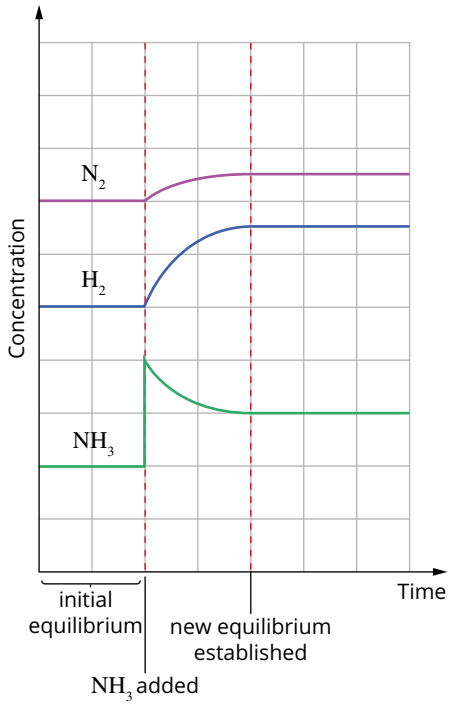


FIGURE 2.2.5 A representation of changes in concentrations that occur when additional ammonia gas is added to the equilibrium: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_2(g)$

Worked example 2.2.1

USING COLLISION THEORY TO EXPLAIN THE EFFECT OF ADDITION OF A REACTANT OR PRODUCT ON AN EQUILIBRIUM SYSTEM

In solution, $Co(H_2O)_6^{2+}$ ions form an equilibrium with $CoCl_4^{2-}(aq)$ ions, as shown by the equation:

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

Use the concepts of rates of reaction and collision theory to predict the effect on the position of equilibrium of the addition of Cl^- ions on the equilibrium.

Thinking	Working
Determine the initial effect of the change on the concentration of the particles.	Adding Cl^- ions increases the concentration of these ions.
Use collision theory to determine the initial effect on the rate of the forward (or reverse) reaction.	Collisions between $Co(H_2O)_6^{2+}$ ions and Cl^- ions become more frequent, increasing the rate of the forward reaction and reducing the concentration of $Co(H_2O)_6^{2+}$ and Cl^- ions.
Consider how the rates of the forward and reverse reactions change as the system reaches a new equilibrium.	As more product ions, $CoCl_4^{2-}$, are formed, the rate of the reverse reaction increases, until the rates of the forward and reverse reactions become equal and a new equilibrium is established.
Predict the overall effect of the change on the position of equilibrium.	A net forward reaction has occurred.

➤ Try yourself 2.2.1

USING COLLISION THEORY TO EXPLAIN THE EFFECT OF ADDITION OF A REACTANT OR PRODUCT ON AN EQUILIBRIUM SYSTEM

Consider the following equilibrium system:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

Use the concepts of rates of reaction and collision theory to predict the effect on the position of equilibrium of the addition of CO gas on the equilibrium.

Chemical balance in wine

Grapes have been cultivated for wine production for thousands of years. The production of wine involves the fermentation of sugars from the grape juice to form ethanol, which can be represented simply by the unbalanced equation:

$$C_6H_{12}O_6(aq) \rightarrow CH_3CH_2OH(aq)$$

However, the chemistry of winemaking is far from simple and still not completely understood. As chemists have learnt more about the reactions involved, their discoveries have contributed greatly to the improvement of wine quality. A number of different chemical equilibria are involved in wines and wine production. Two of the most important equilibria involve sulfur dioxide and tartaric acid.

Sulfur dioxide in wine

Sulfur dioxide gas, SO_2, is used as a preservative in winemaking to prevent the growth of microorganisms. The amount of SO_2 that can be added is controlled by legislation and it can be added directly as a gas or in the form of different sulfite salts. It forms the following equilibrium system in wine, which involves hydrogen sulfite ions (HSO_3^-) and sulfite ions (SO_3^{2-}):

$$SO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq)$$
$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_3^{2-}(aq)$$

The relative positions of these equilibria depend on the concentration of H_3O^+ ions in the wine. As the H_3O^+ concentration increases (and pH decreases), you can see from your knowledge of Le Châtelier's principle that the equilibria will shift to the left and the concentration of SO_2 will increase. Since SO_2 is more effective as a preservative than HSO_3^- or SO_3^{2-}, winemakers adjust the pH to a low value to ensure the free SO_2 is at a safe but effective level. A balance is involved, however, as excess SO_2 gives wine a metallic and bitter taste.

Tartaric acid in wine

There are three main organic acids in wine: malic, tartaric and citric acid. The acids contribute to the acidic taste and flavour of the wine and assist in maintaining its pH in the desired range of about 3.2–3.3. These acids react with water to form equilibria in the wine. For example, tartaric acid, $C_4H_6O_6$ (Figure 2.2.6), is a **diprotic acid** and ionises in water as follows:

$$C_4H_6O_6(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_4H_5O_6^-(aq)$$
$$C_4H_5O_6^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_4H_4O_6^{2-}(aq)$$

(Diprotic acids will be covered in more detail in Chapter 3.)

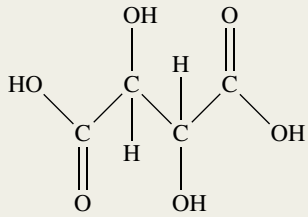


FIGURE 2.2.6 Tartaric acid

Tartaric acid is of particular importance because it is in equilibrium with the hydrogen tartrate ion ($C_4H_5O_6^-$). Winemakers must carefully adjust conditions, including pH, to avoid potassium ions from the skins of the grapes reacting with the hydrogen tartrate ions and forming a precipitate of potassium hydrogen tartrate ($KC_4H_5O_6$). Although soluble in water, potassium hydrogen tartrate is relatively insoluble in aqueous solutions of ethanol:

$$K^+(aq) + C_4H_5O_6^-(aq) \rightleftharpoons KC_4H_5O_6(s)$$

The solid potassium hydrogen tartrate can appear as crystalline deposits on the bottom of the bottle or on the seal, as shown in Figure 2.2.7. Although the crystals are harmless, their presence is regarded as undesirable and unsightly.



FIGURE 2.2.7 Potassium hydrogen tartrate crystals on the bottom of the seal of a bottle of wine. The crystals are normally colourless but have been coloured red by the wine.

As you can see, chemical equilibria and Le Châtelier's principle are fundamental to the chemical balance of wine. Wine is just one of many examples of the importance of chemical equilibria in food and drink.

Review

1 Select the correct words to complete the following statements.
Sulfur dioxide is added to wine to act as a **preservative/flavour enhancer**. It reacts with water to form an equilibrium that involves **sulfate/sulfite** ions. The reaction of sulfur dioxide with water forms an **acidic/basic** solution. The concentration of sulfur dioxide in wine increases as the pH **increases/decreases** and the concentration of H_3O^+ ions **increases/decreases**.

2 Tartaric acid, $C_4H_6O_6$, is involved in the following equilibrium in grape juice and wine:

$$C_4H_6O_6(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_4H_5O_6^-(aq)$$

a Describe the main complication caused by the presence of tartaric acid for winemakers.

b Explain what happens to the relative amounts of $C_4H_6O_6$ and $C_4H_5O_6^-$ as the pH increases.

Carbon dioxide in the atmosphere

The atmosphere consists of a mixture of gases extending about 100 km above Earth's surface. Without the atmosphere, Earth could not support life as we know it. Daily temperatures would be extremely high, while nights would be extremely cold.

Carbon dioxide gas in the atmosphere is essential to life on Earth. Although carbon dioxide occupies only about 0.04% of the total mass of the atmosphere, this concentration is sufficient to sustain life. Through the carbon cycle, shown in Figure 2.2.8, carbon is exchanged between the atmosphere, oceans, rivers, lakes, soils and rocks.

The concentration of carbon dioxide in the atmosphere depends on the rate at which it enters and leaves the different stages of the carbon cycle. An equilibrium will exist if these rates are equal.

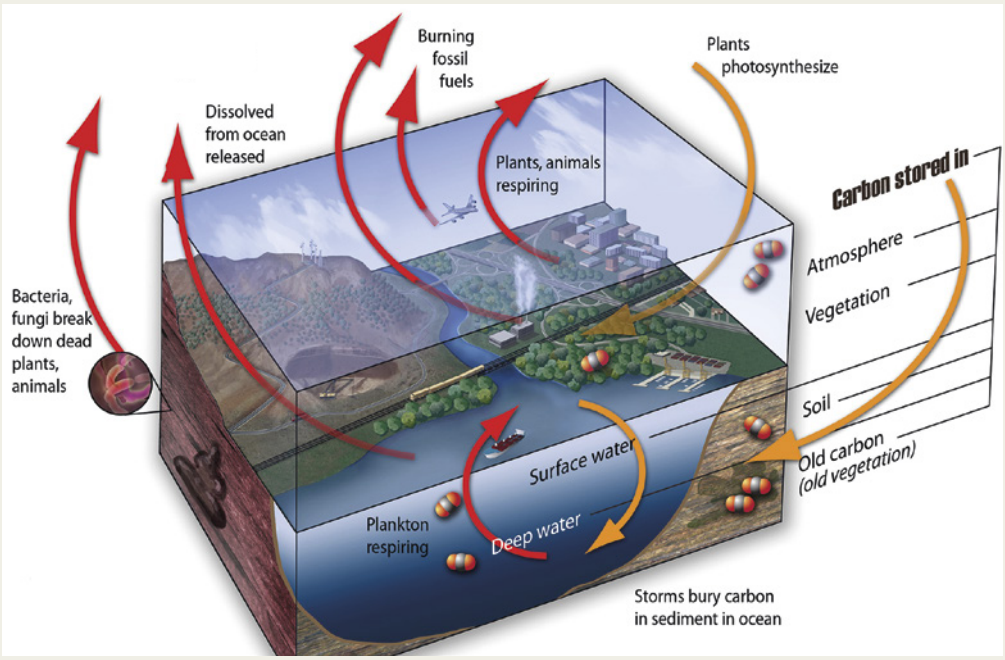


FIGURE 2.2.8 Carbon cycles between land, the atmosphere and the oceans in billions of tonnes each year. It takes about 100 years for half the available carbon atoms to leave and re-enter the atmosphere.

The greenhouse effect

Earth receives visible and ultraviolet radiation from the Sun. This energy can pass through the atmosphere to the Earth's surface. Earth then radiates this energy back into space as lower-energy infrared radiation.

Gases such as carbon dioxide, water vapour and methane are called **greenhouse gases**. They absorb some of the infrared radiation before it can reach space and can re-radiate it back towards Earth as heat. The higher the concentration of greenhouse gases, the more energy is trapped. This natural process is known as the greenhouse effect, because it warms the surface of Earth in a similar way to how the Sun's energy heats a greenhouse.

Figure 2.2.9 shows how the greenhouse effect occurs. Without the atmosphere, Earth would not maintain its average temperature. The effect has been essential for the evolution of life, because it sustains the equilibrium of the elements in the carbon cycle.

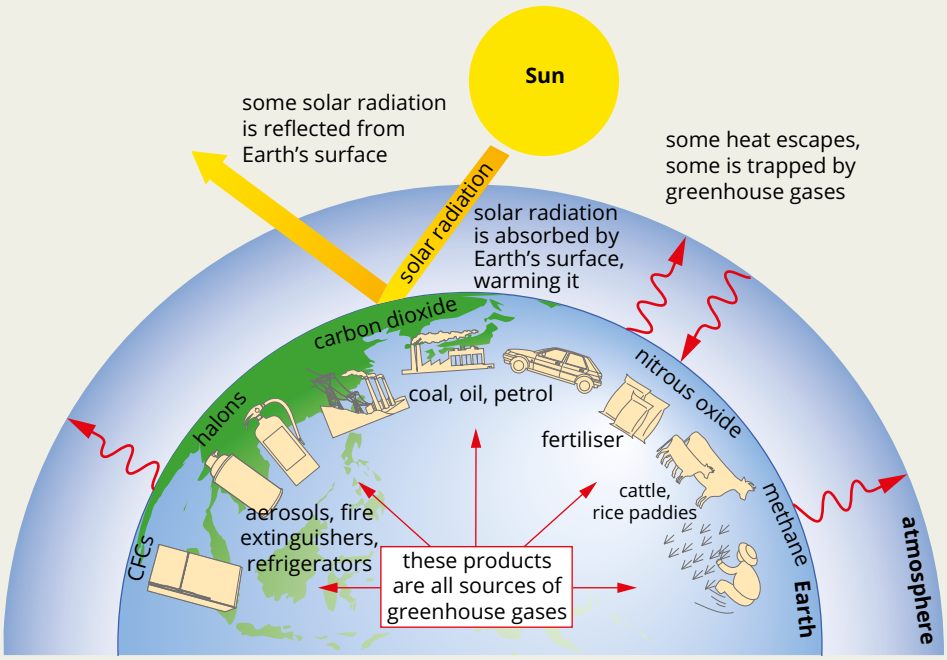


FIGURE 2.2.9 The greenhouse effect. Greenhouse gases help to maintain the temperature at Earth's surface.

Global warming

Studies have shown that the levels of atmospheric carbon dioxide have varied naturally over the last several thousand years. However, since the Industrial Revolution, an increase in the use of fossil fuels has caused the average global concentration of carbon dioxide in the atmosphere to rise by more than 40%. This can be seen in Figure 2.2.10. The result is an increase in the infrared radiation absorbed and re-radiated back towards Earth.

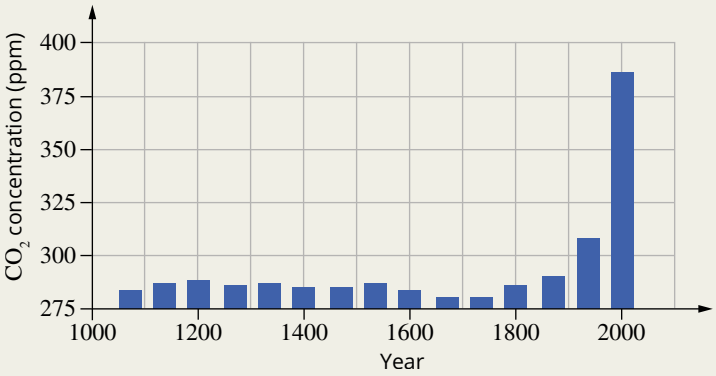


FIGURE 2.2.10 Concentrations of atmospheric carbon dioxide for the last 1000 years.

Scientists are concerned that the increasing levels of greenhouse gases are influencing surface land and sea temperatures and causing **climate change**. This effect is also referred to as the enhanced greenhouse effect. It is proposed that the higher global temperatures are responsible for rising sea levels and triggering shifts in snow and rainfall patterns, as well as some of the more extreme climate events in different parts of the world. These climate events include severe storms and cyclones, more frequent droughts and intense rainfall, causing flooding.

Warmer water temperatures can also result in **coral bleaching**. When water is too warm, the algae living in the tissues of the coral are expelled, causing the coral to turn completely white.

The graph shown in Figure 2.2.11 shows the changes in average global surface temperatures over time. A comparison of Figure 2.2.10 and Figure 2.2.11 shows the correlation between increasing levels of carbon dioxide and increasing surface temperatures.

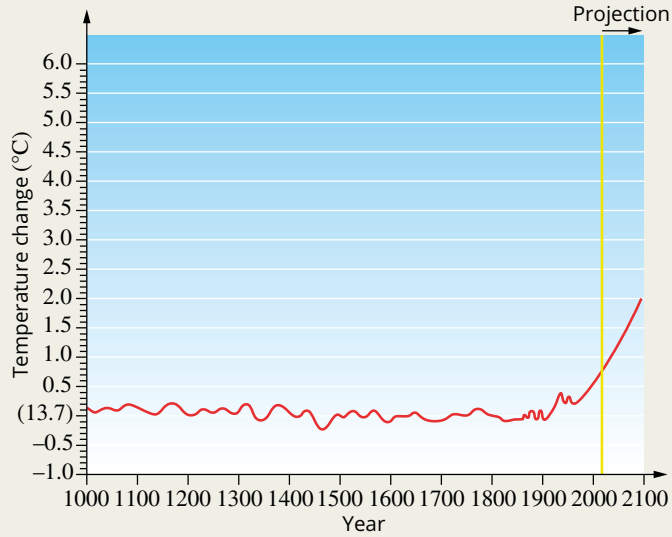


FIGURE 2.2.11 Change in the average surface temperature of Earth from the year 1000 projected to 2100. Estimates of future temperatures vary, depending on what assumptions are made about future energy use. The average surface temperature in the 20th century was 13.7°C.

Carbon dioxide in the hydrosphere

All the bodies of water on Earth's surface, such as lakes and oceans, are collectively known as the **hydrosphere**. The hydrosphere contributes to the maintenance of steady concentrations of atmospheric carbon dioxide because the gas is slightly soluble in water through a range of reversible processes. The oceans contain the largest amount of water in the hydrosphere. A series of inter-related equilibria involving the small concentration of dissolved carbon dioxide in seawater control the pH and carbonate ion (CO_3^{2-}) concentration of the oceans.

Changes in the concentration of carbon dioxide in the oceans will affect the acidity of the water and the concentrations of calcium and carbonate ions. In turn, this can affect coral reefs, fish stocks, algae and entire food chains upon which organisms in the oceans and coastal areas depend.

Equilibria in the ocean

Carbon enters the ocean mainly by the dissolution of carbon dioxide gas. Therefore, as levels of carbon dioxide in the atmosphere increase, more carbon dioxide dissolves in the ocean. The reaction can be written as the equilibrium:

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

Most of the carbon in seawater is present as $CO_2(aq)$, but some reacts further to form carbonic acid:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Carbonic acid is a weak diprotic acid, forming hydrogen carbonate ions, HCO_3^-, and carbonate ions, CO_3^{2-}:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

These equilibria are illustrated in Figure 2.2.12.

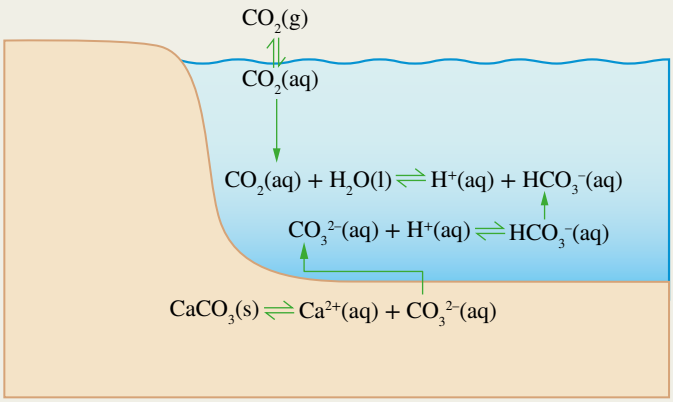


FIGURE 2.2.12 An inter-related set of reactions involving carbon dioxide is present in the ocean.

Applying Le Châtelier's principle to the equilibria above, you can see that as the concentration of dissolved carbon dioxide increases, there will be an increase in the concentration of carbonic acid. This, in turn, increases the concentration of $H^+(aq)$ ions, resulting in an increase in **ocean acidity**. This process is called **acidification**. Over the past 300 years, the pH of the ocean has averaged 8.2. It is currently 8.14 and predicted to fall to about 7.85 by 2100.

Ocean acidification is the decrease in pH that is occurring due to the absorption of carbon dioxide from the atmosphere.

Increasing ocean acidity has a detrimental effect on organisms, such as plankton, that are at the bottom of the food chain. Plankton, such as diatoms, are a food source for krill, which, in turn, are consumed by animals higher up in the food chain. An increase in ocean acidity is predicted to have a harmful effect on the species of plankton and krill upon which other species depend for their survival. A collapse of the krill population coupled with ocean warming could have a disastrous effect on the **ecosystem** of the ocean.

The change in concentration of $H^+(aq)$ also affects the position of the equilibrium with carbonate ions:

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

As the $H^+(aq)$ concentration increases, the equilibrium shifts to the right, consuming carbonate ions. This disturbs an equilibrium between calcium ions, carbonate ions and solid calcium carbonate:

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

As the level of dissolved CO_2 in the oceans increases, $[H^+]$ increases, pH decreases and solid $CaCO_3$ starts to dissolve.

Many marine organisms, such as shells and coral reefs, crabs and lobsters (Figure 2.2.13), use calcium ions and carbonate ions from seawater to build and maintain the calcium carbonate that forms their exoskeletons. If the concentration of CO_3^{2-} in seawater decreases, solid calcium carbonate dissolves and the reaction above shifts to the left, making it more difficult for these creatures to produce and maintain their skeletons.



FIGURE 2.2.13 Queensland's Great Barrier Reef contains complex coral structures made from calcium carbonate. It is predicted that marine organisms such as coral will have greater difficulty producing exoskeletons as the acidity of the ocean increases.

Scientists are concerned that increased levels of carbon dioxide will affect the equilibria that maintain the pH of the oceans and reduce the concentration of carbonate ions in the sea. This can, in turn, affect the health of aquatic ecosystems.

Review

1 **a** Construct balanced equations to represent the reaction of carbon dioxide with water to form carbonic acid and the subsequent dissociation of the acid to form hydrogen carbonate and carbonate ions.

b Select the correct answers from the alternatives provided, to complete the sentence about these equilibria.

If more CO_2 gas were to dissolve in the oceans, the concentration of H_2CO_3 would **increase/decrease** and the pH would **increase/decrease**.

2 Carbon dioxide levels are increasing in the atmosphere. Briefly describe one impact this may have on marine life with calcium carbonate exoskeletons, such as coral and shellfish.

2.2 Review

SUMMARY

- Le Châtelier's principle states that if an equilibrium system is subjected to change, the system will shift to partially oppose the change.
- The effect of a change on an equilibrium system can be predicted from Le Châtelier's principle. The effects of changes can also be explained on the basis of collision theory and reaction rates.

Change to system in equilibrium	Effect of change on equilibrium position
adding more reactant	shifts to the right (net forward reaction)
adding more product	shifts to the left (net reverse reaction)

- There are a number of equilibria that are important in the production of quality wine. Equilibria involving sulfur dioxide and tartaric acid are of particular importance.
- Carbon dioxide is a greenhouse gas in the atmosphere that re-radiates some solar energy to warm Earth's surface. Higher global temperatures are predicted as a result of more greenhouses gases in the atmosphere.
- The oceans contribute to the maintenance of steady concentrations of atmospheric carbon dioxide because the gas is slightly soluble in water through a range of reversible processes.
- An increased concentration of carbon dioxide in the atmosphere causes more carbon dioxide to dissolve in the oceans, producing more carbonic acid. This increases the concentration of hydronium ions in seawater and lowers its pH.
- An increase in ocean acidity causes some of the hydronium ions to react with carbonate ions. Reduced carbonate ion concentration impairs the ability of some marine organisms to build and maintain calcium carbonate structures.

KEY QUESTIONS

Retrieval

1 State Le Châtelier's principle.

Comprehension

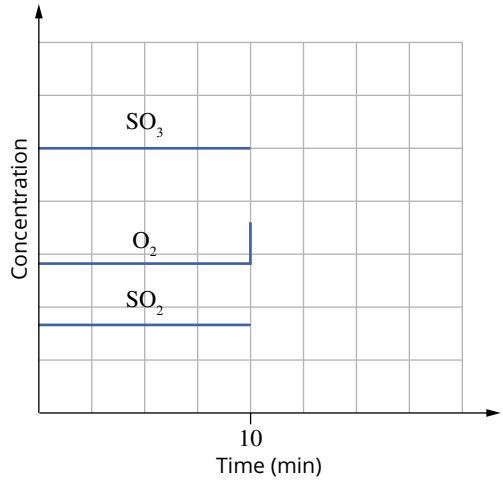
2 Select the correct words in the paragraph below to summarise the effect of adding additional reactant to an equilibrium system.

If a reactant is added to an equilibrium system, the rate of the forward reaction initially becomes **less/greater** than the rate of the reverse reaction. Then, as the concentration of reactants **increases/decreases** and the concentration of products **increases/decreases**, the rate of the forward reaction **increases/decreases** and the rate of the reverse reaction **increases/decreases** until they become equal again and a new equilibrium is formed.

3 Consider the equilibrium:

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

The following graph shows the concentrations of the three gases in an equilibrium mixture of constant volume and temperature. After 10 minutes, additional O_2 was added to the mixture.



Sketch a graph to show how concentrations would change as a consequence of the addition of O_2.

Analysis

4 Predict the effect of adding more hydrogen gas to the following equilibria using Le Châtelier's principle.

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

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

c $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

5 Predict the effect of the following changes on the position of each equilibrium.

a addition of SO_3 to the equilibrium:

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

b removal of CH_3COO^- from the equilibrium:

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

2.3 Applying Le Châtelier's principle and collision theory to equilibria

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- use your knowledge of Le Châtelier's principle, collision theory and rates of reaction to predict the impact of changes in gas pressure and solution concentration on equilibria
- describe the effect of raising and lowering temperature on an equilibrium system
- explain why the presence of a catalyst does not affect the equilibrium position of a reaction.



Le Châtelier's principle can be used to understand how changes to chemical equilibria can affect numerous natural systems, as well as to optimise yields of reactions occurring in industrial processes.

For example, as you learnt in the previous module, the carbon dioxide gas involved in equilibria in the oceans provides the carbonate ions needed for the growth of coral reefs and other marine organisms. Using Le Châtelier's principle, scientists predict that increasing levels of carbon dioxide in the atmosphere will affect the acidity of Earth's oceans. This will put marine ecosystems and organisms at risk, including the cuttlefish (Figure 2.3.1), whose shell is made of calcium carbonate.

In this module, you will continue your study of the effects of changes on chemical systems at equilibrium. Your understanding of chemical equilibrium, Le Châtelier's principle, collision theory and rates of reaction will enable you to predict the impact of changes in gas pressure, solution concentration and temperature, and the addition of a catalyst on an equilibrium system.



FIGURE 2.3.1 Cuttlefish have an internal shell made of calcium carbonate. Cuttlefish and other marine animals could be affected by the increasing acidity of oceans.

CHANGING PRESSURE

The pressure of a gas is inversely proportional to the volume of its container. So the pressure of gases in an equilibrium mixture can be changed by increasing or decreasing the volume of the container, while keeping the temperature constant.

Consider the effect of increasing the pressure on the equilibrium between sulfur dioxide gas, oxygen and sulfur trioxide gas for the following reaction:

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

3 gas particles 2 gas particles

You can see that the forward reaction involves a reduction in the number of particles of gas from three to two. The formation of products would cause an overall reduction in pressure of the system. The reverse reaction involves an increase in the number of gas particles from two to three. So a net reverse reaction causes an overall increase in pressure of the system.

As you saw in Module 2.2, a change in the position of an equilibrium can be predicted by applying either:

- Le Châtelier's principle, or
- an understanding of collision theory and the rates of reactions.

Remember that gas pressure is a measure of the force per unit area, which is proportional to the number and frequency of collisions with the sides of the container. A change in the number of particles will change the pressure.

Predicting the effect of pressure change using Le Châtelier's principle

Le Châtelier's principle tells you that an equilibrium system will respond to an increase in pressure by adjusting to reduce the pressure. Therefore, the position of equilibrium will move in the direction of the fewest gas particles.

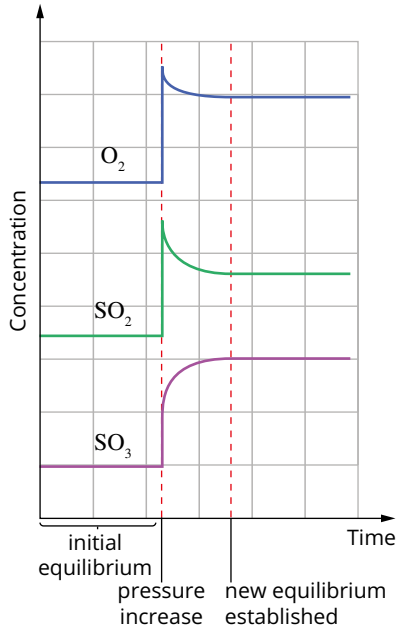


FIGURE 2.3.3 The effect of increased pressure on the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

> **i** An increase in pressure of gas particles will favour the side of the reaction with the least number of particles.

In the example:

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

an increase in pressure will cause a net forward reaction to occur in order to reduce the overall pressure (three gaseous reactant particles become two gaseous product particles). The amount of SO_3 present at equilibrium will increase, as represented in Figure 2.3.2.

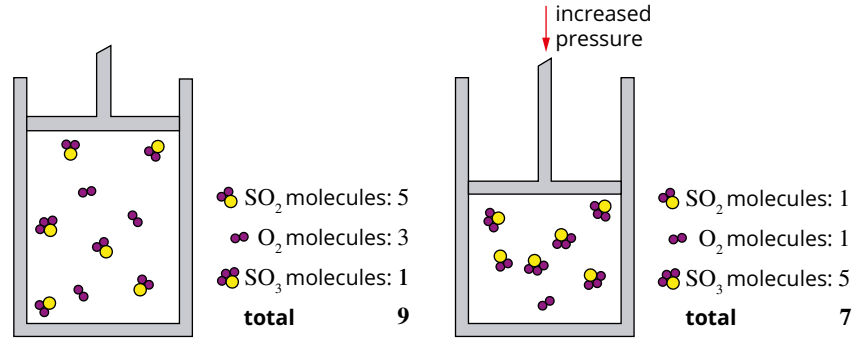


FIGURE 2.3.2 A representation of the effect of increased pressure on the equilibrium: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

The effect of the change can also be illustrated graphically, as shown in Figure 2.3.3. When the system is initially at equilibrium and there is an increase in pressure, the concentrations of all gases increase simultaneously.

As the system adjusts, there is a gradual change in concentration of each of the species until the new equilibrium is established. At the new equilibrium position, the individual concentrations are different to those at the first equilibrium.

Predicting the effect of pressure change using collision theory

The effect of a reduction in volume on the equilibrium can also be understood using collision theory. Because the overall volume occupied by the gases is smaller, the gas molecules are closer to each other and collisions between molecules become more frequent. The rate of the reaction involving the greater number of molecules (the forward reaction in this case) becomes greater than the rate of the reaction between the smaller number of molecules (the reverse reaction). Then, as more product is formed, the rate of the reverse reaction increases and the rate of the forward reaction decreases.

Eventually the rates of the forward and reverse reactions become equal and a new equilibrium is established. Because the forward reaction occurred to a greater extent initially, there has been a net forward reaction.

Pressure changes do not affect the equilibrium position of systems in the liquid or solid phases. Particles in these systems are too tightly packed for an increase in pressure to have a noticeable effect on volume. This means that there is negligible change in the concentration of the species involved and no effect on the position of equilibrium.

Further examples

The effect of a change of pressure or concentration, by changing the container volume, depends on the relative number of particles on both sides of the equation.

When there are equal numbers of reactant and product particles, a change in pressure will not shift the position of equilibrium. This is the case for the reaction between hydrogen and iodine in the following equilibrium:

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

2 gas particles 2 gas particles

According to Le Châtelier's principle, it does not matter which way the system shifts; the number of particles in the container will remain constant (two particles of reactants and two particles of products). Therefore, the system is unable to oppose the change applied and there is no overall net reaction.

In terms of collision theory, the volume decrease causes the rates of the forward and reverse reactions to be increased equally because there are equal numbers of particles on both sides of the equation.

Worked example 2.3.1

USING LE CHÂTELIER'S PRINCIPLE TO DETERMINE THE SHIFT IN EQUILIBRIUM POSITION FOR A VOLUME DECREASE

Consider the equilibrium:

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

Predict the shift in equilibrium position and the effect on the amount of CO when the volume is halved at constant temperature.

Thinking	Working
Determine the immediate effect of the change of volume on the pressure.	Halving the volume will double the pressure of all species at equilibrium.
The system will try to partially oppose the change in pressure by reducing or increasing the pressure of the system. (For a volume decrease, the system will shift in the direction of the fewest gaseous particles, and vice versa for a volume increase.) Decide how the equilibrium will respond.	There are two molecules of gas on the reactant side and four molecules of gas on the product side, so the system will shift to the left (a net reverse reaction). This decreases the amounts of the products, including CO. (Note that the CO concentration will still be higher than it was at the initial equilibrium. The shift in equilibrium position only partially compensates for the change.)

➤ Try yourself 2.3.1

USING LE CHÂTELIER'S PRINCIPLE TO DETERMINE THE SHIFT IN EQUILIBRIUM POSITION FOR A VOLUME INCREASE

Consider the equilibrium:

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

Predict the shift in equilibrium position and the effect on the amount of Cl_2 when the volume is doubled at constant temperature.

Changing pressure by adding an inert gas

The total pressure of an equilibrium mixture of gases may also be changed, without changing the volume of the container, by adding a non-reacting gas such as helium, neon or argon. This can be seen in Figure 2.3.4.



System at equilibrium
Volume 1 L
[•] = 5 particles L^{-1}
[•] = 5 particles L^{-1}

System still in equilibrium but at higher pressure. Volume 1 L
[•] = 5 particles L^{-1}
[•] = 5 particles L^{-1}

FIGURE 2.3.4 The equilibrium of a gaseous system is unaffected by the addition of an inert gas. The total pressure of the system increases without changes in concentrations of the reactants or products.

Because the presence of the additional gas does not change any of the concentrations of the reactants and products, there is no effect on the position of equilibrium. Using collision theory, you can see that any collisions with inert gas molecules will not produce a reaction, so no net reaction occurs.

DILUTION

For equilibria in solution, the situation is similar to the one you saw with pressure and gases. The focus is on the number of particles per volume of solvent.

For an equilibrium occurring in solution, dilution by adding water reduces the number of particles per volume. This results in a shift in the position of equilibrium towards the side that produces the greater number of dissolved particles.

For example, consider the equilibrium system:

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

2 particles in solution 1 particle in solution

The addition of water momentarily lowers the concentration of each species. In terms of Le Châtelier's principle, a net reverse reaction will occur, increasing the total number of particles in solution.

Figure 2.3.5 shows the changes of concentrations that occur. Note that there is an instantaneous decrease in the concentration of all species at the time of dilution.

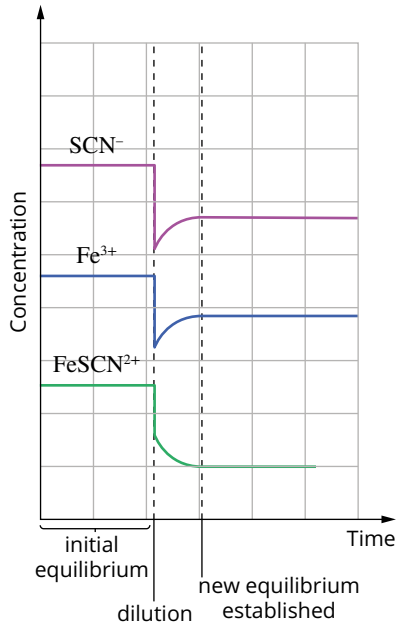


FIGURE 2.3.5 Effect of dilution on the equilibrium $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$. Although the equilibrium position shifts to the left, note that the concentrations of Fe^{3+} and SCN^{-} at the new equilibrium are lower than their concentrations prior to dilution, as the equilibrium shift only partially opposes the change.

CHANGING TEMPERATURE

The effect of a temperature change on an equilibrium reaction depends upon whether the reaction is exothermic or endothermic. The overall effect on equilibrium position can be predicted using Le Châtelier's principle and explained using collision theory and rates of reaction.

For example, consider the conversion of brown nitrogen dioxide gas (NO_2) to colourless dinitrogen tetroxide gas (N_2O_4). The reaction is exothermic, releasing energy to the environment. You could (but would not usually) write an equation for the reaction that includes the energy released:

$$2NO_2(g) \rightleftharpoons N_2O_4(g) + \text{energy}$$

Increasing the temperature of the system increases the energy of the substances in the mixture. Applying Le Châtelier's principle, you can see that the reaction can 'oppose' an increase in energy by absorbing energy. As the reverse reaction is endothermic, this favours a net reverse reaction. Figure 2.3.6 shows the gradual decrease in the concentration of N_2O_4 as the system moves to produce more reactant, NO_2. Note that with a change in temperature, there is no instantaneous change in concentration.

Because the reactants and products of the system are different colours, you can monitor the change in this equilibrium visually. When a new equilibrium is attained, there is less dinitrogen tetroxide and more nitrogen dioxide present so the mixture appears a darker brown. This can be seen in Figure 2.3.7.

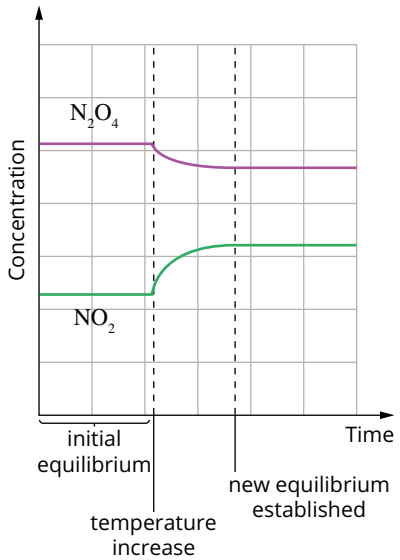


FIGURE 2.3.6 The effect of heating on the equilibrium $2NO_2(g) \rightleftharpoons N_2O_4(g)$



FIGURE 2.3.7 Equilibrium mixtures of NO_2 and N_2O_4 in hot water and ice. Heating the mixture favours the formation of brown NO_2 gas.

Heating an endothermic reaction causes the opposite result to occur. Applying Le Châtelier's principle, you can see that the reaction opposes an increase in energy by absorbing energy, resulting in a net forward reaction.

In summary, increasing the temperature of an equilibrium mixture results in a:

- net reverse reaction (fewer products) for exothermic reactions
- net forward reaction (more products) for endothermic reactions.

Decreasing the temperature has the opposite effect.

Predictions using Le Châtelier's principle of the effect of temperature on equilibria can be explained by collision theory. When there is an increase in temperature, molecules move faster and there are more frequent and more energetic collisions. More molecules now have the necessary energy to overcome the activation energy barrier to undergo successful collisions.

At the higher temperature, the rates of both the forward and reverse reactions increase. One of these reactions is endothermic and the other is exothermic. Because the activation energy for the endothermic reaction is greater than for the exothermic reaction, the increased energy will mean there will be a greater proportion of molecules with the necessary energy to overcome the activation energy barrier for the endothermic reaction. The rate of this reaction will increase more than the rate of the exothermic reaction.

This can be seen from the graph in Figure 2.3.8, which shows the frequency distribution of molecules at different temperatures.

In this example of the equilibrium between NO_2 and N_2O_4, the reverse reaction is endothermic and so there will be a net reverse reaction if the temperature increases. When the system re-establishes equilibrium at a higher temperature, the new equilibrium has a higher concentration of NO_2 and a lower concentration of N_2O_4. Conversely, decreasing the temperature of an equilibrium results in a net reaction in the direction of the exothermic reaction.

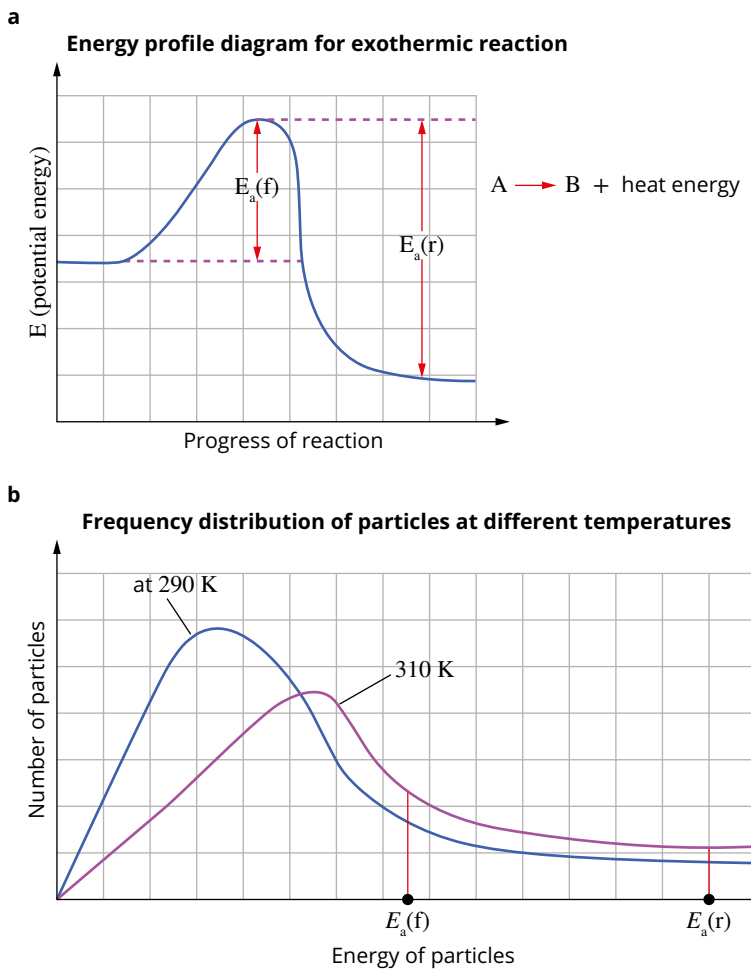


FIGURE 2.3.8 (a) Energy profile diagram for an exothermic reaction. The activation energy of the forward reaction, E_a(f), is less than the activation energy of the reverse reaction, E_a(r). (b) The frequency distribution of molecules at two different temperatures. At the higher temperature, a greater proportion of particles have the necessary energy to overcome the activation energy barrier for the endothermic reaction.

Worked example 2.3.2

USING COLLISION THEORY TO DETERMINE THE EFFECT OF TEMPERATURE ON AN EQUILIBRIUM SYSTEM

Consider the equilibrium:

$$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g) \quad \Delta H = +42\,kJ\,mol^{-1}$$

Using collision theory, explain the effect of an increase in temperature on this endothermic reaction.

Thinking	Working
Decide what effect the temperature change has on the initial rates of reaction. Remember that, for an equilibrium system, an increase in temperature increases the proportion of molecules with the necessary energy to overcome the activation energy barrier for the endothermic reaction to a greater extent than for the exothermic reaction, and so the endothermic reaction will be favoured.	With the temperature increase, all reactant and product molecules have more energy and move faster. Since the forward reaction is endothermic, its rate initially increases more than the rate of the reverse reaction.
Using collision theory, consider what happens to the rates of the forward and reverse reactions.	As H_2 and CO_2 react and the concentration of reactants decreases, the rate of the forward reaction will decrease. As the concentration of CO and H_2O increases, the rate of the reverse reaction will increase. Ultimately, the rates of the forward and reverse reactions become equal and a new equilibrium is established.
Determine the overall effect of the change on the equilibrium.	This results in a net forward reaction, with higher concentrations of the products, CO and H_2O, and lower concentrations of the reactants, CO_2 and H_2.

➤ Try yourself 2.3.2

USING COLLISION THEORY TO DETERMINE THE EFFECT OF TEMPERATURE ON AN EQUILIBRIUM SYSTEM





Consider the equilibrium:

$$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g) \quad \Delta H = -165\,kJ\,mol^{-1}$$

Using collision theory, explain the effect of an increase in temperature on this exothermic reaction.

EFFECT OF A CATALYST ON EQUILIBRIUM

A catalyst lowers the activation energy of the forward and reverse reactions by the same amount. This can be seen in the energy profile diagram shown in Figure 2.3.9.

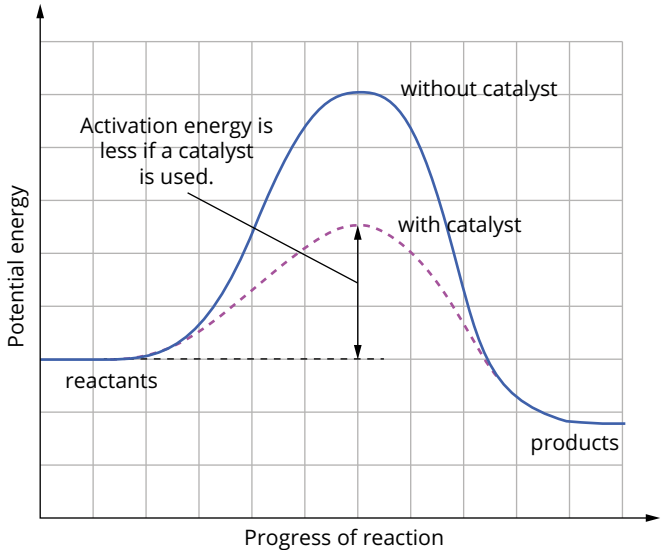


FIGURE 2.3.9 Energy changes in a catalysed and uncatalysed reaction

The lower activation energy causes an increase in the number of effective collisions. As a result, there is an increase in the rate of both forward and reverse reactions. This occurs because more particles have energies greater than the activation energy barrier of the reaction.

A catalyst increases the rate of the forward and reverse reactions equally. Therefore, it will not change the relative concentrations of the reactants and products and the presence of a catalyst does not change the position of equilibrium. A catalyst will increase the rate at which an equilibrium is attained. It is for this reason that catalysts are used in many industrial and biological systems.

Lowering the activation energy of a reaction by the addition of a catalyst does not change the position of equilibrium of a system. Addition of a catalyst only affects how quickly equilibrium is attained.

2.3 Review

SUMMARY

- The effect of a change on an equilibrium can be predicted using Le Châtelier's principle (see table below).
- Alternatively, the effects of changes on an equilibrium can be explained on the basis of collision theory and rates of reaction (see table below).

Summary of the effect of a change on equilibrium

Change on equilibrium	Effect of change on equilibrium position	Collision theory explanation of effect of change on equilibrium position
decreasing pressure by increasing volume (for gases)	shifts in the direction of the most particles	less frequent collisions; the reaction that is less dependent on collisions (fewer particles reacting) occurs to a greater extent
adding an inert gas (container volume remains constant)	no change	no change in concentration of the reacting gases so no change to the rate of the forward and reverse reactions
adding water (dilution of solutions)	shifts in the direction of the most particles	less frequent collisions; the reaction less dependent on collisions (fewer particles reacting) occurs to a greater extent
increasing the temperature for exothermic reactions	shifts to the left (net reverse reaction)	all reactant and product molecules have more energy and move faster; increased temperature favours rate of an endothermic reaction; net reaction in direction of endothermic reaction, i.e. favouring the reverse direction
increasing the temperature for endothermic reactions	shifts to the right (net forward reaction)	all reactant and product molecules have more energy and move faster; increased temperature favours rate of an endothermic reaction; net reaction in direction of endothermic reaction, i.e. favouring the forward direction
adding a catalyst	no change	increases rates of forward and reverse reactions to the same extent; an equivalent change in the number of successful collisions in both directions; no net reaction

KEY QUESTIONS

Retrieval

1 State whether the following statements are true or false.

a Adding a catalyst to an equilibrium system does not affect the position of equilibrium.

b At constant volume, increasing the temperature of an exothermic reaction at equilibrium increases the amount of products.

c At constant temperature, increasing the pressure of a gaseous equilibrium system always increases the amount of products.

d If an aqueous equilibrium system is diluted at constant temperature, the position of equilibrium shifts in the direction that produces the greater number of dissolved particles.

2 Select the correct words in this paragraph to describe the effect of adding a catalyst to an equilibrium system.

A catalyst **raises/lowers** the activation energy of a reaction and increases the rate of the forward and reverse reactions **unequally/equally**. The presence of a catalyst **does/does not** change the position of equilibrium. A catalyst **will increase/does not increase** the rate at which an equilibrium is attained.

Comprehension

3 Summarise the effect of changes on an equilibrium system by completing the following table.

Change to equilibrium	Effect of change on equilibrium position
adding a reactant	
increasing pressure by decreasing the size of the closed container (for gases)	
adding a catalyst	
increasing the temperature for endothermic reactions	
decreasing the temperature for exothermic reactions	
adding water (dilution of solutions)	

4 The total pressure of the equilibrium system below was increased by reducing the volume at constant temperature:

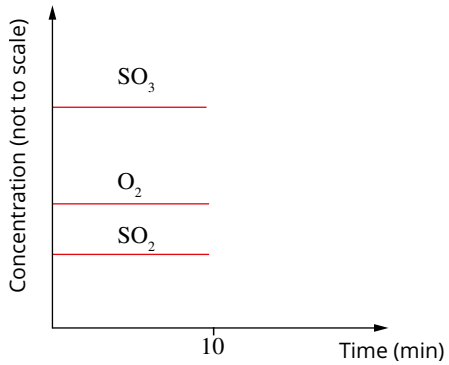
$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Explain why more N_2O_4 is formed in terms of the effect of the change on the rates of the forward and reverse reactions.

5 Consider the equilibrium:

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

The graph below shows the concentrations of the three gases in an equilibrium mixture at constant volume and temperature.



Draw graphs to show how concentrations would change with time if the following changes (**a–c**) occurred separately at 10 minutes. Your graphs should show the relative stoichiometric changes in the concentration of each gas.

a the pressure of the system was suddenly increased by reducing volume

b the temperature of the system was increased at constant volume

c a catalyst was added at constant volume and temperature.

Analysis

6 For each of the three changes to the equilibrium system described in question **5**, predict the effect of the changes in terms of collision theory and rates of reaction.

7 Predict the effect of the following changes on the position of each equilibrium.

a halving the volume (doubling the pressure) of the equilibrium:

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

b increasing the pressure of the equilibrium (by reducing volume):

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

c increasing the temperature of the endothermic equilibrium:

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

8 An equilibrium mixture consists of the gases N_2O_4 and NO_2:

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

The volume of the container is increased at constant temperature and a new equilibrium is established. Predict how each of the following quantities would change at the new equilibrium compared with the initial equilibrium.

a concentration of NO_2

b mass of NO_2

9 Determine how the concentration of hydrogen gas in each of the following equilibrium mixtures will change when the mixtures are cooled and kept at constant volume. Explain your answer.

a $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g) \quad \Delta H = +138\ kJ\ mol^{-1}$

b $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)\ \Delta H = -208\ kJ\ mol^{-1}$

2.4 Equilibrium constants



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand that an equilibrium law expression can be written for equilibrium systems
- state equilibrium law expressions for reactions
- deduce the extent of a reaction from the value of its equilibrium constant
- solve mathematical problems using equilibrium law expressions.

In this module, you will investigate the relationship between the quantities of reactants and the quantities of products present when a system reaches equilibrium. This relationship allows you to qualitatively predict the relative amounts of reactants and products in individual equilibrium systems.

Although the calculations in this section will be restricted to chemical equilibria, the same principles can be applied to other systems in our surroundings. For example, on the African plains of Tanzania, there is a delicate balance of herbivores such as zebras and wildebeest, and carnivores such as lions (Figure 2.4.1). If the populations change through drought or disease, the relative numbers change and a new balance is established. This new balance can be predicted in much the same way as occurs for chemical equilibrium.



FIGURE 2.4.1 The populations of zebras and lions in Africa can be understood using the principles of equilibrium.

THE REACTION QUOTIENT

Consider the equilibrium system you were introduced to in Module 2.1:

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

An unlimited number of different equilibrium mixtures of the three gases, nitrogen, hydrogen and ammonia, can be prepared. Table 2.4.1 shows the concentrations of each of these gases in four different equilibrium mixtures at a constant temperature of 400°C. The values of the fraction $\frac{[NH_3]^2}{[N_2][H_2]^3}$ for each mixture are also given. Note that the coefficients of the reactants and products in the chemical equation above form the indices of the reactant and product concentrations used in this fraction.

The fraction $\frac{[NH_3]^2}{[N_2][H_2]^3}$ is called the **reaction quotient** (Q_c) or **concentration fraction** of the mixture.

TABLE 2.4.1 Concentrations of reactants and products present in equilibrium mixtures

Equilibrium mixture	$[N_2]$ (mol L^{-1})	$[H_2]$ (mol L^{-1})	$[NH_3]$ (mol L^{-1})	$\frac{[NH_3]^2}{[N_2][H_2]^3}$
1	0.25	0.75	0.074	0.052
2	0.55	0.65	0.089	0.052
3	0.0025	0.0055	4.6×10^{-6}	0.051
4	0.0011	0.0011	2.7×10^{-7}	0.051

As you can see in Table 2.4.1, the reaction quotient $\frac{[NH_3]^2}{[N_2][H_2]^3}$ has an almost constant value of 0.052 for each equilibrium mixture regardless of the concentration of each component.

While the reaction quotient can be calculated for any mixture of reactants and products at any time during a reaction, it is only when the mixture is at equilibrium that it gives a constant value. At equilibrium, the value of the reaction quotient is equal to the **equilibrium constant**, K_c.

In general, for chemical reactions at equilibrium:

- different chemical reactions have different values of K_c
- the size of K_c indicates the proportions (relative amounts) of reactants and products in the equilibrium mixture
- for a particular reaction, K_c is constant for all equilibrium mixtures at a fixed temperature.

K_c is the equilibrium constant for a reaction. The value of K_c is different for different reactions.

THE EXPRESSION FOR THE EQUILIBRIUM LAW

By studying a large number of reversible systems, such as the one between nitrogen, hydrogen and ammonia in the previous example, chemists have been able to develop the concept of the **equilibrium law**.

The equilibrium law states that the:

- equilibrium constant, K_c, is given by the concentrations of products divided by the concentrations of reactants at equilibrium
- index of each component concentration is the same as the coefficient for the substances in the balanced chemical equation.

For the general equation $aW + bX \rightleftharpoons cY + dZ$ at equilibrium at a particular temperature, the equilibrium expression can be written as:

$$K_c = \frac{[Y]^c[Z]^d}{[W]^a[X]^b}$$

where K_c is the equilibrium constant.

A useful way of remembering the equilibrium law is that:

K_c can be represented as $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$. Remember that if there is more than one product or reactant, you must multiply the terms.

When you write an equilibrium law expression, the concentrations of the products are always on the top of the expression.

Worked example 2.4.1

WRITING AN EQUILIBRIUM LAW EXPRESSION

The decomposition of N_2O_4 is a reversible reaction that occurs according to the equation:

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

Determine the expression for the equilibrium constant K_c.

Thinking	Working
Identify the coefficients of the products and the reactants in the equation.	The product, NO_2, has a coefficient of 2 and the reactant, N_2O_4, has a coefficient of 1.
Write the expression for K_c. $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$

➤ Try yourself 2.4.1

WRITING AN EQUILIBRIUM LAW EXPRESSION

Determine the equilibrium expression for K_c for the reversible reaction:

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

The reaction quotient and the equilibrium law

An expression for the equilibrium constant, K_c, can be written for any system at equilibrium. As you learnt earlier, a similar expression can be written, called a reaction quotient, Q_c (or concentration fraction), for systems that are not necessarily at equilibrium. For:

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

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

A reaction quotient can be calculated for any mixture of reactants and products at any time during a reaction. However, it is only when the mixture is at equilibrium that the reaction quotient is a constant value. At equilibrium, the value of the reaction quotient is equal to the equilibrium constant, K_c.

If the reaction quotient is:

- greater than K_c, the system 'shifts to the left' to achieve equilibrium and more reactants are formed
- smaller than K_c, the system 'shifts to the right' to achieve equilibrium and more products are formed
- equal to K_c, the system is at equilibrium.

The relationship between Q_c and K_c is illustrated in Figure 2.4.2. By comparing the value of Q_c for a reaction to K_c at a given temperature, it is possible to predict the direction a reaction will proceed in order to reach equilibrium.

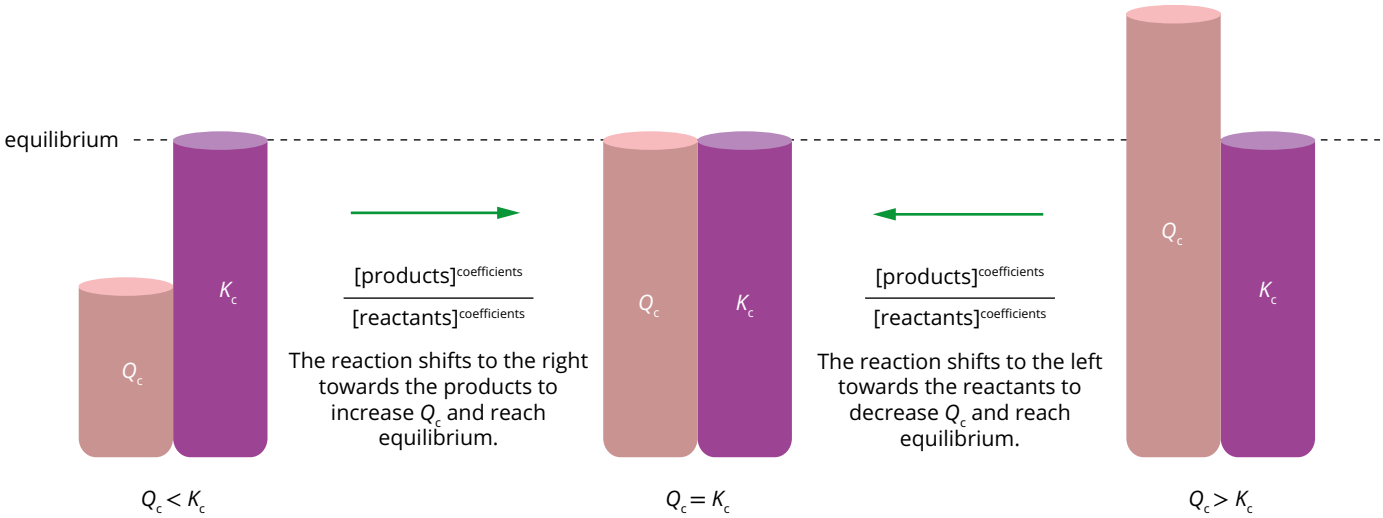


FIGURE 2.4.2 For any reversible reaction at equilibrium $K_c = Q_c$, so comparing these two values for a reaction can indicate which way a reaction must progress to reach equilibrium.

Heterogeneous equilibria

The chemical reactions discussed so far in this module have involved **homogeneous reactions**, in which all reactants and products are in the same phase. However, some equilibria involve **heterogeneous reactions**, in which reactants and products are in different phases.

The important feature of the equilibrium law for heterogeneous reactions is that the concentration of a pure solid or a pure liquid is assigned as 1. This is because these concentrations do not depend on how much of the pure substance is present.

Because the concentration of the solid in the heterogeneous system is considered a constant, it is removed from the equilibrium expression. As a result, the expression for the equilibrium of a heterogeneous system is often much simpler.

For example, for the equation:

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

the expression for the equilibrium constant is $K_c = [CO_2]$. CaO and $CaCO_3$ are both solids and do not appear in the equilibrium law.

You will only be asked to write an equilibrium law expression for homogeneous systems in this course.

DEPENDENCY OF AN EQUILIBRIUM CONSTANT ON THE EQUATION

The equilibrium law depends upon the chemical equation used for a particular reaction.

For example, the equilibrium between the gases N_2O_4 and NO_2 can be represented by several equations. For each equation provided below, the expression for the equilibrium constant, K_c, is given. Values of K_c for this system at 25°C are also shown.

$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 6.2 \times 10^{-4}$

$2NO_2(g) \rightleftharpoons N_2O_4(g) \quad K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{6.2 \times 10^{-4}} = 1.6 \times 10^{3}$

$2N_2O_4(g) \rightleftharpoons 4NO_2(g) \quad K_c = \frac{[NO_2]^4}{[N_2O_4]^2} = (6.2 \times 10^{-4})^2 = 3.8 \times 10^{-7}$

$\frac{1}{2}N_2O_4(g) \rightleftharpoons NO_2(g) \quad K_c = \frac{[NO_2]}{[N_2O_4]^{\frac{1}{2}}} = (6.2 \times 10^{-4})^{\frac{1}{2}} = 2.5 \times 10^{-2}$

You can see from these expressions that if:

- one equation is the reverse of another, the equilibrium constants are the inverse (or reciprocal) of each other
- the coefficients of an equation are doubled, the value of K_c is squared
- the coefficients of an equation are halved, the value of K_c is the square root of the original value of K_c.

Therefore, it is important to specify the equation when quoting an equilibrium constant.

When comparing values of K_c, it is important to know the equation associated with the equilibrium constant.

THE MEANING OF THE VALUE OF AN EQUILIBRIUM CONSTANT

The value of an equilibrium constant is based on the equilibrium concentrations of the products divided by the equilibrium concentrations of the reactants. Therefore, it indicates the extent of reaction at equilibrium (how far the forward reaction proceeds before equilibrium is established) and the **equilibrium yield** (the number of moles of products present at equilibrium).

The concentrations used to determine K_c must be the concentration of each component of the mixture at equilibrium.

The relationship between the value of K_c and the relative proportions of reactants and products at equilibrium is shown in Table 2.4.2.

TABLE 2.4.2 The relationship between the value of K_c and the extent of a reaction provides information on the relative amounts of reactants and products in the reaction mixture at equilibrium.

Value of K_c	Extent of reaction
between about 10^{-4} and 10^{4}	The extent of reaction is significant. Appreciable concentrations of both reactants and products are present at equilibrium. e.g. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_c = 0.052$ at 400°C
very large; $>10^{4}$	Almost complete reaction occurs. The concentrations of products are much higher than the concentrations of the reactants at equilibrium. e.g. $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$ $K_c = 10^{7}$ at 25°C
very small; $<10^{-4}$	Negligible reaction occurs. The concentrations of reactants are considerably higher than the concentrations of products at equilibrium. e.g. $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$ $K_c = 1.8 \times 10^{-5}$ at 25°C

When K_c is very large, the numerator of the equilibrium expression must be large compared to the denominator, which means there is a large amount of products relative to the amount of reactants.

When K_c is very small, the numerator of the equilibrium expression must be very small compared to the denominator, which means there must be a large amount of reactants relative to the amount of products.

Effect of temperature on an equilibrium constant

It has been shown experimentally that the value of the equilibrium constant, K_c, for a particular reaction depends only upon temperature. It is not affected by the addition of reactants or products, changes in pressure, or the use of catalysts.

As you learnt in Module 2.2, the effect of a change in temperature on an equilibrium constant depends on whether the reaction is exothermic or endothermic. As temperature increases, for:

- exothermic reactions, the value of K_c decreases and so the amount of products present at equilibrium decreases
- endothermic reactions, the value of K_c increases and so the amount of products present at equilibrium increases.

Table 2.4.3 summarises the effect on K_c when temperature increases. The opposite is true when temperature decreases.

Only a change in temperature will change the value of K_c for a given reaction.

TABLE 2.4.3 The effect on the value of K_c when the temperature of a system increases

ΔH	T	K_c
exothermic (–)	increases	decreases
endothermic (+)	increases	increases

Because the value of K_c depends on temperature, it is essential to specify the temperature at which an equilibrium constant has been measured.

CALCULATIONS INVOLVING THE EQUILIBRIUM CONSTANT AND CONCENTRATIONS

Calculating an equilibrium constant

An equilibrium constant can be calculated from the molar concentrations of reactants and products at equilibrium, as shown in Worked example 2.4.2.

Worked example 2.4.2

CALCULATING AN EQUILIBRIUM CONSTANT

A 2.00 L vessel contains a mixture of 0.0860 mol of H_2, 0.124 moles of I_2 and 0.716 mol of HI in equilibrium at 460°C according to the equation:

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

Calculate the value of the equilibrium constant, K_c, at 460°C.

Thinking	Working
Find the molar concentrations for all species at equilibrium. Convert the number of moles to mol L^{-1} using $c = \frac{n}{V}$.	The volume of the vessel = 2.00 L $[H_2] = \frac{n(H_2)}{V}$ $= \frac{0.0860}{2.00} = 0.0430 \text{ mol L}^{-1}$ $[I_2] = \frac{n(I_2)}{V}$ $= \frac{0.124}{2.00} = 0.0620 \text{ mol L}^{-1}$ $[HI] = \frac{n(HI)}{V}$ $= \frac{0.716}{2.00} = 0.358 \text{ mol L}^{-1}$
State the expression for K_c.	$K_c = \frac{[HI]^2}{[H_2][I_2]}$
Substitute into the expression for K_c to determine the value of K_c.	$K_c = \frac{0.358^2}{0.0430 \times 0.0620}$ $= 48.1$

➤ Try yourself 2.4.2

CALCULATING AN EQUILIBRIUM CONSTANT

A 3.00 L vessel contains a mixture of 0.120 mol of N_2O_4 and 0.500 mol of NO_2 in equilibrium at 460°C according to the equation:

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

Calculate the value of the equilibrium constant, K_c, for the reaction at that temperature.



Calculating equilibrium concentrations

Another type of calculation involves 'working backwards'. In this situation, you use the equilibrium constant to determine the molar equilibrium concentration of one of the species in the reaction.

Worked example 2.4.3

CALCULATING AN EQUILIBRIUM CONCENTRATION

Consider the following equilibrium with an equilibrium constant of 0.400 at 250°C:

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

An equilibrium mixture contains 0.0020 mol L^{-1} PCl_5 and 0.0010 mol L^{-1} PCl_3 at 250°C. Determine the equilibrium concentration of Cl_2 in this mixture.

Thinking	Working
State the expression for K_c.	$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$
Substitute the known values into the expression for K_c.	$0.400 = \frac{0.0010 \times [Cl_2]}{0.0020}$
Rearrange the expression to make $[Cl_2]$ the subject and calculate the concentration of this species.	$[Cl_2] = \frac{0.400 \times 0.0020}{0.0010}$ $= 0.80 \text{ mol } L^{-1}$

➤ Try yourself 2.4.3

CALCULATING AN EQUILIBRIUM CONCENTRATION

Consider the following equilibrium with an equilibrium constant of 0.72 at 250°C:

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

An equilibrium mixture contains 0.040 mol L^{-1} N_2O_4 at 250°C. Determine the equilibrium concentration of NO_2 in this mixture.

An ICE table (reaction table) sets up the steps for working out equilibrium calculations where the equilibrium concentration of one or more species is unknown. The first letter of each word corresponds to the information that is recorded in each row of the table: Initial, Change, Equilibrium.

Calculating an equilibrium constant using stoichiometry

For some calculations, stoichiometry is used to calculate the molar equilibrium concentrations of the reactants and products from the data provided. Once these are known, the equilibrium constant can then be calculated as you saw in Worked Example 2.4.3.

A popular way to set out calculations of this type is with the use of a **reaction table** (also known as an ICE table). The reaction table shows the initial amounts of reactants and products, the changes that occur as the system reaches equilibrium and the final values at equilibrium, as Worked example 2.4.4 illustrates.

Worked example 2.4.4

USING STOICHIOMETRY TO CALCULATE AN EQUILIBRIUM CONSTANT

An equilibrium is established between A and B at a specified temperature according to the following equation:

$$A(g) \rightleftharpoons 2B(g)$$

0.540 mol of A was placed in an empty 2.00 L vessel. When equilibrium was achieved, 0.280 mol of B was present. Calculate the value of the equilibrium constant at this temperature.

Thinking

Construct a reaction table using each species in the balanced equation as the headings for the columns in the table. Insert three rows in the table labelled 'I' (initial), 'C' (change) and 'E' (equilibrium):

	Reactants ⇌ Products	
I		
C		
E		

Enter the data provided above in the table.

When a species is consumed, the change is negative; when a species is produced, the change is positive.

Working

Initially, there is:

- 0.540 mol of A(g)
- 0.0 mol of the product B(g).

Let x mol of A react; from the coefficients of the equation $2x$ mol of B is produced.

At equilibrium there is 0.280 mol of B(g).

	A(g) ⇌ 2B(g)	
I	0.540 mol	0.0 mol
C	$-x$	$+2x$
E	$0.540 - x$	$2x = 0.280$ mol

Using the coefficients from the equation, calculate the moles of all species at equilibrium.

Initially no B was present, so because 0.280 mol of B has been produced at equilibrium:

$2x = 0.280$ mol

$x = 0.140$ mol

We can enter these values in the table:

	A(g) ⇌ 2B(g)	
I	0.540 mol	0.0 mol
C	$-x = -0.140$	$+2x = 0.280$
E	$0.540 - x$ $= 0.540 - 0.140$ $= 0.400$ mol	0.280 mol

Using the volume of the vessel, calculate the concentrations for all species at equilibrium.

Use the formula $c = \frac{n}{V}$.

The volume of the vessel is 2.00 L.

$$[A] = \frac{n}{V}$$
$$= \frac{0.400}{2.00}$$
$$= 0.200 \text{ mol L}^{-1}$$

$$[B] = \frac{n}{V}$$
$$= \frac{0.280}{2.00}$$
$$= 0.140 \text{ mol L}^{-1}$$

State the expression for K_c and substitute the equilibrium concentrations.

Calculate the equilibrium constant, K_c.

$$K_c = \frac{[B]^2}{[A]}$$
$$= \frac{0.140^2}{0.200}$$
$$= 0.0980$$



➤ Try yourself 2.4.4

USING STOICHIOMETRY TO CALCULATE AN EQUILIBRIUM CONSTANT

At one step during the synthesis of nitric acid, nitrogen dioxide (NO_2) is in equilibrium with dinitrogen tetroxide (N_2O_4) at 60°C:

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

0.350 mol of N_2O_4 was placed in an empty 2.0 L vessel. When equilibrium was achieved, 0.120 mol of NO_2 was present. Calculate the value of the equilibrium constant at this temperature.

Calculations for reactions with small K_c values

If the equilibrium constant for a reaction is very low (less than about 10^{-4}), at equilibrium the concentrations of products will be much less than the concentrations of the reactants. For reactions of this type, it is possible to calculate the concentration of the products by assuming that the equilibrium concentrations of the reactants are the same as their initial concentrations. Worked example 2.4.5 demonstrates this approach.

Although an ICE table can be used for these calculations, it is often unnecessary. Note that you must state any assumptions you make when doing calculations.

Worked example 2.4.5

CALCULATING AN EQUILIBRIUM CONCENTRATION FOR REACTIONS WITH LOW K_C

The following equilibrium has a K_c of 1.6×10^{-6} at 200°C:

$$A(g) \rightleftharpoons B(g) + C(g)$$

0.48 mol of A was placed in an empty 2.0 L vessel at 200°C. Determine the concentrations of B and C at equilibrium.

Thinking	Working
State the expression for K_c.	$K_c = \frac{[B][C]}{[A]}$
Decide if any assumptions can be made in the calculation.	Initially, there is: • 0.48 mol of A(g) • 0.0 mol of the products B(g) and C(g). From the equation, the equilibrium concentration of C will be equal to the concentration of B, i.e. [C] = [B] Since K_c is low, we assume the amount of A at equilibrium is 0.48 mol.
Calculate the concentration of the reactant.	$[A] = \frac{n}{V}$ $= \frac{0.48}{2.0}$ $= 0.24 \text{ mol L}^{-1}$
Substitute into the expression for K_c.	$1.6 \times 10^{-6} = \frac{[B][C]}{0.24}$ Since [C] = [B] $= \frac{[B] \times [B]}{0.24}$
Calculate the unknown concentrations, stating the assumption you made in the calculation.	$1.6 \times 10^{-6} = \frac{[B]^2}{0.24}$ So $3.84 \times 10^{-7} = [B]^2$ Taking the square root of both sides (use your calculator): $[B] = 6.2 \times 10^{-4}$ So $[B] = 6.2 \times 10^{-4} \text{ mol L}^{-1}$ and $[C] = 6.2 \times 10^{-4} \text{ mol L}^{-1}$ Since K_c is low, the concentration of A at equilibrium was assumed to be the same as its initial concentration.

➤ Try yourself 2.4.5

CALCULATING AN EQUILIBRIUM CONCENTRATION FOR REACTIONS WITH LOW K_C

The following equilibrium has a K_c of 4.4×10^{-8} at 200°C:

$$X(g) \rightleftharpoons 2Y(g)$$

0.30 mol of X was placed in an empty 2.0 L vessel at 200°C. Determine the concentration of Y at equilibrium.

2.4 Review

SUMMARY

- The equilibrium constant, K_c, is a constant for a particular chemical reaction at a particular temperature.
- The equilibrium law for the equation:

$$aW + bX \rightleftharpoons cY + dZ$$

$$\text{is } K_c = \frac{[Y]^c[Z]^d}{[W]^a[X]^b}$$

- A reaction quotient (concentration fraction) can be calculated for any stage of a chemical reaction. The reaction quotient, Q_c, has the same mathematical expression as the equilibrium law.
- When a reaction system at a particular temperature has reached equilibrium, the reaction quotient is equal to the equilibrium constant.
- The value of K_c provides a measure of the extent of reaction and the relative concentrations of reactants and products at equilibrium.

Value of K_c	Extent of reaction
between about 10^{-4} and 10^4	indicates significant reaction occurs
$>10^4$	indicates almost complete reaction occurs
$<10^{-4}$	indicates negligible reaction occurs

- When an equation is reversed, the new equilibrium constant is the reciprocal, or inverse, of the original K_c.
- When coefficients are doubled, K_c is squared.
- As temperature increases, the value of K_c increases for endothermic reactions and decreases for exothermic reactions.
- An equilibrium constant for a particular temperature can be calculated from the concentrations of the reactants and products at equilibrium and the expression for the equilibrium constant.
- At equilibrium, the concentration of a reactant or product can be calculated if the concentrations of the other reactants and products and the equilibrium constant are known.
- Stoichiometry may be used to calculate equilibrium concentrations of reactants and products and hence the value of the equilibrium constant using a reaction (ICE) table.

KEY QUESTIONS

Retrieval

1 Define the following terms.
- **a** homogeneous system
- **b** reaction quotient
- **c** equilibrium constant

Comprehension

2 Determine an expression for the reaction quotient for the reaction of hydrogen and chlorine with the equation:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

3 Determine the expression for the equilibrium constant for the following chemical equations.
- **a** $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
- **b** $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$
- **c** $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$
- **d** $4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g)$

continued over page

2.4 Review *continued*

4 A chemist investigated three different reactions and determined the value of the equilibrium constant for each. Select the reaction in which there would be substantially more products produced compared to reactants.

A Reaction 1: $K_c = 0.0057$

B Reaction 2: $K_c = 2.5 \times 10^{9}$

C Reaction 3: $K_c = 3.1 \times 10^{-3}$

Analysis

5 At a particular temperature, the equilibrium constant for the reaction represented by the following equation is 0.667:

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

At a specific point in the reaction, the reaction quotient is found to be 0.234. Predict which way the reaction will shift in order to reach equilibrium with reference to the concentration of the products.

6 Consider the reaction represented by the equation:

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

At 25°C the equilibrium constant is determined to be $K_c = 0.46$. At a particular time during the reaction, the reaction quotient is 1.2.

State an expression for the reaction quotient for this reaction and predict what will happen to the system as it moves to equilibrium.

7 The equilibrium constant for the decomposition of ammonia is 100 at 255°C for the equation:

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

a State an expression for the equilibrium constant for the equation:

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

b Calculate the equilibrium constant for the equation given in part **a**.

c State an expression for the equilibrium constant for the equation:

$$NH_3(g) \rightleftharpoons \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g)$$

d Calculate the equilibrium constant for the equation in part **c**.

e Use your answers to parts **a**–**d** to determine the effect on the value of an equilibrium constant when the:

i equation is reversed

ii coefficients of the equation are halved.

8 Water reacts with chlorine according to the equation:

$$2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$$

At a particular temperature the value of the equilibrium constant for this reaction is determined to be 4.0×10^{-4}. Determine the value for the equilibrium constant for the reaction if it is represented by the following equations, assuming no change in temperature.

a $H_2O(g) + Cl_2(g) \rightleftharpoons 2HCl(g) + \tfrac{1}{2}O_2(g)$

b $2HCl(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons H_2O(g) + Cl_2(g)$

9 For the chemical reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the equilibrium constant is 1.70 at 250°C.

For each equation, calculate the value of K_c at the same temperature.

a $4PCl_5(g) \rightleftharpoons 4PCl_3(g) + 4Cl_2(g)$

b $\tfrac{1}{2}PCl_3(g) + \tfrac{1}{2}Cl_2(g) \rightleftharpoons \tfrac{1}{2}PCl_5(g)$

c $\tfrac{1}{2}PCl_5(g) \rightleftharpoons \tfrac{1}{2}PCl_3(g) + \tfrac{1}{2}Cl_2(g)$

d $2PCl_3(g) + 2Cl_2(g) \rightleftharpoons 2PCl_5(g)$

10 Predict whether the equilibrium constants for each of the following would be increased, decreased or unchanged by an increase in temperature:

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

b $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$ $\quad \Delta H = -113\,kJ\,mol^{-1}$

c $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\quad \Delta H = +42\,kJ\,mol^{-1}$

d $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$ $\quad \Delta H = -564\,kJ\,mol^{-1}$

11 Calculate the equilibrium constant for the reaction represented by the equation $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, if an equilibrium mixture in a 2.0 L container was found to consist of 0.80 mol of N_2O_4 and 0.40 mol of NO_2.

12 Phosgene is a poisonous gas that was used during World War I. It can be formed by the reaction of carbon monoxide with chlorine gas in the equilibrium reaction:

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

The reaction was allowed to proceed at 74°C until equilibrium was reached. The equilibrium concentrations of each species were determined and recorded as follows: $[CO] = 2.4 \times 10^{-2}\,mol\,L^{-1}$, $[Cl_2] = 0.108\,mol\,L^{-1}$ and $[COCl_2] = 0.28\,mol\,L^{-1}$. Determine the equilibrium constant for the reaction at this temperature.

13 The following reaction was allowed to reach equilibrium at a temperature of 230°C:

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

The value of the equilibrium constant was determined to be 6.44×10^{5}.

If the equilibrium concentration of $[NO_2] = 15.5\,mol\,L^{-1}$ and $[NO] = 0.0542\,mol\,L^{-1}$, determine the concentration of O_2 in the equilibrium mixture.

14 4.45 mol of PCl_3 and 5.50 mol of Cl_2 were mixed in a 2.00 L vessel. They reacted according to the equation:

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

When equilibrium was reached, it was found that 0.35 mol of PCl_5 had been formed. Calculate the value of the equilibrium constant.

15 5.89 mol of N_2 and 8.23 mol of H_2 were mixed in a 5.0 L vessel. They reacted according to the equation:

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

When equilibrium was reached, it was found that 0.48 mol of NH_3 had been formed. Calculate the value of the equilibrium constant.

16 The equilibrium constant for the following reaction is 48.8 at 455°C:

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

An equilibrium mixture in a 2.0 L vessel at this temperature contains 0.220 mol of H_2 and 0.110 mol of I_2.

a Calculate the concentration of HI in this mixture.

b Another mixture was prepared by placing 4.00 mol of HI in a 2.0 L vessel at 330°C. At equilibrium, 0.44 mol of H_2 and 0.44 mol of I_2 were present. Determine the value of the equilibrium constant at this temperature.

c A third mixture consisted of 1.0 mol of HI, 0.24 mol of H_2 and 0.32 mol of I_2 in a 2.0 L container at 330°C. Deduce if the mixture is at equilibrium and, if not, predict the direction the reaction will shift to reach equilibrium.

17 A mixture of 0.100 mol of NO, 0.051 mol of H_2 and 0.100 mol of H_2O were added to a reaction vessel with a volume of 1.0 L at 300°C. The reaction at equilibrium is given by the equation:

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

After equilibrium was established, the concentration of NO was found to be 0.062. Determine the equilibrium constant, K_c, for the reaction at 300°C.

18 The following equilibrium has a K_c of 4.4×10^{-8} at 200°C:

$$A(g) \rightleftharpoons 2B(g)$$

0.50 mol of A was placed in an empty 2.0 L vessel at 200°C. Determine the concentration of B at equilibrium.

Chapter review

02

KEY TERMS

acidification
activation energy
catalyst
chemical energy
climate change
closed system
collision theory
concentration fraction
diprotic acid
dynamic equilibrium
ecosystem
endothermic
energy profile diagram
enthalpy
equilibrium
equilibrium constant
equilibrium law
equilibrium yield
exothermic
extent of reaction
greenhouse gas
heat of reaction
heterogeneous reaction
homogeneous reaction
hydrosphere
irreversible reaction
Le Châtelier's principle
ocean acidity
open system
position of equilibrium
rate of reaction
reaction quotient
reaction table
reversible reaction
saturated solution
system
thermochemical equation

KEY QUESTIONS

Retrieval

1 Identify which one of the following statements about a closed system is correct.

A Energy cannot enter or leave a closed system.
B In a closed system, only products remain when the reaction is complete.
C A closed system must be completely sealed to stop reactants or products from escaping.
D In a closed system, the reactants and products cannot be exchanged with the surroundings.

2 Select which one of the following statements about a chemical equilibrium is correct.

A The reaction has stopped.
B The rate of reaction is negligible.
C The rates of the forward and reverse reactions are equal.
D At least one of the reactants has been completely consumed.

3 Hydrogen iodide formed an equilibrium with hydrogen and iodine in a sealed vessel of constant volume, according to the equation:

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

Additional iodine gas was added and the system was allowed to reach a new equilibrium at constant temperature. Compared to the initial equilibrium, at the new equilibrium the:

A concentration of HI would be unchanged.
B concentration of H_2 would be unchanged.
C concentration of HI would have increased.
D concentration of H_2 would have increased.

4 A closed vessel at constant temperature contains H_2 and CO_2 in equilibrium with H_2O and CO, as shown by the following equation:

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \quad \Delta H = +42 \text{ kJ mol}^{-1}$

Select which one of the following procedures will shift the equilibrium position to the right.

A addition of CO gas
B addition of a catalyst to the system
C decreasing the volume of the system
D increasing the temperature of the system

5 SO_2, O_2 and SO_3 were mixed and formed the equilibrium system:

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

Indicate which one of the following ratios is constant at a fixed temperature, irrespective of the initial amounts of gases.

A $\frac{[SO_3]}{[SO_2][O_2]}$
B $\frac{[SO_3]}{[SO_2] + [O_2]}$
C $\frac{[SO_3]^2}{[SO_2]^2[O_2]}$
D $\frac{[SO_2] + [O_2]}{[SO_3]}$

6 Deduce which one of the equations below has the following expression for the equilibrium constant.

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

A $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$
B $4H_2(g) + 2CO(g) \rightleftharpoons 2CH_3OH(g)$
C $2CH_3OH(g) \rightleftharpoons 4H_2(g) + 2CO(g)$
D $CH_3OH(g) \rightleftharpoons 2H_2(g) + CO(g)$

7 Select the correct answers from the list to complete the following paragraph about equilibrium.

concentration, rates, processes, remains constant, increases, decreases, energy, matter, reversible, irreversible

Equilibrium occurs when there is a _____ reaction in a closed system. _____ can be added to the system but _____ cannot be added or removed. At equilibrium, the _____ of the forward and reverse reactions are equal. The total mass of reactants and products present in the reaction _____. There will be no observable change in the _____ of the reactants or products.

Comprehension

8 Determine whether the following systems are open or closed and explain your reasoning.

- **a** a lit candle
- **b** a refrigerator with a door that is shut
- **c** a human being
- **d** a weather balloon

9 Suppose CO gas and Cl_2 gas are added to a sealed container at constant temperature. A reaction occurs according to the following equation:

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

Explain how equilibrium is established by sorting the following statements into the correct order.

- **i** Equilibrium has been reached and the concentrations of CO, Cl_2 and $COCl_2$ will now remain constant.
- **ii** When the rates of the forward and reverse reactions become equal, $COCl_2$ is formed at the same rate as it is breaking down.
- **iii** The forward reaction will occur and, as the concentrations of CO and Cl_2 decrease, the rate of the production of $COCl_2$ decreases.
- **iv** As $COCl_2$ is formed, some $COCl_2$ molecules decompose to re-form CO and Cl_2.

10 Use the concepts of rates of reaction and collision theory to explain the effect on the position of equilibrium of increasing the concentration of hydrogen by adding more hydrogen gas to the equilibrium system:

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

11 The total pressure of the following equilibrium system was increased by reducing the volume at constant temperature:

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

Use the concepts of rates of reaction and collision theory to explain the effect on the position of equilibrium.

12 Explain the difference between the terms 'reaction quotient' (Q_c) and 'equilibrium constant' (K_c).

13 State the expression for the equilibrium constant for the following chemical equations.

- **a** $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
- **b** $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
- **c** $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$
- **d** $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

Analysis

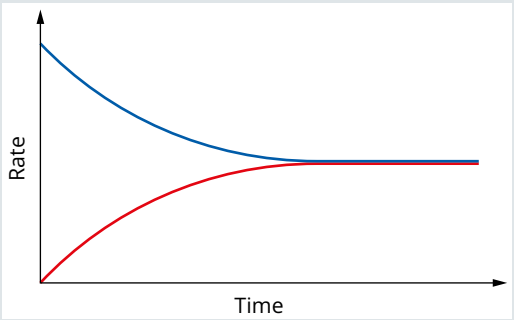
14 Determine whether the following processes occur in open or closed systems.

- **a** a saturated solution of salt in a glass: $NaCl(s) \rightleftharpoons NaCl(aq)$
- **b** solid $(NH_4)_2SO_4$ reacting with NaOH solution in a beaker: $(NH_4)_2SO_4(s) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2NH_3(g) + H_2O(l)$
- **c** a beaker containing a solution of CH_3COOH that dissociates: $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
- **d** burning toast

15 SO_2 and O_2 react to form an equilibrium with SO_3, according to the equation:

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

Analyse, using collision theory, the shape of the rate–time graph below that was obtained when SO_2 and O_2 were mixed in a container at constant temperature.



16 Elderly people, especially women, can become very susceptible to bone breakages. It is thought that as people age they absorb Ca^{2+} from food inefficiently, reducing the concentration of these ions in body fluids. An equilibrium exists between calcium phosphate in bone and calcium ions in body fluids:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Deduce why inefficient absorption of Ca^{2+} ions could cause weakness in bones using your understanding of equilibrium.

17 Determine in which of following reactions the position of the equilibrium is not affected by a change of volume at constant temperature, and justify your answer using collision theory.

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

B $Cl_2(g) + H_2(g) \rightleftharpoons 2HCl(g)$

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

D $2C_2H_6(g) + 7O_2(g) \rightleftharpoons 4CO_2(g) + 6H_2O(g)$

18 Predict how the concentration of hydrogen gas in each of the following equilibrium mixtures will change when the mixtures are heated and kept at constant volume.

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

b $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = +208\,kJ\,mol^{-1}$

19 The following equations represent reactions that are important in industrial processes. Predict the effect on the equilibrium position if each reaction mixture were compressed at constant temperature.

a $C_3H_8O(g) \rightleftharpoons C_3H_6O(g) + H_2(g)$

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

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

20 Deduce the balanced equations for the reactions with the following equilibrium equations.

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

b $K_c = \frac{[H_2S]^2}{[S_2][H_2]^2}$

c $K_c = \frac{[N_2O_4]^{\frac{1}{2}}}{[NO_2]}$

21 The value of K_c for the following reaction is equal to 4 at 25°C:

$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

At time *t*, the reaction quotient, Q_c, for a mixture of ethanol, water, ethyl ethanoate ($CH_3COOC_2H_5$) and ethanoic acid is equal to 6. Assuming that the mixture is also at 25°C, and referring to the values of K_c and Q_c, predict what will happen to the concentration of ethyl ethanoate as the system reaches equilibrium.

22 Apply your knowledge about the equilibrium constant K_c to complete the following statements.

a If $K_c = 0.0001$ for a particular reaction, at equilibrium the concentrations of products will be _____ the concentrations of reactants.

b For the reaction with the equation:

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

the expression for the equilibrium constant, K_c, is _____.

c When the reaction quotient is smaller than K_c, the reaction _____ to establish equilibrium.

23 The equilibrium constant for the following reaction at 25°C is 10^{-10}:

$2Fe^{2+}(aq) + Sn^{4+}(aq) \rightleftharpoons 2Fe^{3+}(aq) + Sn^{2+}(aq)$

a Identify if a significant reaction would occur when solutions of tin(IV) chloride and iron(II) chloride are mixed.

b Determine the value of the equilibrium constant for the reaction:

$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + Sn^{4+}(aq)$

c Explain whether a significant reaction would occur when solutions of tin(II) chloride and iron(III) chloride are mixed.

24 Consider the following equilibrium at 227°C:

$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$

a State the expression for K_c for the equilibrium system.

b Given that the value of K_c at 227°C for the expression in part **a** is 32, deduce the equilibrium constant for each of the following.

i $BrCl(g) \rightleftharpoons \frac{1}{2}Br_2(g) + \frac{1}{2}Cl_2(g)$

ii $Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g)$

iii $4BrCl(g) \rightleftharpoons 2Br_2(g) + 2Cl_2(g)$

iv $\frac{1}{2}Cl_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons BrCl(g)$

25 The reaction used to manufacture ammonia is represented by the equation:

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

The equilibrium constant for the reaction is 0.052 at 400°C.

A gas mixture contains 1.0 mol of N_2 gas, 1.0 mol of H_2 gas and 0.25 mol of NH_3 gas in a 1.0 L vessel at 400°C. Determine if the mixture is at equilibrium and, if not, predict the direction it will shift to reach equilibrium.

26 An equilibrium mixture contains 0.020 mol of H_2O gas, 0.030 mol of H_2 gas, 0.040 mol of CO gas and 0.050 mol of CO_2 gas in a 2.0 L vessel. The gases react according to the equation:

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

Calculate the equilibrium constant at 900°C.

27 At a specified temperature the reaction between solutions of Sn^{2+} and Fe^{3+} reaches equilibrium according to the equation:

$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + Sn^{4+}(aq)$

a Determine the expression for K_c.

b If the equilibrium concentrations are 0.30 mol L^{-1} Fe^{3+}, 0.40 mol L^{-1} Fe^{2+}, 0.20 mol L^{-1} Sn^{4+} and 0.10 mol L^{-1} Sn^{2+} at a particular temperature, calculate the equilibrium constant at that temperature.

28 Propanone (C_3H_6O) is used to remove nail polish. It can be prepared from propan-2-ol (C_3H_8O) using a copper–zinc catalyst, according to the equation:

$$C_3H_8O(g) \rightleftharpoons C_3H_6O(g) + H_2(g)$$

If an equilibrium mixture of these gases consists of 0.018 mol of propan-2-ol, 0.082 mol of acetone and 0.082 mol of hydrogen in a 2.0 L vessel, calculate the value of the equilibrium constant.

29 Consider the equilibrium:

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

A 3.00 L vessel contained 6.00 mol of PCl_3, 4.50 mol of PCl_5 and 0.900 mol of Cl_2 at equilibrium at 250°C.

a State an expression for the equilibrium constant for this reaction.

b Calculate the equilibrium constant for the reaction at 250°C.

c Another equilibrium mixture contains 0.0020 mol L^{-1} of PCl_5 and 0.0010 mol L^{-1} of PCl_3 at 250°C. Determine the concentration of Cl_2 in this mixture.

d Calculate the equilibrium constant at 250°C for the reaction:

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

30 At one stage during the synthesis of nitric acid, dinitrogen tetroxide is in equilibrium with nitrogen dioxide:

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

0.540 mol of N_2O_4 was placed in a 2.00 L vessel. When equilibrium was achieved, 0.280 mol of NO_2 was present. Determine the value of the equilibrium constant at this temperature. (You may wish to set out your calculations using an ICE table.)

31 Consider the reaction:

$$A + 3B \rightleftharpoons 2C + D$$

Analysis of an equilibrium mixture in a 2.0 L container shows that 2.0 mol of A, 0.50 mol of B and 3.0 mol of D are present. If the equilibrium constant of the reaction is 0.024, calculate the:

a concentration of A, B and D at equilibrium

b concentration of C in the equilibrium mixture

c number of moles of C in the equilibrium mixture.

32 Carbon monoxide is used as a fuel in many industries. It reacts according to the equation:

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

In a study of this exothermic reaction, an equilibrium system is established in a closed vessel of constant volume at 1000°C.

a Predict what will happen to the equilibrium position as a result of:

i a decrease in temperature

ii the addition of a catalyst

iii the addition of more oxygen.

b Predict what will happen to the equilibrium constant as a result of each of the changes in part **a**.

c If carbon monoxide can be used as a fuel, what conclusion can you make about the magnitude of the equilibrium constant for the reaction?

33 **a** The equilibrium constant is 0.67 at a particular temperature for the reaction:

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

A mixture of 0.100 mol L^{-1} of CO, 0.200 mol L^{-1} of H_2, 0.300 mol L^{-1} of CH_4 and 0.400 mol L^{-1} of H_2O is heated to this temperature. Predict whether the concentration of the following would increase, decrease or not change.

i CO

ii H_2

iii CH_4

iv H_2O

b When the temperature of the reaction mixture is increased by 10°C, the equilibrium constant for the reaction becomes 0.71. Determine what the enthalpy change of this reaction will be.

34 A step during nitric acid production is the oxidation of nitrogen oxide to nitrogen dioxide:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = -114\,kJ\,mol^{-1}$$

Nitrogen dioxide is a brown gas and nitrogen oxide and oxygen are colourless. An equilibrium mixture was prepared in a 1.0 L container at 350°C. Copy the following table, and for each of the changes listed, predict if the reaction mixture would become darker or lighter. Give a reason for your choice.

	Colour change (lighter or darker)	**Explanation**
a The temperature is increased to 450°C at constant volume.		
b The volume of the container is increased at constant temperature.		
c A catalyst is added at constant volume and temperature.		
d More oxygen is added at constant volume and temperature.		

35 Ethene gas is produced from ethane gas in an endothermic reaction represented by the equation:

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g) \quad \Delta H = +138\,kJ\,mol^{-1}$$

a Predict whether the following changes will result in the equilibrium percentage yield of ethene increasing, decreasing or not changing.

i The volume is reduced at constant temperature.

ii More hydrogen gas is added at constant temperature and volume.

iii The temperature is increased at constant volume.

iv A catalyst is added.

v Argon gas is added at constant temperature and volume.

b Assess how each of the changes in part **a** will affect the rate at which the reaction achieves equilibrium.

36 The reaction used to manufacture ammonia is represented by:

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

The equilibrium constant for the reaction is 0.052 at 400°C.

Each of the following gas mixtures is contained in a 1.0 L vessel at 400°C. Determine if each mixture is in equilibrium. If not, predict the direction the reaction will shift in order to reach equilibrium.

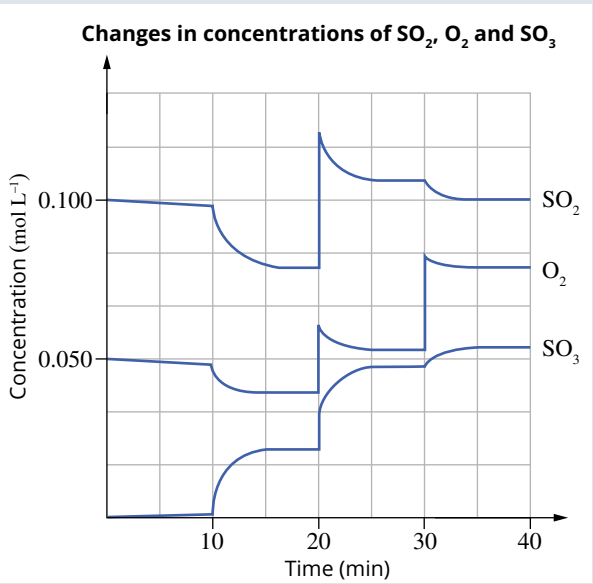
a 0.20 mol of N_2, 0.20 mol of H_2, 0.20 mol of NH_3

b 0.050 mol of N_2 and 0.50 mol of H_2

37 Sulfur dioxide gas and oxygen gas were mixed at 600°C to produce a gaseous equilibrium mixture:

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

A number of changes were then made, including the addition of a catalyst, resulting in the formation of new equilibrium mixtures. The graph below shows how the concentrations of the three gases changed over time.



a State an expression for the equilibrium constant, K_c, of the reaction.

b Determine at what time intervals the reaction was at equilibrium.

c Calculate the value of K_c at 18 minutes.

d Determine at what time was the catalyst added. Explain your reasoning.

e Calculate the value of K_c at 25 minutes.

f Deduce what changes were made to the system at 20 minutes.

Knowledge utilisation

38 Methanol is manufactured for use as a fuel for racing cars. It can be made by the following reaction between carbon monoxide and hydrogen:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -103\,kJ\,mol^{-1}$$

a Predict what conditions of temperature and pressure would be required for a:

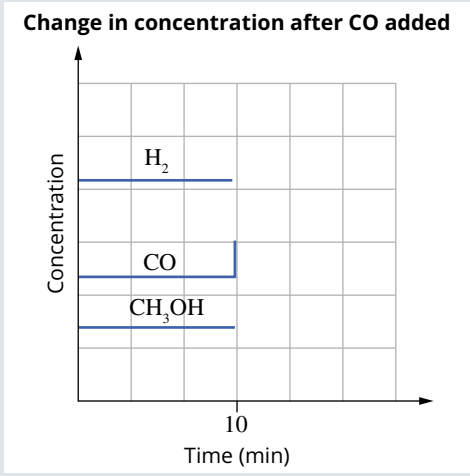
i fast reaction rate

ii high equilibrium yield of methanol.

b State whether a compromise will be needed in the choice of temperature or pressure.

c Propose another method that could be employed at a manufacturing plant to increase the rate of methanol production.

d As part of an investigation of this process, the concentration of a mixture of CO, H_2 and CH_3OH was monitored continuously. The mixture was initially at equilibrium at 400°C and constant volume. After 10 minutes, additional CO was added to the mixture, as shown in the following figure.



i Draw a graph to indicate how concentrations would change as a consequence of the addition of CO.

ii Following the addition of the CO, the mixture again reaches equilibrium. Draw a second graph to show the effect on the concentrations if the temperature was then increased to 450°C.

39 During the process for sulfuric acid manufacture, sulfur dioxide is converted to sulfur trioxide at temperatures of 400–500°C:

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

- **a** Predict the effect of increasing the pressure on:
  - **i** reaction rate
  - **ii** equilibrium yield.
- **b** In practice, this step is usually performed at atmospheric pressure. Propose a reason why.
- **c** During the process, sulfur trioxide is removed from the reaction mixture by converting it to sulfuric acid. The remaining gases are then recycled to the reaction vessel. Explain the reason for recycling the gases.
- **d** Assess what factors would have influenced the choice of the reaction temperature.

40 Carbon disulfide gas (CS_2) is used in the manufacture of rayon. $CS_2(g)$ can be made in an endothermic gas-phase reaction between sulfur trioxide gas (SO_3) and carbon dioxide. Oxygen gas is also produced in the reaction.

- **a** Construct a balanced chemical equation for the reaction.
- **b** State an expression for the equilibrium constant of the reaction.
- **c** An equilibrium mixture of these gases was made by mixing sulfur trioxide and carbon dioxide. The equilibrium mixture consisted of 0.028 mol of CS_2, 0.022 mol of SO_3, 0.014 mol of CO_2 and an unknown amount of O_2 in a 2.0 L vessel. Determine the:
  - **i** number of moles of O_2 present in the equilibrium mixture
  - **ii** value of the equilibrium constant at that temperature.
- **d** Predict how each of the following changes to an equilibrium mixture would affect the yield of CS_2.
  - **i** removing O_2 (at constant total volume)
  - **ii** increasing the temperature
  - **iii** adding a catalyst
  - **iv** increasing the pressure by decreasing the volume of the reaction vessel (at constant temperature)
  - **v** increasing the pressure by introducing argon gas into the reaction vessel (at constant volume).



CHAPTER

03 Equilibrium in acid and base chemistry



Acids and bases have an important and diverse role. They are found in homes and are used extensively in industry and agriculture. Acids and bases are also the reactants and products of many chemical reactions that take place in environmental and biological systems.

In this chapter, you will study a theory that explains the characteristic reactions of acids and bases. You will learn to represent the common reactions of acids and bases using ionic equations and investigate the distinction between strong and weak acids, and concentrated and dilute acids. Finally, you will apply your understanding of acid–base chemistry to a contemporary environmental issue—increasing ocean acidity.

Syllabus subject matter

Topic 1 • Chemical equilibrium systems

PROPERTIES OF ACIDS AND BASES

- understand that acids are substances that can act as proton (hydrogen ion) donors and can be classified as monoprotic or polyprotic depending on the number of protons donated by each molecule of the acid
- distinguish between strong and weak acids and bases in terms of the extent of dissociation, reaction with water and electrical conductivity and distinguish between the terms strong and concentrated for acids and bases.

pH SCALE

- understand that water is a weak electrolyte and the self-ionisation of water is represented by $K_w = [H_3O^+][OH^-]$; K_w can be used to calculate the concentration of hydrogen ions from the concentration of hydroxide ions in a solution
- understand that the pH scale is a logarithmic scale and the pH of a solution can be calculated from the concentration of hydrogen ions using the relationship $pH = -\log_{10} [H_3O^+]$
- use appropriate mathematical representation to solve problems for hydrogen ion concentration $[H^+(aq)]$, pH, hydroxide ion concentrations $[OH^-(aq)]$ and pOH.

BRØNSTED–LOWRY MODEL

- recognise that the relationship between acids and bases in equilibrium systems can be explained using the Brønsted–Lowry model and represented using chemical equations that illustrate the transfer of hydrogen ions (protons) between conjugate acid–base pairs
- recognise that amphiprotic species can act as Brønsted–Lowry acids and bases
- identify and deduce the formula of the conjugate acid (or base) of any Brønsted–Lowry base (or acid)
- appreciate that buffers are solutions that are conjugate in nature and resist a change in pH when a small amount of an acid or base is added; Le Châtelier's principle can be applied to predict how buffer solutions respond to the addition of hydrogen ions and hydroxide ions.



DISSOCIATION CONSTANTS

- recognise that the strength of acids is explained by the degree of ionisation at equilibrium in aqueous solution, which can be represented with chemical equations and equilibrium constants (K_a)
- determine the expression for the dissociation constant for weak acids (K_a) and weak bases (K_b) from balanced chemical equations
- analyse experimental data to determine and compare the relative strengths of acids and bases
- use appropriate mathematical representation to solve problems, including calculating dissociation constants (K_a and K_b) and the concentration of reactants and products.

ACID–BASE INDICATORS

- understand that an acid–base indicator is a weak acid or a weak base where the components of the conjugate acid–base pair have different colours; the acidic form is of a different colour to the basic form
- explain the relationship between the pH range of an acid–base indicator and its pK_a value
- recognise that indicators change colour when the pH = pK_a and identify an appropriate indicator for a titration, given equivalence point of the titration and pH range of the indicator.

SCIENCE AS A HUMAN ENDEAVOUR

- **Development of acid–base models:** 'Superacids', such as carborane acids, have been found to be a million times stronger than sulfuric acid when the position of equilibrium in aqueous solution is considered.

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3.1 The Brønsted–Lowry model of acids and bases

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- use the Brønsted–Lowry model of acids and bases to explain how acids donate protons and bases accept these protons
- identify conjugate acid–base pairs using the Brønsted–Lowry model of acids and bases
- understand that some acids are able to donate more than one proton.



In Unit 2 you were introduced to the Arrhenius model of **acids** and **bases**. This model helps to explain why acids and bases can act as electrolytes in water. Acids form hydrogen ions and bases form **hydroxide ions**. Other properties of acids and bases are summarised in Table 3.1.1.

TABLE 3.1.1 Properties of acids and bases

Properties of acids	Properties of bases
turn litmus indicator red	turn litmus indicator blue
tend to be corrosive	are caustic and feel slippery
taste sour	taste bitter
react with bases	react with acids
solutions have a relatively low pH	solutions have a relatively high pH
solutions conduct an electric current	solutions conduct an electric current

In 1923, Danish physical chemist Johannes Nicolaus Brønsted and English chemist Thomas Martin Lowry were working independently. They each came up with the theory that now bears both of their names. The Brønsted–Lowry model is more general than the one proposed by Arrhenius and provides an explanation for some observed acid–base behaviours that cannot be explained by the earlier theories.

THE BRØNSTED–LOWRY MODEL OF ACIDS AND BASES

According to the **Brønsted–Lowry model**, a substance behaves as an acid when it donates a proton, i.e. H^+, to a base. A substance behaves as a base when it accepts a proton from an acid.

In summary:

- acids are proton donors
- bases are proton acceptors
- an **acid–base reaction** involves an exchange of protons from an acid to a base.

For example, hydrogen chloride (HCl) is a gaseous molecular compound that is very soluble in water. The molecules **ionise** in water according to the following reaction:

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

In an aqueous solution of hydrogen chloride, nearly all the hydrogen chloride is present as ions—virtually no molecules of hydrogen chloride remain. This **solution** is known as hydrochloric acid.

As you work through this chapter, you will notice that the terms 'dissociate' and 'ionise' are often used interchangeably.

While there is a subtle difference between the concepts, the syllabus does not require you to distinguish between the terms.

In general, it is sufficient to understand that strong acids ionise fully, whereas weak acids and bases only partially dissociate.

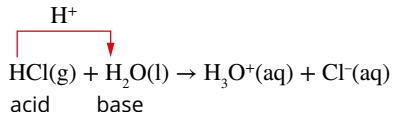


FIGURE 3.1.1 The reaction between hydrochloric acid and water is an example of an acid–base reaction, which involves a transfer of protons from an acid to a base.

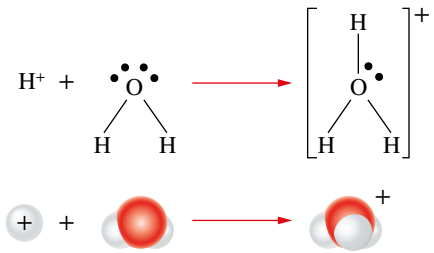


FIGURE 3.1.2 Formation of the hydrogen ion

Remember that $H^+(aq)$ is often used interchangeably with $H_3O^+(aq)$ when discussing acids donating protons.

When acids react with water, hydrogen (H_3O^+) ions are produced. When bases react with water, hydroxide (OH^-) ions are produced.

In this reaction, each HCl molecule has donated a proton to a water molecule, forming the **hydrogen ion** (also referred to as the '**hydronium ion**') $H_3O^+(aq)$. According to the Brønsted–Lowry model, the HCl has acted as an acid. The water molecule has accepted a proton from the HCl molecule, so the water has acted as a base. This is outlined in Figure 3.1.1.

The hydrogen ion can be represented as either $H_3O^+(aq)$ or $H^+(aq)$. The reaction of HCl(g) with water can be written as either:

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

or

$$HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$$

However, writing the hydrogen ion as $H^+(aq)$ in an equation makes it harder to see that a proton transfer has occurred. The hydrogen ion is therefore usually written as $H_3O^+(aq)$ in this chapter.

The structural formulas of the hydrogen ion and the water molecule are shown in Figure 3.1.2.

Advantages of the Brønsted–Lowry model

Acid–base reactions are not restricted to aqueous solutions. A reaction between two gases can be an acid–base reaction. For example, the **salt** ammonium chloride can be formed by a reaction between:

- solutions of hydrochloric acid and ammonia:

$$HCl(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

- gaseous hydrogen chloride and gaseous ammonia:

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

The Brønsted–Lowry model classifies both of these reactions as acid–base reactions because in each case the acid donates a proton to the base.

CONJUGATE ACID–BASE PAIRS

A solution of hydrochloric acid is produced when hydrogen chloride ionises in water:

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

Because Cl^- can be formed from HCl by the loss of a single proton, it is called the **conjugate base** of HCl. Similarly, HCl is described as the **conjugate acid** of Cl^-. HCl and Cl^- are called a **conjugate acid–base pair**. Similarly, H_3O^+ and H_2O are a conjugate pair.

A conjugate acid–base pair is two species that differ by a proton, i.e. H^+. For the reaction between HCl and H_2O, the conjugate pairs are HCl/Cl^- and H_3O^+/H_2O.

The relationship between acid–base conjugate pairs is represented in Figure 3.1.3.

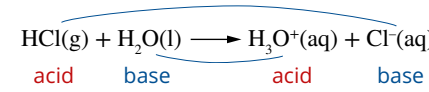


FIGURE 3.1.3 Conjugate acid–base pairs are formed when an acid donates a proton to a base.

In the reaction between NH_3 and H_2O, shown in Figure 3.1.4, the conjugate acid–base pairs are NH_4^+/NH_3 and H_2O/OH^- because each acid differs from its corresponding base by one proton.

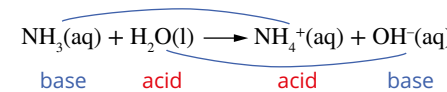


FIGURE 3.1.4 The reaction between ammonia and water, showing the conjugate acid–base pairs

Figure 3.1.5 shows the formulas of some common acids and bases and their conjugate pairs.

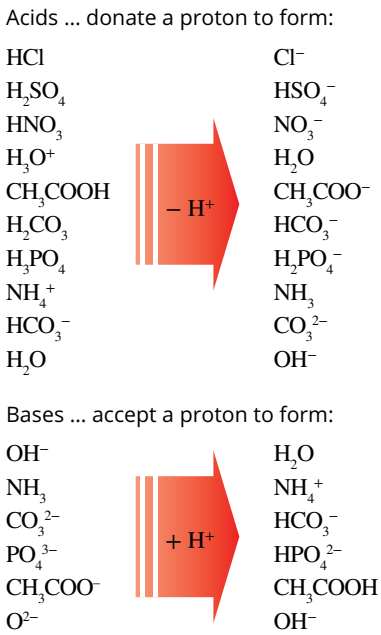


FIGURE 3.1.5 Some common acid–base conjugate pairs

AMPHIPROTIC SUBSTANCES

Some substances can donate or accept protons depending on what they are reacting with. Therefore, they can behave as either acids or bases. Such substances are said to be **amphiprotic**.

For example, in the following reaction, water gains a proton from HCl and acts as a base:

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

However, in the reaction below, water donates a proton to NH_3 and acts as an acid:

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

These reactions are represented in Figure 3.1.6.

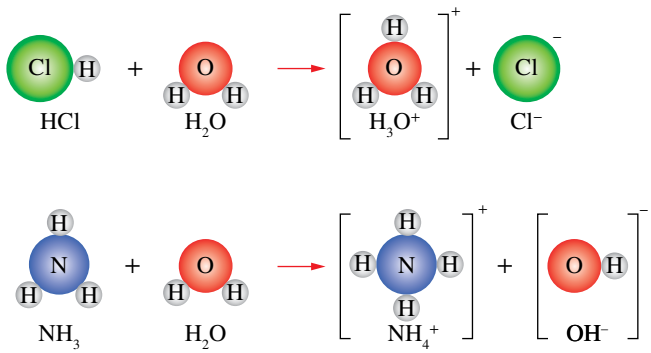


FIGURE 3.1.6 The amphiprotic nature of water is demonstrated by its reactions with HCl and NH_3.

It is evident that water can act as either an acid or a base, depending on the **solute** present.

If the solute is a stronger acid than water, then water will react as a base. If the solute is a stronger base than water, then water will react as an acid.

Some common amphiprotic substances are H_2O, HCO_3^-, $H_2PO_4^-$ and HSO_4^-.

When an amphiprotic substance is placed in water, it reacts as both an acid and a base. For example, the hydrogen carbonate ion (HCO_3^-) reacts according to the equations:

$$\underset{\text{base}}{HCO_3^-}(aq) + \underset{\text{acid}}{H_2O}(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

$$\underset{\text{acid}}{HCO_3^-}(aq) + \underset{\text{base}}{H_2O}(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

Since HCO_3^- can act as both an acid and a base, it is amphiprotic.

Although both reactions are possible for all amphiprotic substances in water, generally one of these reactions dominates. The dominant reaction can be identified by measuring the pH (a measure of the **concentration** of hydrogen ion in solution) of the solution.

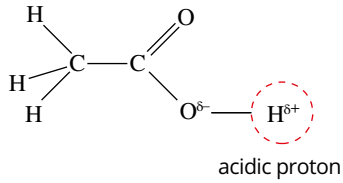


FIGURE 3.1.7 The structure of ethanoic acid. Each molecule can donate only one proton to a water molecule when ethanoic acid reacts with water.

MONOPROTIC AND POLYPROTIC ACIDS

Monoprotic acids can donate only one proton. These acids include hydrochloric acid (HCl), hydrofluoric acid (HF), nitric acid (HNO_3) and ethanoic acid (CH_3COOH).

While ethanoic acid contains four hydrogen atoms, each molecule can donate only one proton to produce an ethanoate ion (CH_3COO^-) and is therefore a monoprotic acid. Only the hydrogen that is part of the highly polar O–H bond is donated. This hydrogen atom is called the **acidic proton**, as shown in Figure 3.1.7.

Polyprotic acids

Some acids can donate more than one proton from each molecule and are said to be **polyprotic acids**. The number of hydrogen ions an acid can donate depends on the structure of the acid. Polyprotic acids do not donate all of their protons at once, but do so in steps when reacting with a base.

Diprotic acids

Diprotic acids, such as sulfuric acid (H_2SO_4) and carbonic acid (H_2CO_3), can donate two protons.

A diprotic acid **dissociates** in two stages; for example sulfuric acid:

Stage 1: $H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$

Sulfuric acid is described as a **strong acid** in water because it readily donates a proton and so this stage occurs almost to completion. Virtually no H_2SO_4 molecules are found in an aqueous solution:

Stage 2: $H_2SO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$

The HSO_4^- ion formed can also act as an acid. In a $1.0\,mol\,L^{-1}$ solution, only a small proportion of those ions react further to produce H_3O^+ ions and SO_4^{2-} ions.

HSO_4^- is described as a **weak acid** because it is only partially dissociated. A double (reversible) arrow indicates that an incomplete reaction occurs. (You will learn more about strong and weak acids later in this chapter.) Therefore, a solution of sulfuric acid contains hydrogen ions, hydrogen sulfate ions and sulfate ions.

Triprotic acids

Triprotic acids can donate three protons. These include phosphoric acid (H_3PO_4) and boric acid (H_3BO_3). A triprotic acid, such as phosphoric acid, dissociates in three stages:

Stage 1: $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$

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

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

Phosphoric acid is a weak acid in water. Therefore, in a $1.0\,mol\,L^{-1}$ solution of phosphoric acid, only a small proportion of the protons is donated at each **dissociation** stage. The extent of the dissociation decreases progressively from stage 1 to stage 3.

PA 3.1.6

3.1 Review

SUMMARY

- The Brønsted–Lowry model describes acid–base properties in terms of proton transfer. A Brønsted–Lowry acid is a proton donor and a base is a proton acceptor.
- When an acid donates a proton, it forms its conjugate base. When a base accepts a proton, it forms its conjugate acid.
- Conjugate acid–base pairs are molecules or ions that differ from each other by a H^+ ion.
- A proton or hydrogen ion in solution can be represented by the hydrogen ion, $H_3O^+(aq)$, or simply as $H^+(aq)$.
- Amphiprotic substances can act as either acids or bases, depending on the substance with which they are reacting.
- A polyprotic acid can donate more than one proton to a base.
- The first dissociation of a diprotic acid occurs to a greater extent than the second dissociation. In a triprotic acid, the third dissociation occurs to the least extent.

KEY QUESTIONS

Retrieval

1 Identify the two acid–base conjugate pairs in the following reaction:

$$H_2SO_4(l) + HNO_3(l) \rightarrow HSO_4^-(l) + H_2NO_3^+(l)$$

2 Identify the conjugate of the acid or base that is written in bold for each of the following equations.

a $HF(aq) + \mathbf{OH^-}(aq) \rightarrow H_2O(l) + F^-(aq)$

b $HCOOH(aq) + \mathbf{H_2O}(l) \rightarrow H_3O^+(aq) + HCOO^-(aq)$

c $CH_3NH_2(aq) + HCl(aq) \rightarrow \mathbf{CH_3NH_3^+}(aq) + Cl^-(aq)$

Comprehension

3 Explain why the reaction between a solution of sodium hydroxide and a solution of hydrochloric acid is a Brønsted–Lowry acid–base reaction.

4 Determine the conjugate acid of the following bases.

a NH_3

b CH_3COO^-

c HPO_4^{2-}

d CO_3^{2-}

5 Construct a structural formula of the monoprotic ethanoic acid molecule. Identify which proton is donated in an acid–base reaction.

Analysis

6 Distinguish between a diprotic and an amphiprotic substance. Use examples.

7 Construct an equation to show each of the following acting as an acid and a base with water.

a HCO_3^-

b HPO_4^{2-}

c HSO_4^-

d H_2O

8 Explain why HSO_4^- is an amphiprotic substance but H_2SO_4 is a diprotic acid.

9 Distinguish between the products formed when water acts as an acid or a base.

10 Describe why the Arrhenius model is useful and explain why the Brønsted–Lowry model is better.

3.2 Strength of acids and bases



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- distinguish between strong and weak acids and bases in terms of the extent of dissociation, reaction with water and electrical conductivity
- distinguish between the terms 'strong' and 'concentrated' for acids and bases
- explain how changing definitions of acids and bases are necessary as new developments and discoveries of solutions, such as superacids, are made.

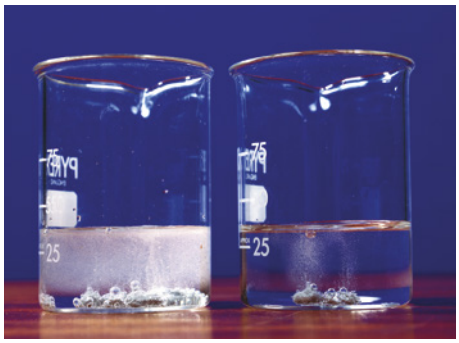


FIGURE 3.2.1 Zinc reacts more vigorously with a strong acid (left) than with a weak acid (right). The acid solutions are of equal concentration and volume.

The acid solutions in the two beakers shown in Figure 3.2.1 are of equal concentration, yet the acid in the beaker on the left reacts more vigorously with zinc than the acid on the right. The acid on the left is described as a stronger acid than the one in the beaker on the right.

In Module 3.1, you learnt that the Brønsted–Lowry model defines acids as proton donors and bases as proton acceptors. In this module, you will investigate the differences between:

- strong and weak acids
- strong and weak bases.

ACID AND BASE STRENGTH

Experiments show that different acid solutions of the same concentration do not have the same pH (a measure of the amount of hydrogen ion in solution—pH will be looked at more closely in the following module).

Some acids can donate a proton more readily than others. The Brønsted–Lowry model describes the strength of an acid as its ability to donate hydrogen ions to a base. The strength of a base is a measure of its ability to accept hydrogen ions from an acid.

Since aqueous solutions of acids and bases are most commonly used, it is convenient to use an acid's tendency to donate a proton to water, or a base's tendency to accept a proton from water, as a measure of its strength. Table 3.2.1 gives the names and chemical formulas of some strong and weak acids and bases.

TABLE 3.2.1 Examples of common strong and weak acids and bases

Strong acids	Weak acids	Strong bases	Weak bases
hydrochloric acid (HCl)	ethanoic acid (CH_3COOH)	sodium hydroxide (NaOH)	ammonia (NH_3)
sulfuric acid (H_2SO_4)	carbonic acid (H_2CO_3)	potassium hydroxide (KOH)	
nitric acid (HNO_3)	phosphoric acid (H_3PO_4)	calcium hydroxide ($Ca(OH)_2$)	

Strong acids

As you saw previously, when hydrogen chloride gas (HCl) is bubbled through water, it ionises completely—virtually no HCl molecules remain in the solution, as shown in Figure 3.2.2a. Similarly, pure HNO_3 and H_2SO_4 are covalent molecular compounds, which also ionise completely in water:

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$
$$H_2SO_4(l) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$$
$$HNO_3(l) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

The single reaction arrow $\rightarrow$ in each equation above indicates that the dissociation reaction is complete.

Acids that readily donate a proton are called strong acids. Strong acids donate protons easily. Therefore, solutions of strong acids contain ions, with virtually no unreacted acid molecules remaining. Hydrochloric acid, sulfuric acid and nitric acid are the most common strong acids.

Weak acids

Vinegar is a solution of ethanoic acid. Pure ethanoic acid is a polar covalent molecular compound that dissociates in water to produce hydrogen ions and ethanoate ions. In a 1.0 mol L^{-1} solution of ethanoic acid (CH_3COOH), only a small proportion of ethanoic acid molecules are dissociated at any one time (Figure 3.2.2b). A 1.0 mol L^{-1} solution of ethanoic acid contains a high proportion of CH_3COOH molecules and only some hydrogen ions and ethanoate ions. At 25°C, in a 1.0 mol L^{-1} solution of ethanoic acid, the concentrations of $CH_3COO^-(aq)$ and H_3O^+ are only about 0.004 mol L^{-1}.

The partial dissociation of a weak acid is shown in an equation using reversible (double) arrows:

$$\underset{\text{acid}}{CH_3COOH(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Therefore, ethanoic acid is described as a weak acid in water. This can be seen in Figure 3.2.2.

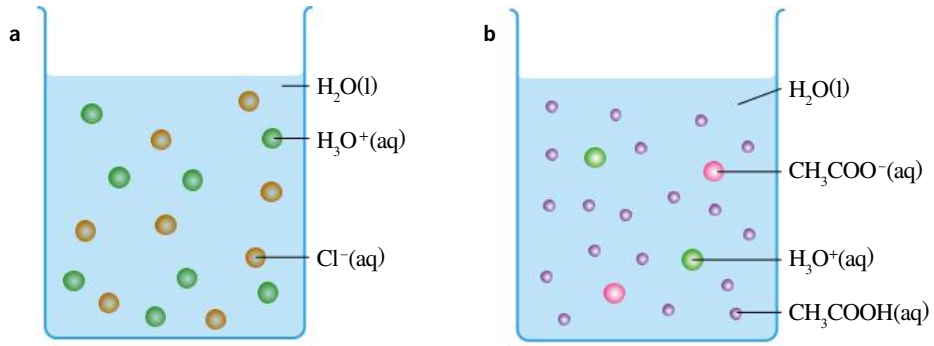


FIGURE 3.2.2 (a) In a 1.0 mol L^{-1} solution of a hydrochloric acid the acid molecules are completely dissociated in water. (b) In a 1.0 mol L^{-1} solution of ethanoic acid only a small proportion of the ethanoic acid molecules are dissociated.

Differences in conductivity

Acids of equal concentrations can have different abilities to conduct an electric current. When copper electrodes are immersed in a 1.0 mol L^{-1} solution of hydrochloric acid and connected to an electric circuit containing a light globe, the globe glows brightly. When the hydrochloric acid is substituted with a 1.0 mol L^{-1} solution of ethanoic acid, the light only glows faintly. This is further evidence that hydrochloric acid is a stronger acid than ethanoic acid. The brighter light indicates the greater number of ions present in a solution of hydrochloric acid than in ethanoic acid.

Strong bases

The ionic compound sodium oxide (Na_2O) ionises in water, releasing sodium ions (Na^+) and oxide ions (O^{2-}). The oxide ions react completely with the water, accepting a proton to form hydroxide ions (OH^-):

$$Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$$

Sodium oxide is an example of a **strong base**. Strong bases accept protons easily.

PA 3.1.5

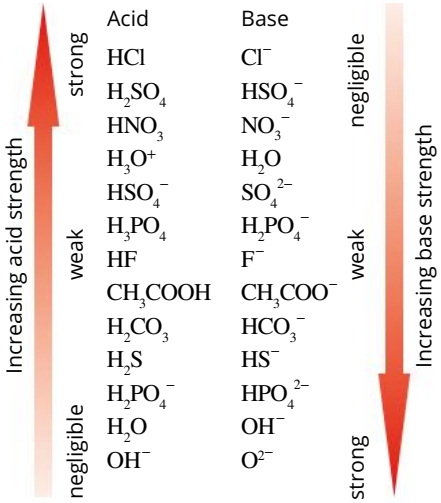


FIGURE 3.2.3 The relative strength of some conjugate acid–base pairs

Weak bases

Ammonia is a covalent molecular compound that dissociates in water by accepting a proton. This dissociation can be represented by the equation:

$$\underset{\text{base}}{NH_3(g)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Ammonia behaves as a base because it gains a proton. Water has donated a proton and so it behaves as an acid.

Only a small proportion of ammonia molecules are dissociated at any instant, so a 1.0 mol L^{-1} solution of ammonia contains mostly ammonia molecules together with a smaller number of ammonium ions and hydroxide ions. This is shown by the double arrow in the equation. Ammonia is a **weak base** in water.

Relative strength of conjugate acid–base pairs

You will recall from Module 3.1 that conjugate acids and bases differ by one proton (H^+). In the reaction represented by the equation:

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

HF is the conjugate acid of F^- and OH^- is the conjugate base of H_2O. HF and F^- are a conjugate acid–base pair. H_2O and OH^- are another conjugate acid–base pair in this reaction.

The stronger an acid is, the weaker is its conjugate base. Similarly, the stronger a base is, the weaker is its conjugate acid. The relative strength of some conjugate acid–base pairs is shown in Figure 3.2.3.

Strength versus concentration

When referring to solutions of acids and bases, it is important not to confuse the terms 'strong' and 'weak' with 'concentrated' and 'dilute'. Concentrated and dilute describe the amount of acid or base dissolved in a given volume of solution. Hydrochloric acid is a strong acid because it readily donates protons. A **concentrated solution** of hydrochloric acid can be prepared by bubbling a large amount of hydrogen chloride into a given volume of water. By using only a small amount of hydrogen chloride, a dilute solution of hydrochloric acid would be produced.

However, in both cases, the hydrogen chloride is completely ionised—it is a strong acid. Similarly a solution of ethanoic acid may be concentrated or dilute. However, as it is partially dissociated, it is a weak acid (Figure 3.2.4).

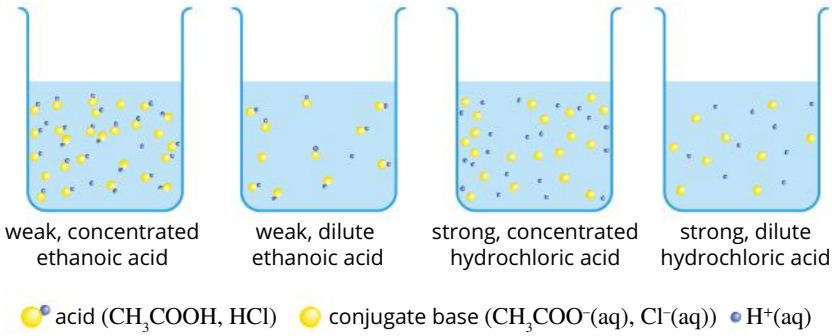


FIGURE 3.2.4 The concentration of ions in an acid solution depends on both the concentration and strength of the acid.

Terms describing acids as 'weak' or 'strong', or solutions as 'dilute' or 'concentrated', are qualitative (or descriptive) terms. Solutions can be given accurate, quantitative descriptions by stating concentrations in mol L^{-1} (M) or g L^{-1}.

Development of acid–base models

Over the years, there have been many attempts to define acids and bases. At first, acids and bases were defined in terms of their observed properties such as taste, effect on an indicator and reactions with other substances.

In 1887, the Swedish scientist Svante Arrhenius passed an electric current through various solutions including acids and bases. As a result of his observations, he developed a theory that explained some of the common properties of acids and bases. (You may recall this from your Unit 2 studies of acids and bases.) You will now be familiar with the Brønsted–Lowry model, which defines an acid as a substance that readily dissociates in water to produce hydrogen ions. The degree of dissociation indicates the strength of the acid.

Fluorosulfuric acid (HSO_3F) is one of the strongest acids known. Fluorosulfuric acid has a similar geometry to that of the sulfuric acid molecule (Figure 3.2.5). The highly electronegative fluorine atom causes the oxygen–hydrogen bond in fluorosulfuric acid to be more polarised than the oxygen–hydrogen bond in sulfuric acid. The acidic proton is easily transferred to a base.

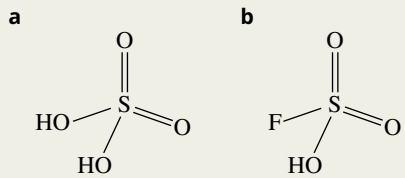


FIGURE 3.2.5 (a) The structure of sulfuric acid and (b) fluorosulfuric acid molecules

Fluorosulfuric acid is classified as a **superacid.** Superacids are defined as acids that have **acidity** greater than the acidity of pure sulfuric acid.

Superacids are produced from combining two strong acids: one a Lewis acid, the other a Brønsted acid. Like the Brønsted–Lowry definition of an acid, 20th-century chemist Gilbert Lewis defined an acid as a substance that can accept and bind two electrons to form a covalent bond.

Superacids such as fluorosulfuric acid and triflic acid (CF_3SO_3H) are about 1000 times stronger than sulfuric acid. The carborane acid ($H(CHB_{11}Cl_{11})$) is 1 million times stronger than sulfuric acid. The strongest known superacid is fluoroantimonic acid (H_2FSbF_6), which is 10^{16} times stronger than 100% sulfuric acid. The position of equilibrium for the dissociation of the proton from carborane acid lies well to the right and readily ionises, releasing the proton. While the carborane acid is considered a strong acid, it is often referred to as 'gentle' as it does not produce corrosive conjugate bases on dissociation, unlike fluorosulfuric acid.

Superacids are used in the production of plastics and high-octane petrol, in coal gasification and in research.

Review

1. Explain why fluorosulfuric acid readily dissociates. Refer to the structure of fluorosulfuric acid shown in Figure 3.2.5b.
2. Carborane acid is often referred to as a 'gentle' acid even though it is so strong. Using the internet, research why it is often used in preference to other superacids. Provide evidence of how it is used in industry.

3.2 Review

SUMMARY

- A concentrated acid or base contains more moles of solute per litre than a dilute acid or base.
- In the context of acids and bases, the terms 'strong' and 'weak' refer to the relative tendency to accept or donate protons.
  - A strong acid donates a proton more readily than a weak acid.
  - A strong base accepts a proton more readily than a weak base.
- The stronger an acid, the weaker its conjugate base. The stronger a base, the weaker its conjugate acid.

KEY QUESTIONS

Retrieval

1 Use balanced equations to show that, in water:
- **a** $HClO_4$ is a strong acid
- **b** HCN is a weak acid
- **c** CH_3NH_2 is a weak base.

Comprehension

2 Identify which of the following is a reaction of a strong acid and which is a reaction of a weak acid. Explain how you came to form this conclusion.
- **A** $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
- **B** $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

3 Construct balanced equations for the three dissociation stages of arsenic acid (H_3AsO_4).

Analysis

4 Perchloric acid is a stronger acid than ethanoic acid. Explain which $1.0\,mol\,L^{-1}$ solution of each acid would be a better conductor of electricity.

5 Determine whether you would expect $H_2PO_4^-$ or HPO_4^{2-} to be a stronger acid.

3.3 Acidity of solutions

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand the pH scale, which is a measure of acidity
- understand the relationship between the concentration of hydrogen and hydroxide ions in different solutions.



IONIC PRODUCT OF WATER

You will recall from Unit 2 that water molecules can react with each other as represented by the equation:

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

The production of the H_3O^+ ion and OH^- ion within this reaction can be seen in Figure 3.3.1.

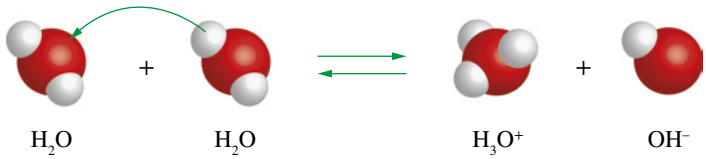


FIGURE 3.3.1 The dissociation of water molecules

Pure water undergoes this **self-ionisation** to a very small extent. In this reaction, water behaves as both a very weak acid and as a very weak base, producing one hydrogen ion (H_3O^+) for every one hydroxide ion (OH^-). Water is displaying amphiprotic properties.

The concentration of hydrogen and hydroxide ions is very low. In pure water at 25°C the H_3O^+ and OH^- concentrations are each $10^{-7}\,mol\,L^{-1}$. For each H_3O^+ ion present in a glass of water, there are 560 million H_2O molecules!

Experimental evidence shows that all aqueous solutions contain both H_3O^+ and OH^- ions, and that the product of their molar concentrations, $[H_3O^+][OH^-]$, is always 1.00×10^{-14} at 25°C. If either $[H_3O^+]$ or $[OH^-]$ in an aqueous solution increases, then the concentration of the other must decrease proportionally.

Remember that $[H_3O^+]$ represents the concentration of hydrogen ions and $[OH^-]$ represents the concentration of hydroxide ions. The expression $[H_3O^+][OH^-]$ is known as **ionic product** (or **ionisation constant**) **of water** and is represented by the symbol K_w:

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\,mol^2\,dm^{-6} \text{ at } 25°C$$

Square brackets [ ] are often used to represent molar concentration.

Acidic and basic solutions

In solutions of acidic substances, H_3O^+ ions are formed by the reaction of the acid with water, as well as from the self-ionisation of water. So the concentration of H_3O^+ ions will be greater than $10^{-7}\,mol\,L^{-1}$ at 25°C. Since the product $[H_3O^+][OH^-]$ remains constant, the concentration of OH^- ions in an **acidic solution** at this temperature must be less than $10^{-7}\,mol\,L^{-1}$.

The opposite is true for **basic solutions**. The concentration of OH^- ions in a basic solution is greater than $10^{-7}\,mol\,L^{-1}$, and that of H_3O^+ ions is less than $10^{-7}\,mol\,L^{-1}$.

In summary, at 25°C:

- pure water and **neutral solutions**: $[H_3O^+] = [OH^-] = 10^{-7}\,mol\,L^{-1}$
- acidic solutions: $[H_3O^+] > 10^{-7}\,mol\,L^{-1}$ and $[OH^-] < 10^{-7}\,mol\,L^{-1}$
- basic solutions: $[H_3O^+] < 10^{-7}\,mol\,L^{-1}$ and $[OH^-] > 10^{-7}\,mol\,L^{-1}$

The higher the concentration of H_3O^+ ions in a solution, the more acidic the solution is.

Calculating the concentration of H_3O^+ in aqueous solutions

The expression for K_w can be used to determine the concentrations of hydrogen and hydroxide ions in solution, knowing that the value of K_w in solutions at 25°C is $1.00 \times 10^{-14}\,mol^2\,dm^{-6}$.

Worked example 3.3.1

CALCULATING THE CONCENTRATION OF HYDROGEN AND HYDROXIDE IONS IN AN AQUEOUS SOLUTION

Calculate the concentration of:
- H_3O^+ ions
- OH^- ions

in a $0.10\,mol\,L^{-1}$ solution of HCl at 25°C.

Thinking	Working
Determine the concentration of the hydrogen (H_3O^+) ions.	HCl is a strong acid, so it will ionise completely in solution. Each molecule of HCl donates one proton to water to form one H_3O^+ ion: $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$ Because HCl is completely ionised in water, $0.10\,mol\,L^{-1}$ of HCl will produce a solution with a concentration of H_3O^+ ions of $0.10\,mol\,L^{-1}$: i.e. $[H_3O^+] = 0.10\,mol\,L^{-1}$
Use the expression for the ionisation constant of water to calculate the concentration of OH^- ions.	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\,mol^2\,dm^{-6}$ $[OH^-] = \frac{1.00 \times 10^{-14}}{[H_3O^+]}$ Since $[H_3O^+] = 0.10\,mol\,L^{-1}$ $[OH^-] = \frac{1.00 \times 10^{-14}}{0.10}$ $= 1.0 \times 10^{-13}\,mol\,L^{-1}$

➤ Try yourself 3.3.1

CALCULATING THE CONCENTRATION OF HYDROGEN AND HYDROXIDE IONS IN AN AQUEOUS SOLUTION

Calculate the concentration of:
- H_3O^+ ions
- OH^- ions

in a $5.6 \times 10^{-6}\,mol\,L^{-1}$ solution of HNO_3 at 25°C.

THE pH SCALE

Definition of pH

The range of H_3O^+ concentrations in solutions is so great that a convenient scale, called the **pH scale**, has been developed to measure acidity. The pH scale was first proposed by the Danish scientist Sören Sörenson in 1909 as a way of expressing levels of **acidity**. The pH of a solution is defined as:

$$pH = -\log_{10}[H_3O^+]$$

Alternatively, this expression can be rearranged to give:

$$[H_3O^+] = 10^{-pH}\,mol\,L^{-1}$$

The pH scale eliminates the need to write cumbersome powers of 10 when we describe hydrogen ion concentration. The use of pH greatly simplifies the measurement and calculation of acidity. Since the scale is based upon the negative logarithm of the hydrogen ion concentration, the pH of a solution *decreases* as the concentration of hydrogen ions *increases*.

pH of acidic and basic solutions

Figure 3.3.2 shows a pH meter, which is used to accurately measure the pH of a solution.

Acidic, basic and neutral solutions can be defined in terms of their pH at 25°C.

- Neutral solutions have a pH equal to 7.0.
- Acidic solutions have a pH less than 7.0.
- Basic solutions have a pH greater than 7.0.

On the pH scale, the most acidic solutions have pH values slightly less than 0.0 and the most basic solutions have values of about 14.0. The pH values of some common substances are provided in Table 3.3.1.



FIGURE 3.3.2 A pH meter is used to measure the acidity of a solution.

TABLE 3.3.1 pH values of some common substances at 25°C

Solution	pH	$[H_3O^+]$ (M)	$[OH^-]$ (M)	$[H_3O^+] \times [OH^-]$
1.0 mol L^{-1} HCl	0.0	1	10^{-14}	10^{-14}
lemon juice	3.0	10^{-3}	10^{-11}	10^{-14}
vinegar	4.0	10^{-4}	10^{-10}	10^{-14}
tomatoes	5.0	10^{-5}	10^{-9}	10^{-14}
rain water	6.0	10^{-6}	10^{-8}	10^{-14}
pure water	7.0	10^{-7}	10^{-7}	10^{-14}
seawater	8.0	10^{-8}	10^{-6}	10^{-14}
soap	9.0	10^{-9}	10^{-5}	10^{-14}
oven cleaner	13.0	10^{-13}	10^{-1}	10^{-14}
1.0 mol L^{-1} NaOH	14.0	10^{-14}	10^{-0}	10^{-14}

A solution with pH 2.0 has 10 times the concentration of hydrogen ions as one of pH 3.0. The solution of pH 2.0 has one-tenth the concentration of hydroxide ions as one of pH 3.0.

The reactions of acids and bases are important in a large variety of everyday applications. The high acidity of gastric juices is essential for protein digestion in the stomach. There is a complex system of pH control in your blood because even small deviations from the normal pH range of 7.35–7.45 for any length of time can lead to serious illness and death.

Calculations involving pH

pH can be calculated using the formula $pH = -\log_{10}[H_3O^+]$. Your scientific calculator has a logarithm function that will simplify pH calculations.

Worked example 3.3.2

CALCULATING THE pH OF AN AQUEOUS SOLUTION FROM $[H_3O^+]$

Calculate the pH of a solution in which the concentration of $[H_3O^+]$ is 0.14 mol L^{-1}. Express your answer to two decimal places.

Thinking	Working
Identify the concentration of $[H_3O^+]$ ions in the solution.	$[H_3O^+] = 0.14$ mol L^{-1}
Substitute the value of $[H_3O^+]$ into: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine the answer.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(0.14)$ $= 0.85$

➤ Try yourself 3.3.2

CALCULATING THE pH OF AN AQUEOUS SOLUTION FROM $[H_3O^+]$

Calculate the pH of a solution in which the concentration of $[H_3O^+]$ is $6 \times 10^{-9}\,mol\,L^{-1}$.

Express your answer to two decimal places.

Worked example 3.3.3

CALCULATING pH IN A SOLUTION OF A BASE

Calculate the pH of a $0.005\,mol\,L^{-1}$ solution of $Ba(OH)_2$ at 25°C.

Thinking	Working
Identify the reaction in which $Ba(OH)_2$ dissociates.	In water, each mole of $Ba(OH)_2$ completely dissociates to release 2 moles of OH^- ions: $Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$
Determine the concentration of $[OH^-]$ ions.	$[OH^-] = 2 \times [Ba(OH)_2]$ $= 2 \times 0.005\,mol\,L^{-1}$ $= 0.01\,mol\,L^{-1}$
Determine the $[H_3O^+]$ in the diluted solution by substituting the $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-]$ $= 1.00 \times 10^{-14}\,mol^2\,dm^{-6}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\,mol^2\,dm^{-6}$ $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.00 \times 10^{-14}}{0.01}$ $= 1 \times 10^{-12}\,mol\,L^{-1}$
Substitute the value of $[H_3O^+]$ into: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine the answer.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(1 \times 10^{-12})$ $= 12.0$

➤ Try yourself 3.3.3

CALCULATING pH IN A SOLUTION OF A BASE

Calculate the pH of a $0.01\,mol\,L^{-1}$ solution of $Ba(OH)_2$ at 25°C.

Worked example 3.3.4

CALCULATING pH IN A SOLUTION WHERE THE SOLUTE CONCENTRATION IS NOT GIVEN

Calculate the pH of a solution at 25°C that contains 1.0 g sodium hydroxide (NaOH) in 100 mL of solution.

Thinking	Working
Determine the number of moles of NaOH.	$n(NaOH) = \frac{m}{M}$ $n(NaOH) = \frac{1.0}{40.00}$ $= 0.025\,mol$
Construct the equation for dissociation of NaOH.	$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$ NaOH is completely dissociated in water.
Determine the number of moles of OH^- based on the dissociation equation.	$n(OH^-) = n(NaOH)$ $= 0.025\,mol$

Use the formula for determining concentration given number of moles and volume: $c = \frac{n}{V}$	$n = 0.025\,\text{mol}$ $V = 0.100\,\text{L}$ $c = \frac{0.025}{0.100}$ $= 0.25\,\text{mol L}^{-1}$
Determine the $[H_3O^+]$ in the diluted solution by substituting the $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-]$ $= 1.00 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}$ $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.00 \times 10^{-14}}{0.25}$ $= 4.0 \times 10^{-14}\,\text{mol L}^{-1}$
Substitute the value of $[H_3O^+]$ into: $\text{pH} = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine the answer.	$\text{pH} = -\log_{10}[H_3O^+]$ $= -\log_{10}[4.0 \times 10^{-14}]$ $= 13.40$

➤ Try yourself 3.3.4

CALCULATING pH IN A SOLUTION WHERE THE SOLUTE CONCENTRATION IS NOT GIVEN

Calculate the pH of a solution at 25°C that contains 0.50 g of potassium hydroxide (KOH) in 500 mL of solution.

Worked example 3.3.5

CALCULATING $[H_3O^+]$ IN A SOLUTION OF A GIVEN pH

Calculate the $[H_3O^+]$ in a solution of pH 5.0 at 25°C.

Thinking	Working
Determine which form of the relationship between pH and $[H_3O^+]$ should be used: $\text{pH} = -\log_{10}[H_3O^+]$ or $[H_3O^+] = 10^{-\text{pH}}$	As you have the pH and are calculating $[H_3O^+]$, use: $[H_3O^+] = 10^{-\text{pH}}$
Substitute the value of pH into the relationship expression and use a calculator to determine the answer.	$[H_3O^+] = 10^{-\text{pH}}$ $= 10^{-5.0}$ $= 1 \times 10^{-5}\,\text{mol L}^{-1}$ (or $0.00001\,\text{mol L}^{-1}$)

➤ Try yourself 3.3.5

CALCULATING $[H_3O^+]$ IN A SOLUTION OF A GIVEN pH

Calculate the $[H_3O^+]$ in a solution of pH 10.4 at 25°C.

Effect of temperature on pH

Earlier, the **ionisation** constant of water was described as:

$$K_w = [H_3O^+]\,[OH^-] = 1.00 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6} \text{ at } 25°C$$

You can use this relationship to calculate either $[H_3O^+]$ or $[OH^-]$ at 25°C in different solutions. But what happens if the temperature is not 25°C?

From experimental data we know that the value of K_w increases as the temperature increases, as shown in Table 3.3.2.

The pH of pure water is only 7.00 at 25°C. At other temperatures, even though the pH of pure water is not equal to 7.00, it can still be described as neutral because the concentrations of H_3O^+ and OH^- ions are equal.

TABLE 3.3.2 The effect of temperature on pH of pure water

Temperature (°C)	K_w	pH
0	1.14×10^{-15}	7.47
5	1.85×10^{-15}	7.37
15	4.51×10^{-15}	7.17
25	1.00×10^{-14}	7.00
35	2.09×10^{-14}	6.83
45	4.01×10^{-14}	6.70
55	7.29×10^{-14}	6.57

Effect of dilution on pH of strong acids and bases

The number of moles of a solute in a solution does not change when a solution is diluted; the volume of the solution increases and the concentration decreases. The change in concentration or volume can be calculated using the formula

$$c_1V_1 = c_2V_2$$

where c_1 and V_1 are the initial concentration and volume, and c_2 and V_2 are the concentration and volume after dilution.

You can calculate the concentration of a dilute acid if you know the:

- volume of the concentrated solution
- concentration (**molarity**) of the concentrated solution
- total volume of water added.

Consider a $0.1\,mol\,L^{-1}$ solution of hydrochloric acid. HCl is a strong acid, so the concentration of H_3O^+ ions in this solution is $0.1\,mol\,L^{-1}$. Since $pH = -\log_{10}[H_3O^+]$, the pH of this solution is 1.0 (see earlier in this module if you need to review this formula).

If this 1.0 mL solution is diluted by a factor of 10 to 10.0 mL by the addition of 9.0 mL of water, the concentration of H_3O^+ ions decreases to $0.01\,mol\,L^{-1}$ and the pH increases to 2.0. A further dilution by a factor of 10 to 100 mL will increase the pH to 3.0. However, note that when acids are repeatedly diluted, the pH cannot increase above 7.0.

Similarly, the progressive dilution of a 0.10 mL NaOH solution will cause the pH to decrease until it reaches very close to 7.0.

You will now look at how to calculate the pH of solutions of strong acids and bases after dilution. (A discussion of the effect of dilution on the pH of solutions of weak acids and bases is complex and beyond the scope of this course.)

Worked example 3.3.6

CALCULATING THE pH OF A DILUTED ACID

Calculate the pH of a solution after 5.0 mL of $0.010\,mol\,L^{-1}$ HNO_3 is diluted to 100.0 mL.

Thinking	Working
Identify given values for concentrations and volumes before and after dilution.	$c_1 = 0.010\,mol\,L^{-1}$ $V_1 = 5.0\,mL$ $V_2 = 100.0\,mL$ $c_2 = ?$

Calculate c_2, which is the concentration of H_3O^+ after dilution, by transposing the formula: $c_1V_1 = c_2V_2$	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= \frac{0.010 \times 5.0}{100.0}$ $= 0.00050\ \text{mol L}^{-1}$
Calculate pH using: $\text{pH} = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine pH.	$\text{pH} = -\log_{10}[H_3O^+]$ $= -\log_{10}(0.00050)$ $= 3.30$

➤ Try yourself 3.3.6

CALCULATING THE pH OF A DILUTED ACID

Calculate the pH of a solution after 10.0 mL of 0.1 mol L^{-1} hydrochloric acid (HCl) is diluted to 30.0 mL.

Calculation of the pH of a base after dilution

The following steps and flow chart shown in Figure 3.3.3 show the sequence used to calculate the pH of a base after it has been diluted. Remember that pH is a measure of the hydrogen ion concentration.

1 Calculate $[OH^-]$ in the diluted solution.
2 Calculate $[H_3O^+]$ using the expression for the ionic product of water:
$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$$
3 Calculate the pH of the solution using $\text{pH} = -\log_{10}[H_3O^+]$, as shown in Figure 3.3.3.

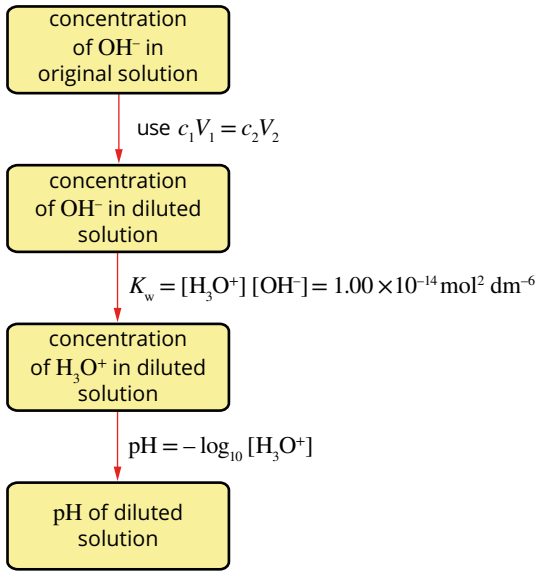


FIGURE 3.3.3 Calculating the pH of a diluted solution of a base

Worked example 3.3.7

CALCULATING THE pH OF A DILUTED BASE

Calculate the pH of a solution after 10.0 mL of 0.1 mol L^{-1} sodium hydroxide (NaOH) is diluted to 100.0 mL.

Thinking	Working
Identify given values for concentrations and volumes before and after dilution.	$c_1 = 0.1\ \text{mol L}^{-1}$ $V_1 = 10.0\ \text{mL}$ $V_2 = 100.0\ \text{mL}$ $c_2 = ?$
Calculate c_2, which is the concentration of $[OH^-]$ after dilution, by transposing the formula: $c_1V_1 = c_2V_2$	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= \frac{0.1 \times 10.0}{100.0}$ $= 0.01\ \text{mol L}^{-1}$
Determine $[H_3O^+]$ in the diluted solution by substituting $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-]$ $= 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$	$K_w = [H_3O^+][OH^-]$ $= 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$ $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.00 \times 10^{-14}}{0.01}$ $= 1 \times 10^{-12}\ \text{mol L}^{-1}$
Calculate pH using: $\text{pH} = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine pH.	$\text{pH} = -\log_{10}[H_3O^+]$ $= -\log_{10}(1 \times 10^{-12})$ $= 12.0$

➤ Try yourself 3.3.7

CALCULATING THE pH OF A DILUTED BASE

Calculate the pH of a solution after 15.0 mL of 0.02 mol L^{-1} KOH is diluted to 60.0 mL.

3.3 Review

SUMMARY

- Water self-ionises according to the equation:
  $$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
- The ionic product for water is:
  $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\,mol^2\,dm^{-6}$ at 25°C
- The concentration of $[H_3O^+]$ is measured using the pH scale:
  $$pH = -\log_{10}[H_3O^+]$$
- At 25°C the pH of a neutral solution is 7.0. The pH of an acidic solution is less than 7.0 and the pH of a basic solution is greater than 7.0.
- The number of moles of acid or base in solution do not change during a dilution. The volume of the solution increases and as a result its concentration decreases.
- Solutions of acids and bases of a required concentration can be prepared by diluting more concentrated solutions using the formula
  $$c_1V_1 = c_2V_2$$
  where c_1 and V_1 are the initial concentration and volume, and c_2 and V_2 are the final concentration and volume after dilution.
- The pH increases when a solution of an acid is diluted.
- The pH of a diluted acid can be determined by calculating the concentration of hydrogen ions in the diluted solution.
- The pH decreases when a solution of a base is diluted. The pH of a diluted base can be determined by:
  - calculating the concentration of hydroxide ions in the diluted base, and
  - using the ionic product of water to calculate the concentration of hydrogen ions in the diluted base.

KEY QUESTIONS

Retrieval

1 Human blood has a pH of 7.4. Identify if blood is acidic, basic or neutral.

Comprehension

2 The pH of a cola drink is 3.0 and the pH of black coffee is 5.0. Determine how many more times acidic the cola is than the black coffee.

Analysis

3 Determine the pH of a 200 mL solution that contains 0.365 g of HCl.

4 Calculate $[OH^-]$ at 25°C in an aqueous solution in which $[H_3O^+] = 0.001$ mol L^{-1}.

5 Calculate $[H_3O^+]$ at 25°C in an aqueous solution in which $[OH^-] = 1.0 \times 10^{-5}$ mol L^{-1}.

6 The pH of water in a lake is 6.0. Calculate $[H_3O^+]$ in the lake.

3.4 Buffers

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand that solutions known as buffers resist a change in pH when a small amount of acid or base is added to the solution
- understand how Le Châtelier's principle can be applied to predict how buffer solutions respond to the changes in concentration of acid or base to the solution.



THE CONJUGATE NATURE OF BUFFERS

Buffer solutions are conjugate in nature and resist a change in pH when a small amount of an acid or base is added. Acidic buffer solutions can be made in two ways:

- a weak acid and half the amount of base
- weak acid and **salt** of the acid and a strong base. That is, a weak acid with a salt that contains its conjugate base.

The weak acid is only partially dissociated in solution but the salt fully dissociates. Consider the following example of ethanoic acid mixed with sodium hydroxide (base):

$$2CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l) + CH_3COOH(aq)$$

ethanoic acid limited base conjugate base/salt excess acid

The salt formed, CH_3COONa, fully dissociates into Na^+ ions and CH_3COO^- ions. The ethanoic acid, being a weak acid, only partially dissociates into CH_3COO^- and H^+ ions in the following reaction:

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

Combined, this means the concentration of CH_3COO^- ions is high.

If an acidic solution is added to the ethanoic acid equilibrium reaction above, the H^+ ions from the acid will combine with the ethanoate ions to form undissociated ethanoic acid and the concentration of H^+ ions will remain the same. As a result, the pH is unchanged.

Hydroxide ions from an alkaline solution will react with the undissociated ethanoic acid and form water. Again, the pH will remain unchanged.

A general equation for buffer solution reactions is:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

If a strong acid is added to a buffer, the weak base (A^-) will react with the H^+ from the strong acid to form the weak acid HA, so the pH changes only slightly.

You will remember from Chapter 2 that Le Châtelier's principle states that a system at equilibrium will act to partially oppose the effects of a change to the equilibrium position. With weak acids (HA), the equilibrium position is already shifted to the left given their partial dissociation. Therefore, adding additional A^- ions will only further shift this position to the left. Because of this, the pH will not change very much, but it will fall slightly.

Basic buffer solutions can be made in two ways:

- a weak base and half the amount of acid
- weak base and salt of the base and a strong acid. That is, a weak base with a salt that contains its conjugate acid.

An example of such a buffer solution is ammonia:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Strong acids will fully ionise in water and donate all their H^+ ions to the base present; however, weak acids do not fully ionise in water. A better way to describe their behavious is to say that weak acids partially dissociate in solution.

Scientists also say that bases will dissociate into their components rather than ionise.

Buffer solutions are those that resist a change in pH when a small amount of acid or base is added to them.

In this buffer, if an acid is added, the H^+ ions react with the OH^- ions to form water and the pH changes only slightly as the equilibrium position shifts to the right as more ammonia dissociates to replace the OH^- ions. If more hydroxide ions are added in the case of an alkaline solution, they will react with the ammonium ions to form more undissociated ammonia and water. The pH change will be only slight in both cases.

In the next module you will look at **dissociation constants** involving acid–base equilibria (similar to equilibrium constants examined in Chapter 2) and how these can indicate the pH change of a buffer in different circumstances.

3.4 Review

SUMMARY

- Buffer solutions are those that resist a change in pH when a small amount of acid or base is added to them.
- An acidic buffer solution can be formed by reacting an amount of a weak acid with the salt of the acid and a strong base.
- An alkaline buffer solution can be formed by reacting an amount of a weak base with the salt of the base and a strong acid.

KEY QUESTIONS

Retrieval

1 Define 'buffer'.

Comprehension

2 Describe the relationship between ammonia and its conjugate acid (NH_4^+) when a small amount of sodium hydroxide (NaOH) is added to the solution.

3 Explain why hydrochloric acid is not a suitable acid for use in preparing a buffer solution.

Analysis

4 Determine what will happen to the pH of a sodium ethanoate buffer solution if concentrated HCl solution is continually added to it.

3.5 Dissociation constants

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- apply your knowledge of dissociation of acids and bases in solution to determine the strength of acids and bases at equilibrium in aqueous solution
- apply your knowledge of dissociation of acids and bases in solution to determine the expression for the dissociation constant for acid–base equilibria
- analyse experimental evidence to explain the strengths of acids and bases
- perform calculations involving acid–base dissociation constants.



ACID DISSOCIATION CONSTANTS

You will recall from Module 3.2 that a strong acid is one that fully dissociates in water forming hydrogen ions and its conjugate base. A weak acid only partially dissociates and can be represented by HA in the following equilibrium expression:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

As you saw in Chapter 2, equilibrium reactions do not go to completion, and some of the products formed can react to form reactants. The equilibrium constant is a measure of the relative amounts of products and reactants at a given temperature. It can give an indication of the extent of a reaction.

In acid–base equilibria involving weak acids and bases, an acid dissociation constant, K_a, can also be used to indicate the extent of dissociation of the acid or base at a given temperature. It is written in a similar way to the equilibrium constant. For the above general equation, the K_a will be given by:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

You will remember that equilibrium constants can be written for reactants and products in the same state. In this case, weak acids and their dissociated products are all in the aqueous state. The acid dissociation constant therefore follows this same general rule.

In Chapter 2 you learnt that the size of the equilibrium constant gives an indication of the extent of the reaction. In the same way, the acid dissociation constant indicates the extent of dissociation of the acid to its conjugate base.

If the value of K_a is large, the concentration of the products of the dissociation reaction are high and therefore favoured. That is, the acid dissociates readily and is therefore referred to as a strong acid.

If the value of K_a is small, the acid does not readily dissociate making it a weak acid.

The value of K_a for ethanoic acid is 1.75×10^{-5} at 25°C. This relatively small value means that in ethanoic acid solutions, the position of equilibrium favours the reactants and there are relatively low concentrations of products. Ethanoic acid is classified as a weak acid because at equilibrium less than 1% of the CH_3COOH molecules in a $1.0\,mol\,L^{-1}$ solution are dissociated.

In contrast, hydrochloric acid, HCl(aq), has an acidity constant of 10^7 at 25°C. This means that the degree of dissociation for hydrochloric acid in water is almost 100%:

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

Almost all of the HCl molecules have been converted to H^+ and Cl^-. Hydrochloric acid is therefore classified as a strong acid. Therefore, equilibrium arrows are not used.

The acidity constant is used as a measure of acid strength. The acidity constants of several common acids are shown in Table 3.5.1. You can see, for example, that while phosphoric acid is stronger than citric acid, it is weaker than nitric acid.

TABLE 3.5.1 K_a values of some common acids at 25°C

Name	Formula	K_a
hydrochloric acid	HCl	10^7
sulfuric acid*	H_2SO_4	10^3
nitric acid	HNO_3	2.4×10^1
phosphoric acid*	H_3PO_4	7.1×10^{-3}
citric acid*	$H_3C_6H_5O_7$	7.2×10^{-4}
ethanoic acid	CH_3COOH	1.75×10^{-5}

* Sulfuric acid, citric acid and phosphoric acid are polyprotic acids. The value of K_a is for the dissociation of the first proton.

K_a values for polyprotic acids

Polyprotic acids donate their protons in stages. For example, in the case of phosphoric acid, a triprotic acid, K_a decreases from the first dissociation reaction through to the third dissociation reaction.

Stage 1: $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$ $\quad K_a = 7.1 \times 10^{-3}$

Stage 2: $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$ $\quad K_a = 6.3 \times 10^{-8}$

Stage 3: $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$ $\quad K_a = 4.2 \times 10^{-13}$

The first dissociation reaction occurs to a greater extent than the second. The second dissociation reaction occurs to a greater extent than the third.

The value of the dissociation constant, K_a, gives an indication of the strength of an acid.

In general, for polyprotic acids, it becomes increasingly harder for positively charged protons to be lost as the acid species becomes increasingly negative and K_a values decrease for each dissociation stage.

Similarly, the strength of a base can be determined by the dissociation constant, K_b. The dissociation constant for the reaction involving the weak acid ammonia (NH_3) is shown below:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

CALCULATIONS USING DISSOCIATION CONSTANTS

As you saw with equilibrium constants in Chapter 2, the equilibrium constant can be calculated from the concentration of reactants and products in a reaction at a particular temperature. Similar calculations can be used to determine the acid dissociation constant of the products of a dissociation reaction involving weak acids and bases. Conversely, concentration of the acid and its conjugate base at equilibrium can also be determined if given the value of the K_a. Knowing these values also allows you to determine the pH of the final solution. The following worked examples show you how.

Worked example 3.5.1

CALCULATING CONCENTRATIONS USING DISSOCIATION CONSTANTS

The concentration of CH_3COOH at 25°C is 1.00 mol L^{-1}. The value for the equilibrium constant for this reaction is 1.75×10^{-5}. Calculate the concentration of the ethanoate ion at this temperature.

Thinking	Working
Construct an equation for the dissociation reaction.	$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$
Formulate an expression for the dissociation constant.	$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$
Draw up an ICE table to determine the initial and final concentrations of the species present. Assume that the concentration of hydrogen ions will be x mol L^{-1} at equilibrium.	See table below
Substitute the values in the ICE table into the dissociation constant expression.	$1.75 \times 10^{-5} = \frac{x \times x}{1.00 - x}$
Rearrange the equation to solve for x. Since x is very small, $1.00 - x$ approximates to 1.00, given the dissociation of this weak acid is low.	$1.75 \times 10^{-5} = \frac{x^2}{1.00}$ $1.75 \times 10^{-5} \times 1.00 = x^2$ $x = \sqrt{1.75 \times 10^{-5}}$ $= 0.00418$ mol L^{-1}

Species	CH_3COOH	H^+	CH_3COO^-
Initial	1.00	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$1.00 - x$	$+x$	$+x$

➤ Try yourself 3.5.1

CALCULATING CONCENTRATIONS USING DISSOCIATION CONSTANTS

The concentration of CH_3COOH at 25°C is $2.00\,mol\,L^{-1}$. The value for the equilibrium constant for this reaction is 1.75×10^{-5}. Calculate the concentration of the ethanoate ion at this temperature.

Worked example 3.5.2

CALCULATING THE pH OF A BASE USING THE DISSOCIATION CONSTANT

Calculate the pH of a $1.00\,mol\,L^{-1}$ solution of ammonia (NH_3) if the K_b for its dissociation at 25°C is 1.80×10^{-5}.

Thinking	Working
Formulate an expression for the dissociation constant.	$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$
Substitute in the values for concentration for each of the reactants and products. As ammonia is a weak base we can assume that the equilibrium concentration of ammonia will be the same as its initial concentration.	$1.80 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{1.00}$
As the concentrations of NH_4^+ and OH^- will be equal at equilibrium, the equation can be simplified.	$1.80 \times 10^{-5} = \frac{[OH^-]^2}{1.00}$
Rearrange and solve for $[OH^-]$.	$1.80 \times 10^{-5} = \frac{[x]^2}{1.00}$ $[x]^2 = 1.80 \times 10^{-5} \times 1.00$ $[x]^2 = 1.80 \times 10^{-5}$ $[x] = \sqrt{1.80 \times 10^{-5}}$ $= 0.00424\,mol\,L^{-1}$
Determine the $[H_3O^+]$ in the diluted solution by substituting the $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-]$ $= 1.00 \times 10^{-14}\,mol^2\,dm^{-6}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\,mol^2\,dm^{-6}$ $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.00 \times 10^{-14}}{0.00424}$ $= 2.36 \times 10^{-12}\,mol\,L^{-1}$
Use the formula $pH = -\log_{10}[H_3O^+]$ to calculate pH.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10} 2.36 \times 10^{-12}$ $= 11.6$

➤ Try yourself 3.5.2

CALCULATING THE pH OF A BASE USING THE DISSOCIATION CONSTANT

Calculate the pH of a $0.500\,mol\,L^{-1}$ solution of ammonia (NH_3) if the K_b for its dissociation at 25°C is 1.80×10^{-5}.





3.5 Review

SUMMARY

- The equilibrium expression for the dissociation of a monoprotic acid in water:

  $$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

  is written as $K_a = \frac{[H^+][A^-]}{[HA]}$
- K_a is known as the acidity constant and is a measure of the strength of an acid.
- K_b is known as the dissociation constant for a base and is a measure of the strength of a base.

KEY QUESTIONS

Retrieval

1 Formulate an expression for the dissociation constant for ethanoic acid (CH_3COOH).

Comprehension

2 Determine the strongest acid using the following information.

$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$
$K_a = 7.1 \times 10^{-3}$

$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$
$K_a = 6.3 \times 10^{-8}$

$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$
$K_a = 4.2 \times 10^{-13}$

Analysis

3 Calculate the pH of the base $C_6H_5NH_2$ of 0.500 mol L^{-1}, which has a K_b of 3.80×10^{-10}.

4 The hydrogen sulfate ion and the hydrogen carbonate ion are both amphiprotic, as shown by the following equations. The equilibrium constants for the reaction of these ions with water are also provided.

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$
$K_a = 1.0 \times 10^{-2}$

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_2SO_4(aq) + OH^-(aq)$
$K_b = 1.0 \times 10^{-12}$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$
$K_a = 4.7 \times 10^{-11}$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$
$K_b = 2.1 \times 10^{-4}$

Using the K_a of these solutions, determine which of the above is the strongest acid.

3.6 Indicators

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- explain the action of acid–base indicators
- understand that the pH range of an indicator is related to its pK_a value
- determine the appropriate indicator for a titration given the equivalence point for the reaction.



Indicators have a different colour in acidic and basic solutions and are used to distinguish between acids and bases. Indicators are also used to determine the pH of a solution. Indicators exist in two forms: as a weak acid and its weak conjugate base.

COMMON INDICATORS

One of the characteristic properties of acids and bases is their ability to change the colour of certain plant extracts. Litmus is a purple dye obtained from lichen. In the presence of acids, litmus turns red. The colouring of rose petals, blackberries and red cabbage is also altered by acids and bases. Such plant extracts are called **indicators**. Common indicators and their pH ranges can be seen in Figure 3.6.1. Today most indicators used in laboratories and industry, such as bromothymol blue, methyl orange and phenolphthalein, are synthetic.

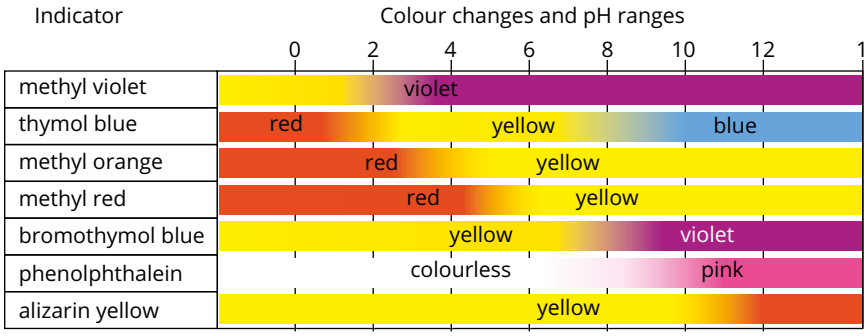


FIGURE 3.6.1 Common indicators and their pH ranges

Indicators themselves are weak acids or weak bases. The conjugate acid form of the indicator is one colour and the conjugate base form is another. The indicators that undergo a single colour change are also used for many analyses.

Figure 3.6.2 shows the variation in colour that can be achieved using red cabbage as an indicator. As you can see, the colour of juice extracted from the leaves of red cabbage is dependent upon the pH of the solution.



FIGURE 3.6.2 The colour of extract from red cabbage in solutions (from left to right) of pH 1, pH 3, pH 5, pH 8 and pH 10

pH RANGE OF AN INDICATOR

Indicators are large organic molecules whose colour changes in response to changes in the pH of the solution they are dissolved in. They are either weak acids or weak bases. In solution, the acid form of the indicator is in equilibrium with its conjugate base, as shown in the following equation:

$$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$

The position of equilibrium changes depending on the pH. The colour of the acid form of an indicator, HIn, and the colour of its conjugate base, In^-, are different. The acid or base colour of an indicator is visible at low indicator concentrations.

The dissociation constant for the acid–base indicator dissociation is:

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

The indicator changes colour when the concentration of the acid, HIn, is equal to the concentration of its conjugate base, In^-. That is, the colour change will occur when $[H^+] = K_a$. This means that the colour change occurs when the pK_a is equal to the pH.

According to the Brønsted–Lowry model of acids and bases, an acid and its conjugate base differ by the presence of a proton (H^+).

For example, methyl orange is an indicator with a pK_a value of 3.7. It changes colour over a pH range of 3.2 to 4.4. Methyl orange and other common indicators will be discussed in the following sections.

Universal indicator

Universal indicator is widely used to estimate the pH of a solution. It is a mixture of several indicators and changes through a range of colours from red through yellow, green and blue, to violet. This can be seen in Figure 3.6.3. If a more accurate measurement of pH is needed, you can use a pH meter instead of universal indicator.



FIGURE 3.6.3 Universal indicator pH scale. When universal indicator is added to a solution, it changes colour depending on the solution's pH. The tubes contain solutions of pH 1 to 12 from right to left. The light green tube (centre) is neutral, pH 7.

Bromothymol blue

Bromothymol blue is a widely used indicator. The indicator is yellow in acidic solutions and blue in basic solutions. In a neutral solution of pH 7.0, the colour of the indicator is green, midway between yellow and blue.

A chart showing the variation in colour of bromothymol blue from pH 0 to pH 14 is shown in Figure 3.6.4.

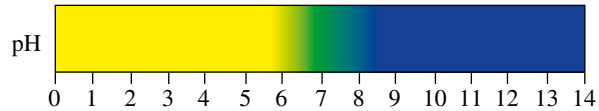


FIGURE 3.6.4 Bromothymol blue is yellow in acidic solutions and blue in basic solutions. The indicator changes colour over the pH range 6.0 to 7.6.

The equilibrium principles studied in Chapter 2 also apply to indicators. Le Châtelier's principle can be used to explain why indicators have different colours in acidic and basic solutions.

The equation for the dissociation of bromothymol blue in water is shown here. Bromothymol blue is a complex organic compound. For the sake of simplicity, the acid form of bromothymol blue can be represented as HBB and the base form as BB^-.

$$\underset{\text{yellow}}{HBB(aq)} + H_2O(l) \rightleftharpoons \underset{\text{blue}}{BB^-(aq)} + H_3O^+(aq)$$

The indicator colour you see depends upon the relative concentrations of HBB and BB^-.

When a few drops of bromothymol blue indicator are added to HCl solution, the additional H_3O^+ ions from HCl shift the indicator equilibrium system to the left:

$$HBB(aq) + H_2O(l) \rightleftharpoons BB^-(aq) + H_3O^+(aq)$$

The concentration of HBB molecules is now much greater than the concentration of BB^- ions and the solution has a yellow colour.

When the indicator is added to a solution of a base, the OH^- ions react with the HBB:

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

The concentration of BB^- ions is now much greater than the concentration of HBB molecules and the solution is blue in colour, as shown in Figure 3.6.5.

At a pH of 7.0 the concentration of HBB molecules and the concentration of BB^- ions are equal. This is referred to as the transition point of bromothymol blue. At this point the solution appears green, a mixture of blue and yellow.



FIGURE 3.6.5 Bromothymol blue is yellow in acidic solutions (left), blue in basic solutions (right) and green in neutral solutions (centre).

Methyl orange

Methyl orange is a synthetic indicator often used in the analysis of weak bases. It is also used as a textile dye.

Methyl orange is red in acidic solutions and yellow in basic solutions. The indicator changes colour between pH 3.1 and pH 4.4. Between these pH values the indicator has an orange colour.

A colour chart for methyl orange indicator is shown in Figure 3.6.6.

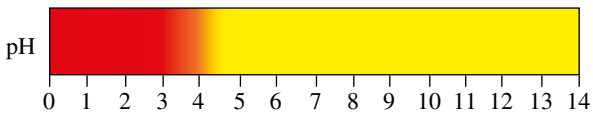
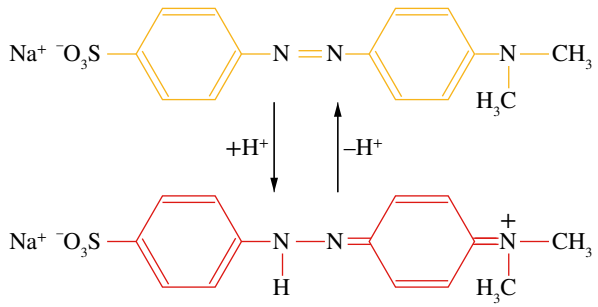


FIGURE 3.6.6 Methyl orange is red in acidic solutions and yellow in basic solutions. The indicator changes colour over the pH range 3.1 to 4.4.

Methyl orange is a weak acid. The acidic and basic forms of the indicator are in equilibrium in solution. Their structures are shown in Figure 3.6.7

yellow form of methyl orange at pH values greater than about 4.5



red form of methyl orange at pH values less than about 3.0

FIGURE 3.6.7 The structure of methyl orange is dependent upon the pH of the solution. The red form of methyl orange has a different structure than the yellow form.

Phenolphthalein

Phenolphthalein is a synthetic indicator used in the analysis of weak acids. In the past it was also used as the active ingredient in some laxatives.

In acidic solutions phenolphthalein is colourless, whereas in basic solutions it has a pink to magenta colour. Phenolphthalein changes colour over the pH range 8.3 to 10.0.

Le Châtelier's principle states that if an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of the change. Therefore, in reactions with weak acids and their conjugate bases, the addition of the base will cause the system to move the equilibrium position towards the reactants. This causes the colour of the indicator to appear as it would in acidic solution.

A colour chart for phenolphthalein indicator is shown in Figure 3.6.8.

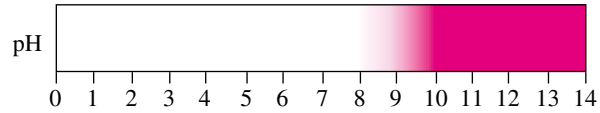


FIGURE 3.6.8 Phenolphthalein is colourless in solutions when the pH is below 8.3 and pink when the pH is greater than 10. The indicator changes colour over the pH range 8.3 to 10.0.

EQUIVALENCE POINT

As you have seen, the colour of an indicator in acidic solution is distinctly different to its appearance in basic solution. Indicators do not change colour at exactly pH 7.0. Bromothymol blue changes colour between pH 6.0 and pH 7.6. Methyl orange changes colour between pH 3.1 and pH 4.4. Phenolphthalein changes colour over a pH range of 8.3 to 10.0. The range of pH values over which an indicator changes colour is known as the **indicator range**.

The acid and base colours and pH ranges of some common laboratory indicators were shown in Figure 3.6.1 on page 77. Table 3.6.1 summarises common indicators and their pH ranges.

TABLE 3.6.1 Common indicators and their pK_as and pH ranges

Indicator	Colour in acidic solution	Colour in basic solution	pK_a	pH range
methyl violet	yellow	violet	0.8	0.0–1.6
methyl orange	red	yellow	3.7	3.1–4.4
bromophenol blue	yellow	violet	4.2	3.0–4.6
bromocresol green	yellow	blue	4.7	3.8–5.4
methyl red	red	yellow	5.1	4.4–6.2
bromothymol blue	yellow	blue	7.0	6.0–7.6
phenolphthalein	colourless	pink	9.6	8.3–10.0
alizarin yellow	yellow	red	11.0	10.0–12.0
phenol red	yellow	red	7.9	6.8–8.4

USING INDICATORS

A neutralisation reaction occurs when an acid reacts with a base to form a salt and water.

The reactions of acids are discussed in Chapter 4. Indicators are particularly useful in determining the **equivalence point** of a **neutralisation reaction** between an acid and a base. The equivalence point is the moment during a neutralisation reaction when the amount of acid and base are in stoichiometric ratios represented by the reaction equation.

For example, hydrochloric acid and sodium hydroxide react according to the following equation:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

The equivalence point during this reaction is when the number of moles of HCl is equal to the number of moles of NaOH in the 1:1 ratio given by the equation.

Indicators are commonly used in **volumetric analysis** or **titrations** to help visualise the equivalence point of a reaction. Volumetric analysis is a quantitative technique in which volumes of solutions of known concentrations are added to volumes of concentrations of unknown solution. This will be discussed in more detail in Chapter 4. The **end point** is when the indicator changes colour. In the reaction the end point corresponds closely with the equivalence point.

The colour of the indicator will be the intermediate colour between how it is found in acidic solution and alkaline solution colour. The change in pH when a strong acid, such as HCl, is titrated against a strong base, such as NaOH, can be represented on a graph called a **titration curve** or **pH curve**. The equivalence point occurs when the gradient of the pH curve is steepest. An example of a pH curve is shown in Figure 3.6.9.

Near the equivalence point the addition of a very small volume of HCl produces a large change in pH. In this titration the pH changes from 10.0 to 4.0 with just one drop of acid! By using an indicator that changes colour in this pH range, such as bromothymol blue which changes between 6.0 and 7.6, one drop will cause a colour change. This is referred to as a sharp end point. Therefore, knowing the pH range of an indicator is an important tool to ensuring a sharp end point. Other indicators, including phenolphthalein (pH range 8.3 to 10.0), could also be used for this titration because they would also produce a sharp end point.

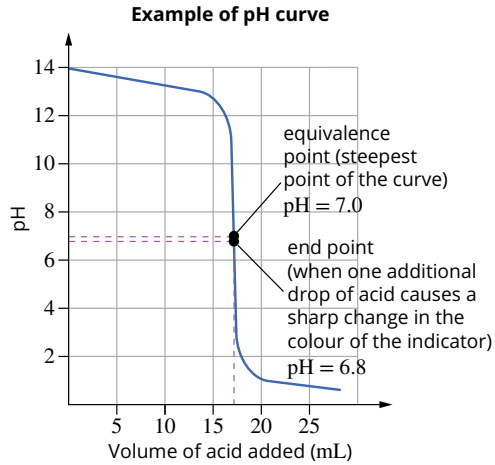


FIGURE 3.6.9 Titration curve for a strong acid being added to a strong base

Determining the transition point and pH range of an indicator

Remember that indicators are weak Brønsted–Lowry acids. The acid–base equilibrium can be represented by the general equation:

$$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$

HIn represents the acidic form of the indicator and In^- the basic form.

The expression for the **acidity constant** for this general reaction is:

$$K_a = \frac{[In^-][H_3O^+]}{[HIn]}$$

The pH at which the indicator changes colour depends upon the value of the indicator's acidity constant, K_a. At the midpoint of the indicator colour change, the **transition point**, the concentrations of the acidic and basic forms of the indicator are equal, i.e. [HIn] = [In^-].

At the transition point, the equilibrium expression simplifies to:

$$[H_3O^+] = K_a$$

The pH at the transition point can be calculated using $pH = -\log_{10}[H_3O^+]$. As a rule of thumb, the indicator range is one pH unit either side of the pH at the transition point.

For example, phenol red indicator (Figure 3.6.10) has a K_a of 10^{-8}. The concentration of hydrogen ions at the transition point is 10^{-8} mol L^{-1} and the pH is 8. The pH range of this indicator is approximately 8 ± 1, i.e. between pH 7.0 and pH 9.0.



FIGURE 3.6.10 Phenol red indicator at pH 5, pH 8 and pH 11

3.6 Review

SUMMARY

- The colour of an indicator in acidic solution is distinctly different to its appearance in basic solution.
- Indicators are solutions of a weak acid or base in solution with its conjugate base or conjugate acid.
- The pH range of an indicator is related to the dissociation constant of the acid–base indicator dissociation reaction.
- An indicator changes colour when the pH is equal to the value of the pK_a for the indicator.
- The point in a titration at which the reactants have reacted in their correct mole ratios is called the equivalence point.
- The end point is the point during the titration at which the indicator changes colour.
- Indicators used in titrations must have a sharp end point.

KEY QUESTIONS

Retrieval

1 Construct the general equation for the equilibrium that exists between a weak acidic indicator and its conjugate base.

2 Refer to Table 3.6.1 on page 80 to determine what colour the following indicators will produce in pure water.

a methyl orange

b phenolphthalein

c bromothymol blue

Comprehension

3 Explain why universal indicator appears coloured across a range of pH values.

4 Bromothymol blue is added to a solution of pH 5.

a Determine the colour of the solution.

b Explain what this indicates about the position of the equilibrium of the indicator reaction.

5 Determine the pH at which phenolphthalein would provide a sharp end point during a titration and what colour you would expect to see at the end point of a titration.

6 Use Le Châtelier's principle to explain why indicators appear coloured differently in acidic or basic solutions.

Analysis

7 Congo red is an acid base indicator. The acid colour of the indicator is blue and the base colour is red. The acid form of the Congo red molecule can be written as HCgr.

At pH 4 (the transition point) the concentration of HCgr is the same as the concentration of its conjugate base, Cgr^-.

a Represent the dissociation of Congo red in aqueous solution by completing the following equation.

$HCgr(aq) + H_2O(l) \rightleftharpoons$ ____ + _____

b Determine the colour of the solution at the following pH values.

i pH 4

ii neutral solution

iii pH 2

iv pH 12

Chapter review

03

KEY TERMS

acid
acid–base reaction
acidic proton
acidic solution
acidity
acidity constant
amphiprotic
base
basic solution
Brønsted–Lowry model
buffer
concentrated solution
concentration
conjugate acid
conjugate acid–base pair
conjugate base
dissociate
dissociation
dissociation constant
end point
equivalence point
hydrogen ion
hydronium ion
hydroxide ion
indicator
indicator range
ionic product of water
ionisation
ionisation constant of water
ionise
molarity
monoprotic acid
neutral solution
neutralisation reaction
pH scale
pH curve
polyprotic acid
salt
self-ionisation
solute
strong acid
strong base
superacid
titration
titration curve
transition point
triprotic acid
universal indicator
volumetric analysis
weak acid
weak base

KEY QUESTIONS

Retrieval

1 Select the reaction representing the reaction of a strong acid with water.
- **A** $LiOH(aq) \rightarrow Li^+(aq) + OH^-(aq)$
- **B** $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
- **C** $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$
- **D** $NH_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_4^-(aq)$

2 A solution is yellow in both bromothymol blue and methyl orange. Select which one of the following is the most accurate approximation of the pH of this solution.
- **A** between 3.1 and 6.0
- **B** between 3.1 and 7.6
- **C** between 4.4 and 7.6
- **D** between 4.4 and 6.0

3 The acid form of alizarin yellow is yellow, whereas its base form is red. At pH 11.0 the concentrations of the indicator and its conjugate base are equal. Select which one of the following statements about alizarin yellow is correct.
- **A** Alizarin yellow changes colour at exactly pH 11.0..
- **B** A solution of alizarin yellow at pH 11.0 is neutral.
- **C** The indicator can be used to distinguish between a solution of pH 10.0 and a solution of pH 12.0.

4 Identify what the $[H_3O^+]$ in a solution is at 25°C with an $[OH^-]$ equal to $2.84 \times 10^{-2}\,mol\,L^{-1}$.
- **A** $3.98\,mol\,L^{-1}$
- **B** $10.5\,mol\,L^{-1}$
- **C** $2.84 \times 10^{12}\,mol\,L^{-1}$
- **D** $3.52 \times 10^{-13}\,mol\,L^{-1}$

5 Identify what the $[OH^-]$ in a solution is at 25°C with a $[H_3O^+]$ equal to $5.70 \times 10^{-9}\,mol\,L^{-1}$.
- **A** $8.3\,mol\,L^{-1}$
- **B** $2.46\,mol\,L^{-1}$
- **C** $5.70 \times 10^{6}\,mol\,L^{-1}$
- **D** $1.75 \times 10^{-6}\,mol\,L^{-1}$

6 The acid form of an indicator is blue and the base form is red. It is purple when there are equal amounts of acid and conjugate base. The acid–base equation for the indicator is:

$$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$

Drops of a purple solution of the indicator are added to $1.0\,mol\,L^{-1}$ NaOH solution. Select which one of the following correctly identifies the direction of the equilibrium shift and the colour of the resulting solution.
- **A** left, red
- **B** left, blue
- **C** right, red
- **D** right, blue

7 Identify the reactant that acts as an acid in each of the following reactions.
- **a** $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
- **b** $NH_4^+(aq) + H_2O(l) \rightarrow NH_3(aq) + H_3O^+(aq)$
- **c** $HCO_3^-(aq) + OH^-(aq) \rightarrow H_2O(l) + CO_3^{2-}(aq)$
- **d** $SO_4^{2-}(aq) + H_3O^+(aq) \rightarrow HSO_4^-(aq) + H_2O(l)$
- **e** $CO_3^{2-}(aq) + CH_3COOH(aq) \rightarrow HCO_3^-(aq) + CH_3COO^-(aq)$

8 Referring to Figure 3.6.1 on page 77, identify at what pH range would you expect the following to happen.
- **a** methyl violet to appear yellow
- **b** phenolphthalein to appear pink
- **c** methyl red to transition from red to yellow

9 Show the formula for the conjugate of:
- **a** the acid HCl
- **b** the base OH^-
- **c** the base O^{2-}
- **d** HSO_4^- when it acts as an acid.

10 Identify which of the following reactions are Brønsted–Lowry acid–base reactions.
- **A** $HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$
- **B** $CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$
- **C** $2HNO_3(aq) + Mg(s) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$
- **D** $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

Comprehension

11 Construct balanced equations to show that in water:
- **a** PO_4^{3-} acts as a base
- **b** $H_2PO_4^-$ acts as an amphiprotic substance
- **c** H_2S acts as an acid.

12 Construct an equation to show that perchloric acid ($HClO_4$) acts as a strong acid in water.

13 Construct an equation to show that hypochlorous acid ($HClO_3$) acts as a weak acid in water.

14 Four beakers contain solutions of the following substances: lemon juice, ammonia solution, sugar and sodium hydroxide. Some phenolphthalein is added to each beaker. Identify in which beakers the phenolphthalein changes colour.

15 Explain the term transition point in terms of K_a using methyl orange as an example.

Analysis

16 Calculate $[OH^-]$ at 25°C in aqueous solutions with $[H_3O^+]$ equal to:
- **a** $0.001\ mol\,L^{-1}$
- **b** $10^{-5}\ mol\,L^{-1}$
- **c** $5.7 \times 10^{-9}\ mol\,L^{-1}$
- **d** $3.4 \times 10^{-12}\ mol\,L^{-1}$
- **e** $6.5 \times 10^{-2}\ mol\,L^{-1}$
- **f** $2.23 \times 10^{-13}\ mol\,L^{-1}$

17 Calculate the concentration of these ions in solutions, at 25°C, with the following pH values.
- **i** hydrogen ions
- **ii** hydroxide ions

- **a** 1
- **b** 3
- **c** 7
- **d** 11.7

18 Calculate the concentration of H^+ and OH^- ions in solutions, at 25°C, with the following pH values.
- **a** 3.0
- **b** 10.0
- **c** 8.5
- **d** 5.8
- **e** 9.6
- **f** 13.5

19 The pH of tomato juice is 5.3 at 25°C. Calculate the concentration of hydroxide ions in tomato juice.

20 A solution of hydrochloric acid has a pH of 2.0 .
- **a** Calculate the molar concentration of hydrogen ions in the solution.
- **b** Calculate the number of moles of hydrogen ions that would be present in 500 mL of this solution.

21 Calculate the pH of each of the following mixtures at 25°C.
- **a** 10 mL of $0.025\ mol\,L^{-1}$ HCl is diluted to 50 mL of solution.
- **b** 20 mL of $0.0050\ mol\,L^{-1}$ KOH is diluted to 500 mL of solution.
- **c** 10 mL of $0.15\ mol\,L^{-1}$ HCl is diluted to 1.5 L of solution.

22 The molarity of concentrated sulfuric acid is $18.0\ mol\,L^{-1}$. Calculate the volume of concentrated sulfuric acid required to prepare a 1.00 L solution of $2.00\ mol\,L^{-1}$ H_2SO_4.

23 When a 10.0 mL solution of hydrochloric acid is diluted, the pH changes from 2.0 to 4.0. Determine the volume of water that is added to the acid solution.

24 40.0 mL of $0.10\ mol\,L^{-1}$ HNO_3 is diluted to 500.0 mL. Describe the effect this would have on the pH.

25 Determine the effect on the pH of a monoprotic acid solution of pH 0.1 when it is diluted by a factor of 10.

26 Calculate the pH of the base $C_6H_5NH_2$ of $0.0800\ mol\,L^{-1}$, which has a K_b of 3.80×10^{-10}.

27 The concentration of CH_3COOH at 25°C is $0.500\ mol\,L^{-1}$. The value for the equilibrium constant for this reaction is 1.75×10^{-5}. Calculate the concentration of the ethanoate ion at this temperature.

28 The general equation for buffer solution reactions is:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

Determine the pH of a solution containing $0.010\ mol\,L^{-1}$ of HA and $0.020\ mol\,L^{-1}$ of A^- with a K_a value of 4.5 (a strong acid).

29 Explain what a high K_a value of an acid indicates in terms of the position of equilibrium and whether it is a potential acid for use in a buffer.

Knowledge utilisation

30 Haemoglobin binds to oxygen in the blood enabling oxygen to be transported around the body and deposited at tissues and cells where it is needed. This is a reversible process that can be represented by the following equilibrium reaction:

$$HHb(aq) + O_2(g) \rightleftharpoons H^+(aq) + HbO_2^-(aq)$$

The human body, and bloodstream in particular, requires buffering systems to control the level of acidity to ensure biological reactions take place at an optimum rate. Determine why these buffering systems are necessary given the above reaction using Le Châtelier's principle and your knowledge of pH.

31 Carbon dioxide is slightly soluble in water. As levels of carbon dioxide in the atmosphere are increasing, more carbon dioxide is dissolving into the oceans. Some of this carbon dioxide remains as $CO_2(aq)$, but some reacts further to produce carbonic acid in the following reaction:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Carbonic acid is diprotic, meaning it can dissociate in two stages.

a Construct equations for these two stages.

b Determine what effect more CO_2 released from the burning of fossil fuels has on the position of equilibrium in each reaction.

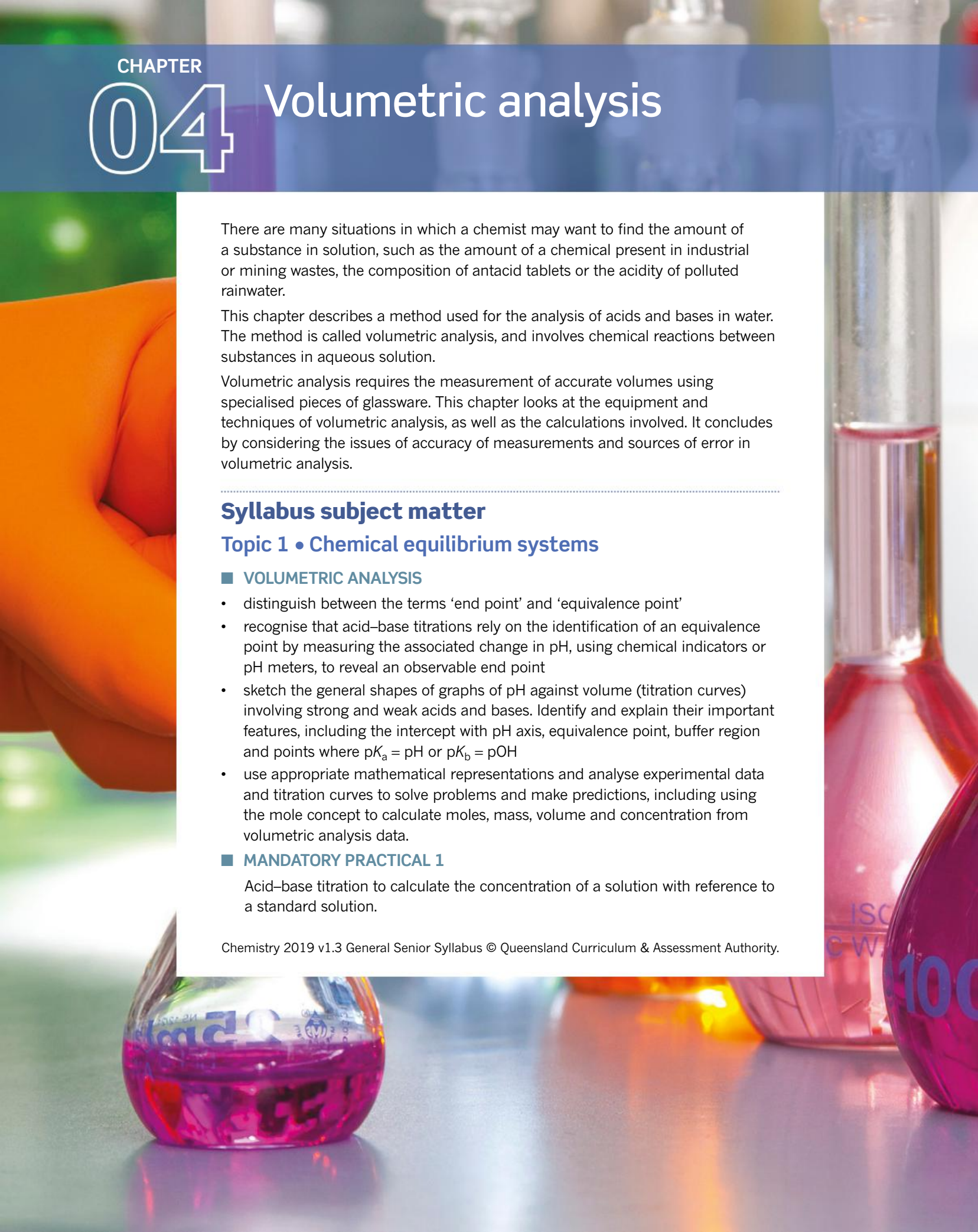
c Explain the effect of this in terms of pH.

d Since the beginning of the Industrial Revolution, the pH of the oceans has decreased by 0.11 units. Calculate the change in H_3O^+ concentration in this time.



CHAPTER

04 Volumetric analysis



There are many situations in which a chemist may want to find the amount of a substance in solution, such as the amount of a chemical present in industrial or mining wastes, the composition of antacid tablets or the acidity of polluted rainwater.

This chapter describes a method used for the analysis of acids and bases in water. The method is called volumetric analysis, and involves chemical reactions between substances in aqueous solution.

Volumetric analysis requires the measurement of accurate volumes using specialised pieces of glassware. This chapter looks at the equipment and techniques of volumetric analysis, as well as the calculations involved. It concludes by considering the issues of accuracy of measurements and sources of error in volumetric analysis.

Syllabus subject matter

Topic 1 • Chemical equilibrium systems

VOLUMETRIC ANALYSIS

- distinguish between the terms ‘end point’ and ‘equivalence point’
- recognise that acid–base titrations rely on the identification of an equivalence point by measuring the associated change in pH, using chemical indicators or pH meters, to reveal an observable end point
- sketch the general shapes of graphs of pH against volume (titration curves) involving strong and weak acids and bases. Identify and explain their important features, including the intercept with pH axis, equivalence point, buffer region and points where pK_a = pH or pK_b = pOH
- use appropriate mathematical representations and analyse experimental data and titration curves to solve problems and make predictions, including using the mole concept to calculate moles, mass, volume and concentration from volumetric analysis data.

MANDATORY PRACTICAL 1

Acid–base titration to calculate the concentration of a solution with reference to a standard solution.

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4.1 Principles of volumetric analysis



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- explain how standard solutions can be prepared
- use stoichiometry to determine unknown concentrations of acids and bases
- use titration curves to determine the equivalence point of a reaction
- differentiate between the end point and equivalence point in a titration
- select suitable indicators for different acid–base titrations using the titration curve.

Volumetric analysis is a common technique used by analytical chemists and it will be the focus of this chapter. Volumetric analysis can be used to accurately determine the concentration of solutions of acids and bases. This involves reacting solutions of unknown concentration with a solution of accurately known concentration (a **standard solution**).

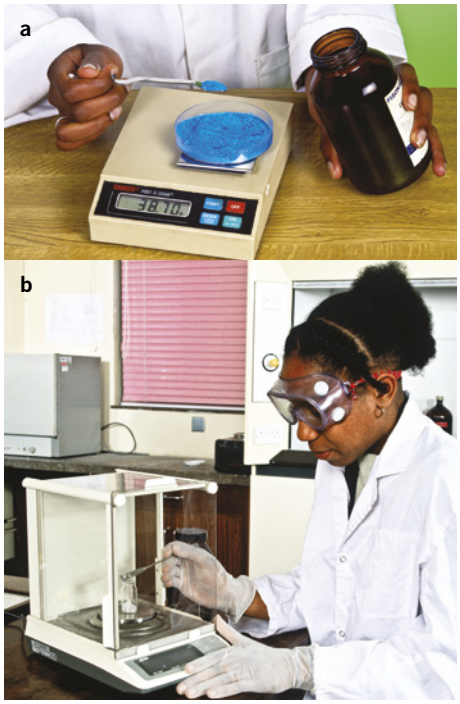


FIGURE 4.1.1 (a) A top-loading balance. (b) An analytical balance can be used to accurately weigh substances used in chemical analysis.



FIGURE 4.1.2 Volumetric flasks of various sizes are used to prepare standard solutions.

STANDARD SOLUTIONS

A standard solution is a solution of accurately known concentration. Pure substances that are widely used in the laboratory to prepare solutions of accurately known concentrations are called **primary standards**.

Primary standards are substances that are so pure that the number of moles of a substance can be calculated accurately from their mass.

A primary standard should:

- be readily obtainable in a pure form
- have a known chemical formula
- be easy to store without deteriorating or reacting with the atmosphere
- have a high molar mass to minimise the effect of errors in weighing
- be inexpensive.

Examples of primary standards are:

- bases: anhydrous sodium carbonate (Na_2CO_3) and sodium borate ($Na_2B_4O_7 \cdot 10H_2O$). (The term anhydrous indicates there is no water present in the compound.)
- acids: hydrated oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) and potassium hydrogen phthalate ($KH(C_8H_4O_4)$).

Standard solutions are prepared by dissolving an accurately measured mass of a primary standard in an accurately measured volume of water.

Digital balances are used in analytical laboratories to accurately weigh primary standards. A top-loading balance can weigh to an accuracy of between 0.1 g and 0.001 g depending on the model. Analytical balances can weigh to an accuracy of between 0.0001 g and 0.00001 g. The two types of balances commonly used can be seen in Figure 4.1.1.

A **volumetric flask** or standard flask, as shown in Figure 4.1.2, is used to prepare a solution that has an accurately known volume. Volumetric flasks of 50.00 mL, 100.00 mL and 250.00 mL are frequently used in the laboratory.

A volumetric flask is filled so that the bottom of the meniscus is level with the graduation line on the neck of the flask. This can be seen in Figure 4.1.3. Your eye should be level with the line to avoid **parallax errors**.

To prepare a standard solution from a primary standard, you need to dissolve an accurately known amount of the substance in deionised water to produce a solution of known volume. The steps in this process are shown in Figure 4.1.4.

The molar concentration of the standard solution is then found using these formulas:

$$\text{number of moles, } n = \frac{\text{mass of solute (in g)}}{\text{molar mass (in g mol}^{-1}\text{)}} = \frac{m}{M}$$

$$\text{concentration, } c = \frac{\text{number of moles of solute (mol)}}{\text{volume of solution (L)}} = \frac{n}{V} = \frac{m}{M \times V}$$

In practice, making a standard solution directly from a primary standard is only possible for a few of the chemicals found in the laboratory. Many chemicals are impure because they decompose or react with chemicals in the atmosphere. For example, strong bases such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) absorb water and react with carbon dioxide in the air, and many hydrated salts, such as sodium carbonate ($Na_2CO_3 \cdot 10H_2O$), lose water to the atmosphere over time.

In addition, the concentrations of commercial supplies of strong acids (for example, HCl, H_2SO_4 and HNO_3) cannot be accurately specified.

Solutions such as HCl(aq), H_2SO_4(aq), NaOH(aq) and KOH(aq) must be standardised to determine their concentration. An accurately measured volume of the solution is reacted with a known amount of a standard solution such as Na_2CO_3(aq) or $KH(C_8H_4O_4)$(aq). This is done by titration, which is discussed in Module 4.2.



FIGURE 4.1.3 This close-up view of the neck of a standard flask shows the bottom of the meniscus level with the graduation line.

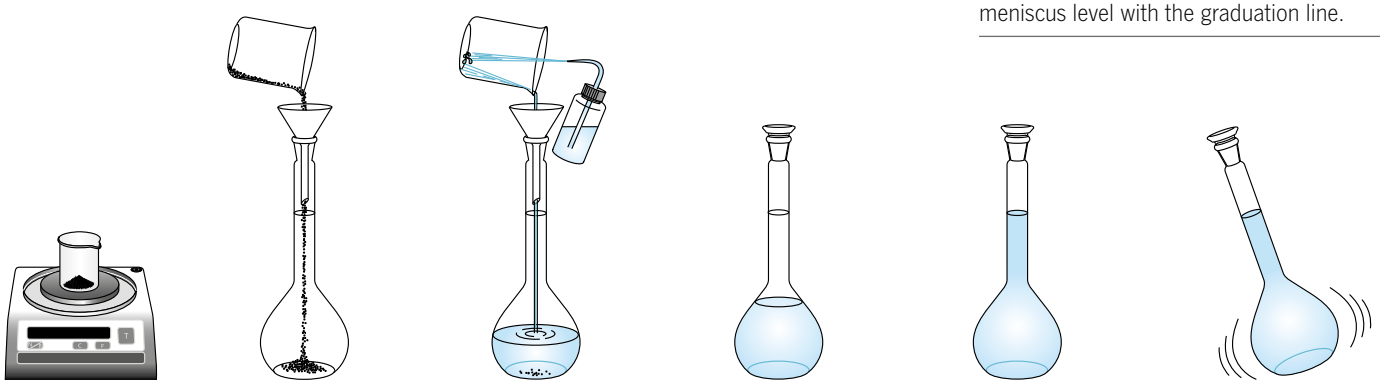


FIGURE 4.1.4 Preparing a standard solution from a primary standard

Concentration of standard solutions

In Unit 2 you looked at calculating the concentration of a solution and determining how much solute is required to prepare a solution of a specific concentration.

Figure 4.1.5 summarises the steps involved in calculating the concentration of a standard solution from the accurately measured mass of a primary standard.

A standard solution is a solution of an accurately known concentration.

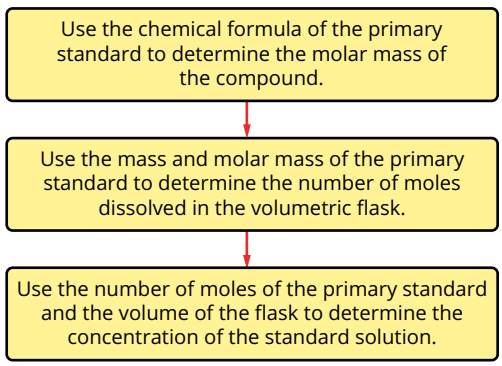


FIGURE 4.1.5 A summary of the steps used in the calculation of the concentration of a standard solution prepared from a primary standard

Worked example 4.1.1

CALCULATING THE CONCENTRATION OF A STANDARD SOLUTION PREPARED FROM A PRIMARY STANDARD

Calculate the concentration of a standard solution prepared from 29.22 g of sodium chloride (NaCl) dissolved in a 1.00 L volumetric flask.

Thinking	Working
Use the chemical formula to determine the molar mass (M) of the compound.	The molar mass (M) of NaCl is $22.99 + 35.45 = 58.44\,g\,mol^{-1}$
Use the mass (m) and molar mass (M) of the compound and the formula $n = \frac{m}{M}$ to determine the number of moles.	$n = \frac{29.22}{58.44}$ $= 0.500\,mol$
Use the number of moles to determine the concentration of the solution using the formula $c = \frac{n}{V}$. Remember, volume is in L.	$c = \frac{0.500}{1.00}$ $= 0.500\,mol\,L^{-1}$

➤ Try yourself 4.1.1

CALCULATING THE CONCENTRATION OF A STANDARD SOLUTION PREPARED FROM A PRIMARY STANDARD

Calculate the concentration of a standard solution prepared from 117.00 g of sodium chloride (NaCl) dissolved in a 500.00 mL volumetric flask.

SOLUTION STOICHIOMETRY

In Unit 2 you learnt to predict the products for the reactions of acids with bases, carbonates or metals. In this module, you will learn how to calculate how much product is produced, or how much reactant is required in these reactions.

Being able to answer the 'how much' question has many useful applications, including determining how much:

- lime should be added to soil to increase its pH
- calcium carbonate should be used to neutralise hazardous acidic wastes from an industrial plant or a mine site
- phosphoric acid is in a cola drink
- stomach acid can be neutralised by an antacid tablet.

You will use your knowledge of the reactions of acids, your ability to write balanced chemical equations, and your understanding of the mole concept and mole relationships to answer 'how much' questions like these.

Reacting quantities of acids and bases

Calculations based on the reactions of acids usually involve determining the number of moles of a substance.

You will recall from Unit 2 that:

- the coefficients in a balanced chemical equation give the ratio in which substances react
- the number of moles of solid can be calculated from the expression $n = \frac{m}{M}$, where m is the mass in grams and M is the molar mass in $g\,mol^{-1}$
- the number of moles of solute in a solution is given by $n = cV$, where c is the concentration in mol L^{-1} and V is the volume in litres (L).

As you will see in Worked examples 4.1.2 and 4.1.3, there are four main steps in solving calculation problems involving solutions of acids and bases:

1 Construct a balanced equation for the reaction.
2 Calculate the number of moles of the substance with known volume and concentration.

3 Use the mole ratio from the equation to calculate the number of moles of the required substance.
4 Calculate the required volume or concentration.

The steps in a stoichiometric calculation can be summarised as shown in the flow chart in Figure 4.1.6.

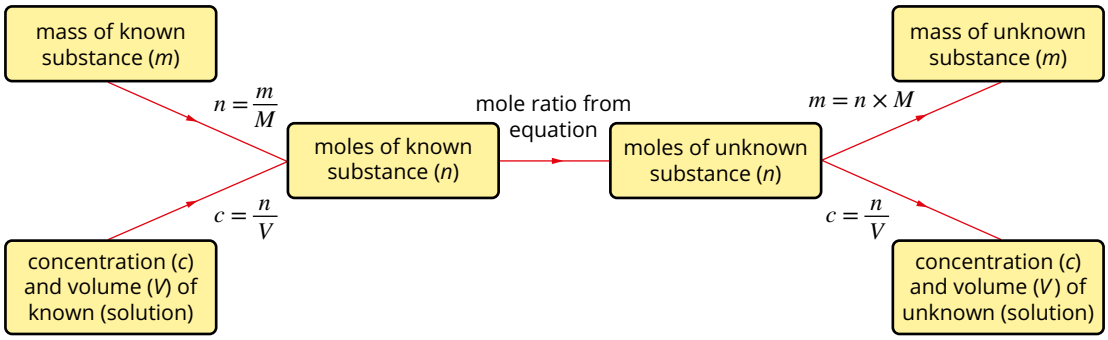


FIGURE 4.1.6 Flow chart for mass and solution calculations

Worked example 4.1.2

A SOLUTION VOLUME–VOLUME CALCULATION

Calculate the volume of 0.100 mol L^{-1} sulfuric acid (H_2SO_4) that reacts completely with 17.8 mL of 0.150 mol L^{-1} potassium hydroxide (KOH) solution.

Thinking	Working
Construct a balanced full equation for the reaction.	$2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$
Calculate the number of moles of the substances with known volume and concentration.	The volume and concentration of the potassium hydroxide solution are given, so you can use $n = cV$ (remember that volume must be expressed in litres). $n(KOH) = cV$ $= 0.150 \times 0.0178$ $= 0.00267$ mol
Use the mole ratio from the equation to calculate the number of moles of the required substance.	The balanced equation shows that 1 mol of sulfuric acid reacts with 2 mol of potassium hydroxide. $\frac{n(H_2SO_4)}{n(KOH)} = \frac{1}{2}$ $n(H_2SO_4) = \frac{1}{2} \times n(KOH)$ $= \frac{1}{2} \times 0.00267$ $= 0.00134$ mol
Calculate the volume or concentration required.	The volume of H_2SO_4 is found by using $n = cV$. $V(H_2SO_4) = \frac{n}{c}$ $= \frac{0.00134}{0.100}$ $= 0.0134$ L $= 13.4$ mL

➤ Try yourself 4.1.2

A SOLUTION VOLUME–VOLUME CALCULATION

Calculate the volume of 0.500 mol L^{-1} hydrochloric acid (HCl) that reacts completely with 25.0 mL of 0.100 mol L^{-1} calcium hydroxide ($Ca(OH)_2$) solution. The salt formed in this acid–base reaction is calcium chloride.

Stoichiometry problems involving excess reactants

Reactants are not always mixed in stoichiometric amounts in acid–base reactions. There are occasions when one of the reactants, an acid or a base, is in excess. The issue of excess and limiting reactants was discussed in Unit 2. The same principles for identifying whether or not an acid or a base is in excess in a reaction mixture apply:

- calculate the number of moles of each reactant
- determine which reactant is in excess and which is the limiting reactant
- use the number of moles of the limiting reactant to work out the number of moles of product formed or the number of moles of reactant in excess.

Worked example 4.1.3

SOLUTION STOICHIOMETRY—A LIMITING REACTANT PROBLEM

20.0 mL of a 1.00 mol L^{-1} solution of lithium hydroxide (LiOH) is added to 30.0 mL of a 0.500 mol L^{-1} solution of nitric acid (HNO_3). The equation for the reaction that occurs is:

$$HNO_3(aq) + LiOH(aq) \rightarrow LiNO_3(aq) + H_2O(l)$$

a Determine which reactant is the limiting reactant.

Thinking	Working
Calculate the number of moles of each of the reactants using $n = cV$.	$n(HNO_3) = 0.500 \times 0.0300$ $= 0.0150$ mol $n(LiOH) = 1.00 \times 0.0200$ $= 0.0200$ mol
Use the coefficients of the equation to find the limiting reactant.	The equation shows that 1 mol of HNO_3 reacts with 1 mol of LiOH. So, the HNO_3 is the limiting reactant (it will be completely consumed).

b Calculate the mass of $LiNO_3$ that will be produced by this reaction.

Thinking	Working
Find the mole ratio of the unknown substance to the limiting reactant from the equation coefficients: $\frac{\text{coefficient of unknown}}{\text{coefficient of limiting reactant}}$	From the equation coefficients: $\frac{n(LiNO_3)}{n(HNO_3)} = \frac{\text{coefficient of } LiNO_3}{\text{coefficient of } HNO_3} = \frac{1}{1}$
Calculate the number of moles of the unknown substance using the limiting reactant: $n(\text{unknown}) = n(\text{limiting reactant}) \times \text{mole ratio}$	$n(LiNO_3) = n(HNO_3) \times \frac{1}{1}$ $= 0.0150 \times \frac{1}{1}$ $= 0.0150$ mol
Calculate the mass of the unknown substance using: $m(\text{unknown}) = n(\text{limiting reactant}) \times \text{molar mass}$	Molar mass of $LiNO_3 = 68.95$ g mol^{-1} $m(LiNO_3) = 0.0150 \times 68.95$ $= 1.03$ g

➤ Try yourself 4.1.3

SOLUTION STOICHIOMETRY—A LIMITING REACTANT PROBLEM

30.0 mL of a 0.100 mol L^{-1} solution of sulfuric acid (H_2SO_4) is added to 40.0 mL of a 0.200 mol L^{-1} solution of potassium hydroxide (KOH). The equation for the reaction that occurs is:

$$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$$

a Determine which reactant is the limiting reactant.

b Calculate the mass of K_2SO_4 that will be produced by this reaction.

TITRATION CURVES

The change in pH when a strong acid such as hydrochloric acid (HCl) is titrated against a strong base such as sodium hydroxide (NaOH) can be represented on a graph called a titration curve or pH curve. The equivalence point occurs when the gradient of the titration curve is steepest. An example of a titration curve is shown in Figure 4.1.7.

You may remember from Chapter 3 that the equivalence point is the time during a neutralisation reaction when the amount of acid and base are in stoichiometric ratios represented by the reaction equation. For example, hydrochloric acid and sodium hydroxide react according to the following equation:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

The equivalence point during this reaction is when the number of moles of HCl is equal to NaOH in the 1:1 ratio given by the equation.

Near the equivalence point, the addition of a very small volume of HCl produces a large change in pH. In this titration the pH changes from 10 to 4 with just one drop of acid! By using an indicator that changes colour within this pH range, such as bromothymol blue which changes between pH 6.0 and 7.6, one drop will cause a colour change. This is referred to as a sharp end point. Therefore, knowing the pH range of an indicator is an important tool to ensuring a sharp end point.

The volume of acid added at this point indicates the amount needed to react according to the balanced equation. This volume is the titre that is recorded for the titration.

For a reaction between a strong acid and a strong base, the pH at the equivalence point is 7. The equation for the reaction can be written as:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Only $H_2O(l)$ and NaCl(aq) are present at the equivalence point, making the solution neutral.

Other indicators, including phenolphthalein (pH range 8.3 to 10.0), could be used for this titration because they would also produce a sharp end point for this reaction. (Indicator pH ranges are discussed in Chapter 3 on page 77 and Appendix J.)

Figure 4.1.8 compares the titration curves obtained when a strong acid is added to a strong base, and when a strong acid is added to a weak base. Note that there is a sharp drop in pH in both graphs at the equivalence point. However, because this drop occurs over different ranges, the choice of indicator is important in detecting the equivalence point. Phenolphthalein can be used successfully for the first titration but not for the second.

Phenolphthalein, which changes colour in the pH range 8.3 to 10.0, gives a sharp end point in Figure 4.1.8a but a broad end point in Figure 4.1.8b. Methyl orange, which changes colour in the pH range 3.1 to 4.4, would be a more suitable indicator for the second titration.

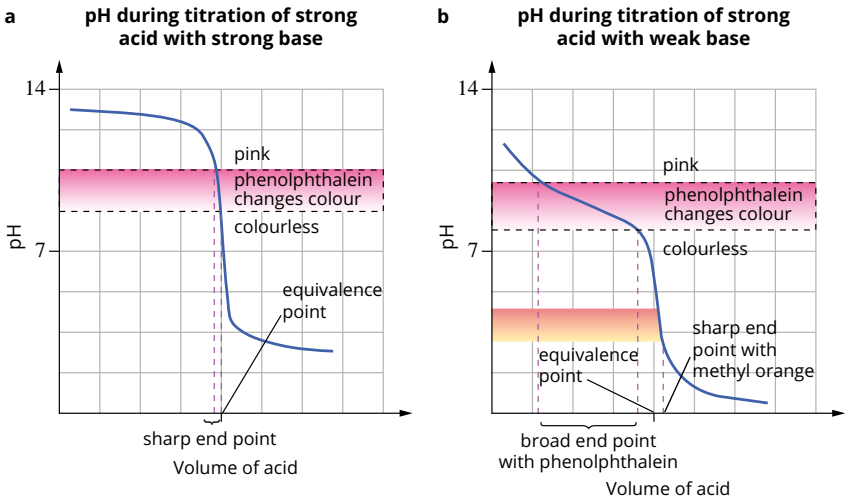


FIGURE 4.1.8 Titration curves showing the pH during a titration of (a) a strong acid with a strong base, and (b) a strong acid with a weak base.

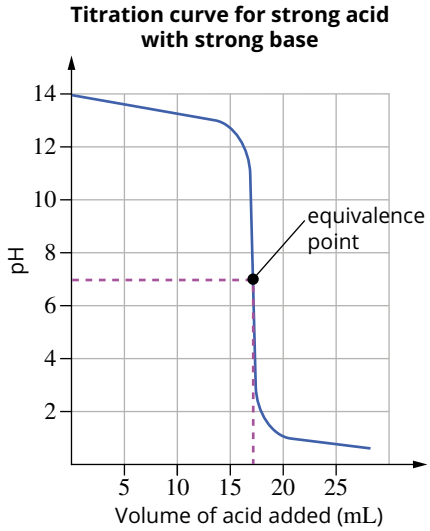


FIGURE 4.1.7 Titration curve for a strong acid being added to a strong base

The point during a titration at which the reactants are present in equivalent amounts, as indicated by coefficients in the equation for the reaction, is called the equivalence point.



FIGURE 4.1.9 A student uses a pH meter during a titration.

> **i** The equivalence point occurs when the gradient of the pH curve is steepest.

TABLE 4.1.1 pH change during a titration

Volume of HCl added (mL)	pH of conical flask solution
0.0	11.76
5.0	10.06
10.0	9.88
15.0	9.50
20.0	9.01
21.0	8.87
22.0	8.71
23.0	8.41
24.0	7.60
25.0	2.20
30.0	1.35
35.0	1.16

Figure 4.1.9 shows a student using a digital pH meter to measure the pH of a solution as acid is added during a titration.

As small amounts of solution in the burette are progressively added to the titration flask, the student records the pH measurements and the corresponding burette reading.

The pH measurements shown in Table 4.1.1 were recorded during the titration of an ammonia solution with a standard solution of 0.10 mol L^{-1} hydrochloric acid. You can see from the graph in Figure 4.1.10 that the titre needed to reach the equivalence point was about 24.5 mL and the equivalence point occurs at a pH of 5.

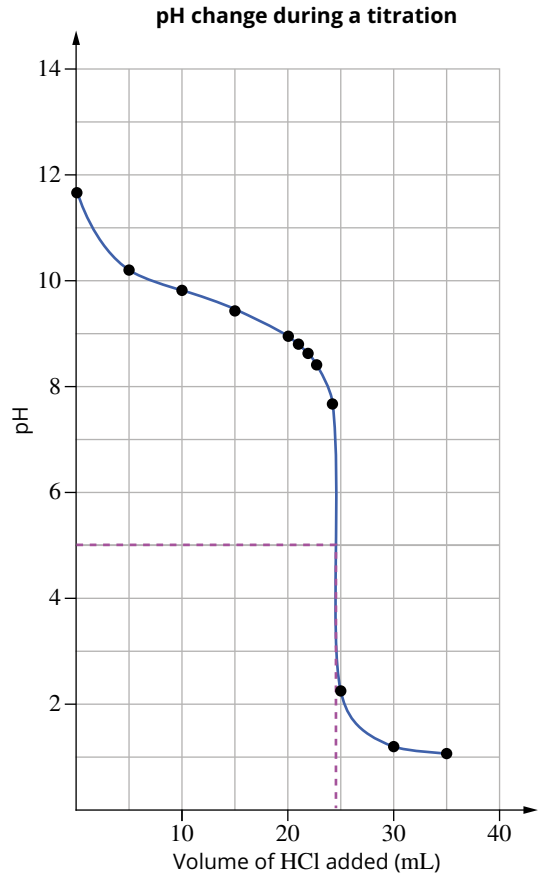


FIGURE 4.1.10 Titration curve showing how the pH of a solution of 0.1 mol L^{-1} NH_3(aq) changes as 0.1 mol L^{-1} HCl(aq) is added from a burette.

pH meters need to be calibrated before use. Some pH probes linked to a computer can automatically store data into a spreadsheet and are able to simultaneously record pH and time elapsed. By adjusting the burette to a constant dripping rate (e.g. one drop per second) and reading data every three seconds for five minutes, a pH curve can be automatically generated and stored.

INDICATORS IN VOLUMETRIC ANALYSIS

You will remember from Chapter 3 that an indicator is in equilibrium with its conjugate base represented by the following equation:

$$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$

The position of equilibrium changes depending on the pH. The colour of the acid form of an indicator, HIn, and the colour of its conjugate base, In^-, are different. The acid or base colour of an indicator is visible at low indicator concentrations.

The dissociation constant for the acid–base indicator dissociation is:

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

The indicator changes colour when the concentration of the acid, HIn, is equal to the concentration of its conjugate base, In^-. That is, the colour change will occur when $[H^+] = K_a$. This means that the colour change occurs when the pK_a is equal to the pH. For a basic indicator, the colour change occurs when the pK_b is equal to the pOH.

For example, methyl orange is an acidic indicator with a pK_a value of 3.7. It changes colour over a pH range of 3.1 to 4.4. Table 4.1.2 summarises some of the pH ranges of common acid–base indicators.

TABLE 4.1.2 The pH ranges of a number of common acid–base indicators

Indicator	Colour of acid form	Colour of base form	pH range
methyl orange	red	yellow	3.1–4.4
bromothymol blue	yellow	blue	6.0–7.6
phenolphthalein	colourless	pink	8.3–10.0

When choosing an indicator for a titration, it is important to know the titration curve for the reaction.

Strong acid–strong base titration

The graph in Figure 4.1.11 shows the pH changes that take place when a solution of a strong base, such as 1.0 mol L^{-1} sodium hydroxide (NaOH), is titrated with a solution of a strong acid, such as 1.0 mol L^{-1} hydrochloric acid (HCl). The equivalence point occurs when the gradient of the pH curve is steepest.

Near the equivalence point, addition of a very small volume of HCl produces a large change in pH. By using an indicator that changes colour within this pH range, such as bromothymol blue which changes between pH 6.0 and pH 7.6, one drop will cause a colour change. This is referred to as a sharp end point.

The volume of acid added at this point indicates the amount needed to react according to the balanced equation. This volume is the titre that is recorded for the titration.

For a reaction between a strong acid and a strong base, the pH at the equivalence point is 7.0. The equation for the reaction can be written as:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Only $H_2O(l)$ and NaCl(aq) are present at the equivalence point, making the solution neutral.

Other indicators, including phenolphthalein (pH range: 8.3 to 10.0), could be used for this titration because they would also produce a sharp end point for this reaction.

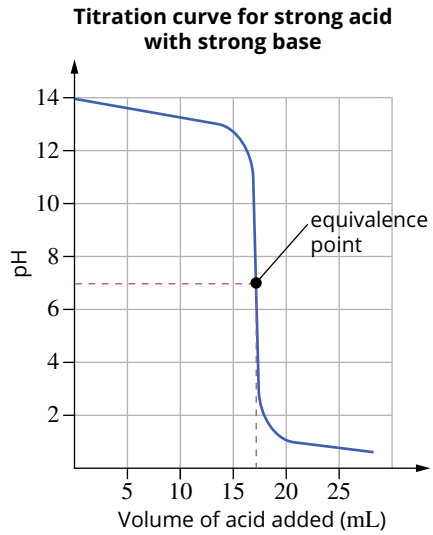


FIGURE 4.1.11 Titration curve for a strong acid being added to a strong base

Weak acid–strong base titration

The titration curve obtained when a strong base (0.1 mol L^{-1} sodium hydroxide) is added to a weak acid (0.1 mol L^{-1} ethanoic acid) is shown in Figure 4.1.12.

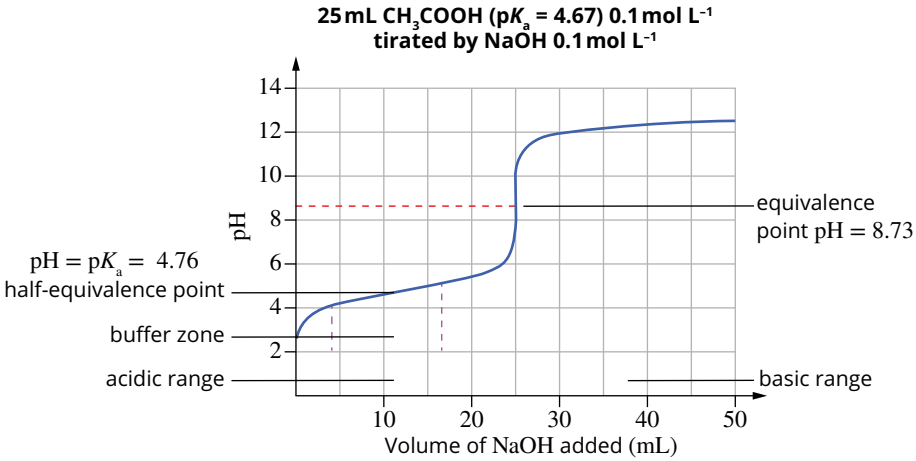


FIGURE 4.1.12 Titration curve for a strong base being added to a weak acid

WS 3.1.6 WS 3.1.7

Features of the titration curve

The shape of the curve reflects the weakly acidic nature of the acid. Before the acid is titrated the pH of the solution is 2.87. Remember from Chapter 3 that a weak acid represented by the balanced equation

$$HA \rightleftharpoons H^+ + A^-$$

has an acid dissociation constant, K_a, determined using the formula

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Since the dissociation of the weak acid is very small, [HA] can be approximated to be $0.1\,mol\,L^{-1}$.

Thus, for ethanoic acid ($K_a = 1.8 \times 10^{-5}$) the expression rearranges and simplifies to:

$$[H^+][A^-] = K_a \times 0.1$$
$$= 1.8 \times 10^{-6}$$

Since ethanoic acid dissociates equally into hydrogen ions and ethanoate ions, the $[H^+]$ can be calculated by taking the square root of 1.8×10^{-6}, which means $[H^+] = 1.34 \times 10^{-3}\,mol\,L^{-1}$.

Since $pH = -\log_{10}[H^+]$, the hydrogen ion concentration of the original acid solution can be determined to be 2.87.

As sodium hydroxide is added to the solution the pH increases; however, this region is relatively flat and is known as the buffer zone. The buffer zone is the part of the titration curve prior to reaching the equivalence point and is the region in which lots of volume of the titrant is added with little change to the pH of the solution. On the graph, it appears as a relatively horizontal (flat) portion of the curve.

A buffer is a solution of weak acid and conjugate base, or weak base and conjugate acid.

Buffer solutions resist the change in pH because of the equilibrium between the acid (HA) and its conjugate base (A^-), as shown in the balanced equation:

$$HA \rightleftharpoons H^+ + A^-$$

When more base is added to the mixture, the OH^- ions react with the H^+ reducing the concentration of H^+ in the solution. By Le Châtelier's principle this causes the equilibrium to shift to the right resulting in more of the ethanoic acid dissociating. Therefore, the hydrogen ion concentration decreases by less than the amount expected for the quantity of base added.

If H^+ was added to the equilibrium mixture of the weak acid and its conjugate base, the equilibrium is shifted to the left in accordance with Le Châtelier's principle. This causes the hydrogen ion (H^+) concentration to increase by less than the amount expected for the quantity of acid added.

Halfway between the start of the titration and the equivalence point is a point where the pH is equal to the pK_a of the weak acid.

Using the balanced equation:

$$HA \rightleftharpoons H^+ + A^-$$

in which K_a is defined as:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

By taking $\log_{10}$ of both sides the expression can be written as:

$$\log_{10} K_a = \log_{10}[H^+] + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

Rearranging the expression gives:

$$-\log_{10}[H^+] = -\log_{10} K_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

By definition $-\log_{10}[H^+] = pH$ and $-\log_{10}K_a = pK_a$; therefore, the expression can be written as:

$$pH = pK_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

Therefore, when $\log_{10}\left(\frac{[A^-]}{[HA]}\right)=0$, $pH = pK_a$.

This happens when $[HA]=[A^-]$ and is the point halfway to the equivalence point.

The change in pH at the equivalence point is not as large as in the earlier strong acid–strong base titration. An indicator that changes colour within the pH range 6.0–10.0, such as phenolphthalein, would be suitable to identify the end point of such a titration.

The reaction occurring is:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

In this case the equivalence point has a pH greater than 7.0 because $CH_3COONa(aq)$ is present. CH_3COO^- is a weak base that undergoes hydrolysis with water to produce hydroxide ions, making the solution slightly basic at that point.

After the equivalence point is reached, and more of the strong base is added, the pH continues to increase up to a maximum of 13.0.

This can be determined using the ionic product of water:

$$K_w = 1\times10^{-14} = [H^+][OH^-]$$
$$[H^+] = \frac{1\times10^{-14}}{[OH^-]}$$

Therefore, a 0.1 mol L^{-1} solution of NaOH, where $[OH^-]$ is 0.1, would have a $[H^+]=1\times10^{-13}$ and thus a maximum pH of 13.0 is achievable.

Strong acid–weak base titration

The titration curve obtained when a strong acid (0.1 mol L^{-1} hydrochloric acid) is added to a weak base (0.1 mol L^{-1} ammonia) is shown in Figure 4.1.13.

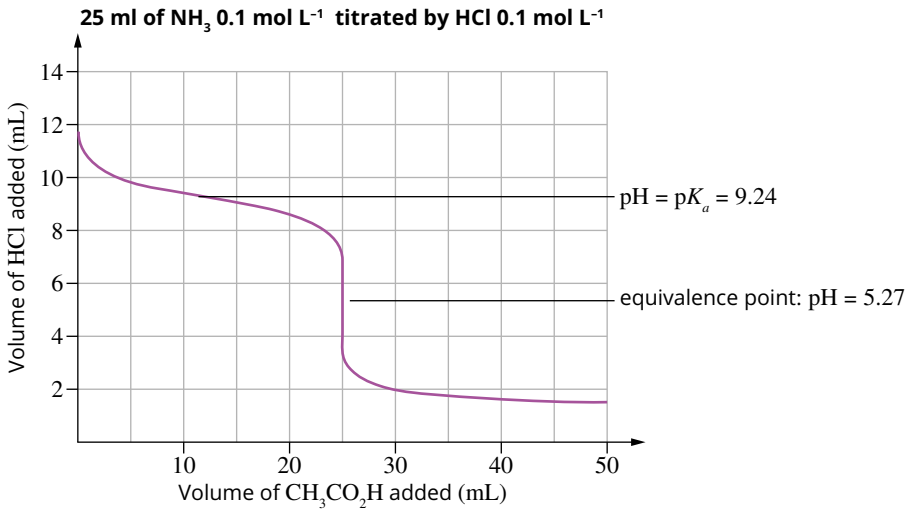


FIGURE 4.1.13 Titration curve for a strong acid added to a weak base

Features of the titration curve

Since aqueous ammonia solution is a weak base, ($K_b = 1.75 \times 10^{-5}$), it only partially dissociates and so the $[OH^-]$ concentration is much less than 0.1. Therefore, the pH of the 0.1 mol L^{-1} solution is approximately 11.

As the hydrochloric acid is added, the pH decreases slightly; however, this region is relatively flat and is known as the buffer zone. The buffer zone is the part of the titration curve prior to reaching the equivalence point and is the region in which lots of volume of the titrant is added with little change to the pH of the solution. On the graph, it appears as a relatively horizontal (flat) portion of the curve.

As with the weak acid–strong base titration, the addition of the acid creates an equilibrium with the weak base (NH_3) and its conjugate acid (NH_4^+).

Buffer solutions resist the change in pH because of the equilibrium between the base (B) and its conjugate acid (BH^+), as shown in the balanced equation:

$$B + H^+ \rightleftharpoons BH^+$$

When more acid is added to the mixture, by Le Châtelier's principle this causes the equilibrium to shift to the right resulting in more of the base reacting with the H^+ and reducing the concentration of H^+ in solution. Therefore, the hydrogen ion concentration increases by less than the amount expected for the quantity of acid added.

If base is added to the equilibrium mixture of the weak acid and its conjugate base, the base reacts with the H^+ thus reducing the concentration of hydrogen ions in solution. The reduction in H^+ ions causes the equilibrium above to shift to the left, in accordance with Le Châtelier's principle, which means that the hydrogen ion (H^+) concentration decreases by less than the amount expected for the quantity of base added.

As with the weak acid titration, halfway between the start of the titration and the equivalence point is a point where the pOH is equal to the pK_b of the weak base.

The dissociation constant, K_b, for the weak base represented by the equation

$$BOH \rightleftharpoons B^+ + OH^-$$

is defined as:

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

By taking $\log_{10}$ of both sides, the expression can be written as:

$$\log_{10} K_b = \log_{10}[OH^-] + \log_{10}\left(\frac{[B^+]}{[BOH]}\right)$$

Rearranging the expression:

$$-\log_{10}[OH^-] = -\log_{10} K_b + \log_{10}\left(\frac{[OH^-]}{[BOH]}\right)$$

By definition $-\log_{10}[OH^-] = pOH$ and $-\log_{10}K_b = pK_b$; therefore, the expression can be written as:

$$pOH = pK_b + \log_{10}\left(\frac{[OH^-]}{[BOH]}\right)$$

Therefore, when $\log_{10}\left(\frac{[OH^-]}{[BOH]}\right) = 0$, $pOH = pK_b$.

This happens when $[BOH] = [OH^-]$ and is the point halfway to the equivalence point.

There is a large drop in pH between about 7.0 and 3.0. Methyl orange would be a suitable indicator for this titration because it changes colour between the pH range 3.1 to 4.4, which falls within the pH range near the equivalence point. Once again, a sharp end point would be obtained.

The reaction occurring in this instance is:

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

The pH of about 5.0 at the equivalence point can be explained by the presence of the weakly acidic ammonium ion, NH_4^+, when the reaction between HCl and NH_3 is complete.

4.1 Review

SUMMARY

- A substance is suitable for use as a primary standard if it:
  - is readily obtainable in a pure form
  - has a known chemical formula
  - is easy to store without deteriorating or reacting with the atmosphere
  - has a high molar mass to minimise the effect of errors in weighing
  - is inexpensive.
- A standard solution is a solution of an accurately known concentration.
- The concentration, in mol L^{-1}, of a prepared standard solution can be determined by measuring the mass of solid dissolved and the volume of solution prepared.
- Given the quantity of one of the reactants or products in a chemical reaction, the quantity of all other reactants and products can be predicted by working through the following steps.
  1. Construct a balanced equation for the reaction.
  2. Calculate the number of moles of the given substances.
  3. Use the mole ratios of reactants and products in the balanced chemical equation to calculate the number of moles of the required substance.
  4. Convert the number of moles of the required substance to the quantity required in the question.
- The equivalence point of a reaction occurs when the reactants have been mixed in the mole ratio shown by the equation for the reaction.
- An acid–base indicator can usually be used to identify the equivalence point of a reaction.
- The stage at which an indicator changes colour is called the end point.
- For accurate analysis, the indicator's end point must closely match the equivalence point of the reaction.
- pH meters can be used to produce a graph that shows the change in pH during an acid–base titration, called the titration curve (or pH curve).
- The shape of a titration curve depends on the strength and concentration of the acids and bases involved.
- Titration curves can be used to identify the equivalence point of titrations.

KEY QUESTIONS

Retrieval

1 Describe the steps required for the correct preparation of a standard solution.

2 State the difference between the end point and the equivalence point of a titration.

3 Describe the importance of selecting an indicator with an end point close to the equivalence point for the reaction.

Comprehension

4 Determine the volume of 0.200 mol L^{-1} KOH required to react with 30.0 mL of 0.100 mol L^{-1} HNO_3.

5 Explain why NaOH is not suitable for use as a primary standard in the titration of a strong acid.

Analysis

6 Potassium hydrogen phthalate ($KH(C_8H_4O_4)$) is used as a primary standard for the analysis of bases. Use the following information to calculate the concentration of a standard solution prepared in a 50.00 mL volumetric flask by dissolving 2.042 g of potassium hydrogen phthalate in deionised water. The molar mass of $KH(C_8H_4O_4)$ is 204.23 g mol^{-1}.

7 Determine the mass of anhydrous sodium carbonate (Na_2CO_3) required to prepare 250.0 mL of a 0.500 mol L^{-1} standard solution.

8 A 0.100 mol L^{-1} solution of H_2SO_4 is neutralised with 10.0 mL of a 0.300 mol L^{-1} solution of KOH.

a Represent this reaction using a balanced chemical equation.

b Determine the volume of sulfuric acid that was neutralised.

9 15.0 mL of a nitric acid solution is required to react completely with 10.0 mL of a 0.100 mol L^{-1} solution of $Ca(OH)_2$.

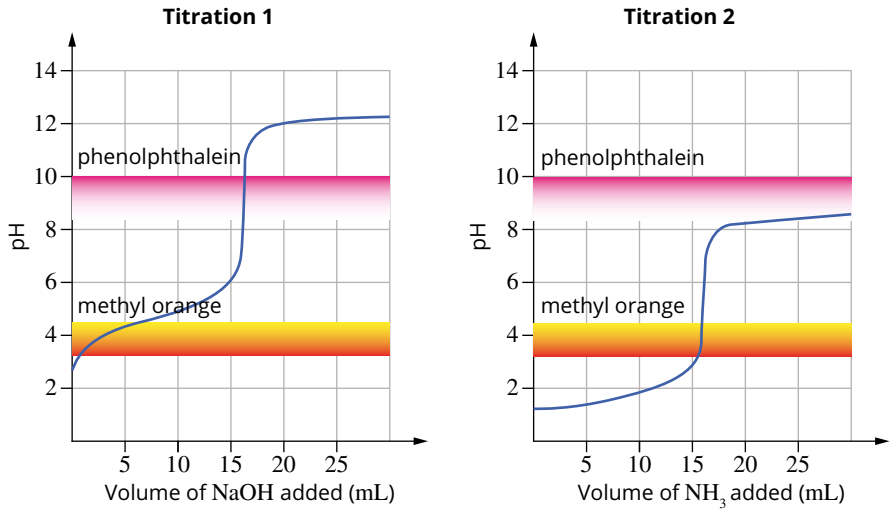
a Represent this reaction using a balanced chemical equation.

b Determine the concentration of the nitric acid solution.

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4.1 Review *continued*

10 A student used a pH meter to produce titration curves for two different acid–base reactions. The range in which two indicators change colour was then superimposed on each graph as shown below. Determine which indicator is best used for each titration.



11 During a titration of ethanoic acid with sodium hydroxide the solution in the conical flask changed from pink to colourless after 20 mL of the solution in the burette had been added.

a Determine the most likely indicator used.

b Explain if the pH is progressively increasing or decreasing during the titration.

c When equal amounts of the acid and base have been mixed, deduce what the pH of the solution will be. Determine if it will be less than 7, greater than 7 or equal to 7. Explain your answer.

4.2 Performing volumetric analysis

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- determine the equipment used in volumetric analysis and explain its use and measurement uncertainty
- calculate stoichiometric calculations using the results of volumetric analysis.



EQUIPMENT USED IN VOLUMETRIC ANALYSIS

Often the concentrations of acids and bases used in industry are unknown. The laboratory equipment shown in Table 4.2.1 is used to make precise measurements of mass and volume. These instruments, combined with calculations similar to those in Module 4.1, can help scientists determine unknown concentrations of acids and bases.

If you want to find the concentration of a solution of hydrochloric acid, you can react the hydrochloric acid with a standard solution of sodium carbonate. Precisely calibrated glassware is used to carry out the analysis.

The solution of sodium carbonate is slowly added (titrated) to the acid solution in the conical flask until the reactants are present in equivalent amounts. These amounts are indicated by the coefficients in the equation for the reaction. You will recall from Chapter 3 that this is called the equivalence point.

TABLE 4.2.1 Laboratory equipment used to determine the concentration of a solution of hydrochloric acid by volumetric analysis

Equipment	Visual reference	Use
volumetric flask		A volumetric flask is used to prepare a standard solution of sodium carbonate. An accurately weighed sample of sodium carbonate is placed in the flask and dissolved in deionised water to form a specific volume of solution.
pipette		A **pipette** is used to accurately measure a specific volume of the solution of hydrochloric acid. This known volume, or **aliquot**, is then poured into a conical flask ready for analysis.
burette		The standard solution of sodium carbonate is placed in a **burette**, which delivers accurately known, but variable, volumes of solution. The volume of liquid delivered by a burette is called a **titre**.

For the reaction between hydrochloric acid and sodium carbonate solution:

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

The equivalence point occurs when exactly 2 moles of HCl has been added for each 1 mole of Na_2CO_3. This whole process is called a titration.

As you will remember from Module 4.1, the reaction is complete when the equivalence point is reached. The concentration and volume of sodium carbonate (from the burette) required is now known, as is the volume of the aliquot of hydrochloric acid used. The concentration of the acid can now be calculated.

As both acid and base solutions are often colourless, an indicator is added to determine when the reaction is complete. (The indicator chosen should change colour when the solutions are neutralised.) You will recall from Chapter 3 that the end point is the point during the titration at which the indicator changes colour. For an accurate analysis, the end point should be very close to the equivalence point. See Appendix J on page 599 for the pH range of various indicators.

Figure 4.2.1 shows how the equipment listed would be used to complete the titration for the reaction of NaOH and HCl.

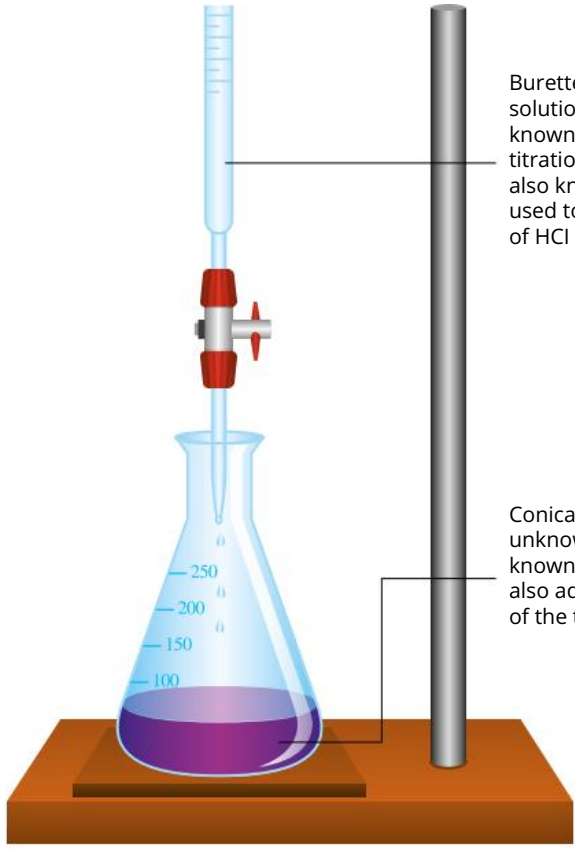


FIGURE 4.2.1 The equipment used in the titration of NaOH (in the burette) to determine the concentration of HCl (in the conical flask)

Reading a burette scale

Burettes are usually calibrated in intervals of 0.10 mL. The volume of liquid in a burette is measured at the bottom of the meniscus of the liquid. The reading is estimated to half the smallest division, 0.05 mL, as shown in Figure 4.2.2.

To minimise errors, the titration is repeated several times and the **average titre** is found. Usually three **concordant titres** (titres that are within 0.10 mL from highest to lowest of each other) are used to find this average.

The volume of one single drop from a burette is about 0.05 mL, so taking the average of three results assumes that the results will be no more than one drop over or one drop under the accurate titre.

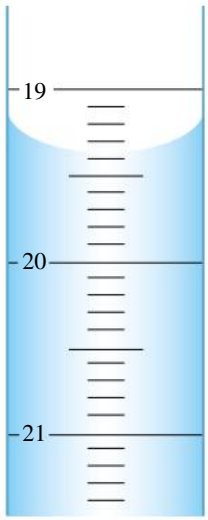


FIGURE 4.2.2 The burette is read from the bottom of the meniscus and the volume is estimated to the second decimal place. The volume measurement in this case is 19.38 mL.

Consider the titration data represented in Table 4.2.2.

TABLE 4.2.2 Titration data collected over five trials

Titration number	1	2	3	4	5
Final burette reading	20.20	40.82	20.64	41.78	21.86
Initial burette reading	0.00	21.00	1.00	22.00	2.00
Titre (mL)	20.20	19.82	19.64	19.78	19.86

The first reading is a rough reading that gives an idea of the approximate end point. Titres 2, 4 and 5 are the concordant titres: they are within 0.10 mL from highest to lowest of each other. The difference between the highest and lowest readings is 19.86–19.78 = 0.08 mL, which is within the acceptable range for concordant results. Since titration number 3 is not within the acceptable range (19.78–19.82), it is not included in any calculation. The mean (average) titre is:

$$\frac{19.82+19.78+19.86}{3} = 19.82\,\text{mL}$$

CALCULATIONS IN VOLUMETRIC ANALYSIS

Consider the data gained in an acid–base titration in which the concentration of a dilute solution of hydrochloric acid was determined by titration with a standard solution of sodium hydroxide.

The data gained from the titration is summarised in Table 4.2.3.

TABLE 4.2.3 Sample data obtained from a volumetric analysis

Volume of aliquot of HCl	25.00 mL
Concentration of standard NaOH solution	1.00 mol L^{-1}
Titre volumes of NaOH	25.05 mL, 22.10 mL, 22.00 mL, 22.05 mL

The concentration of hydrochloric acid is calculated by following a number of steps. These steps are summarised in the flow chart shown in Figure 4.2.3.

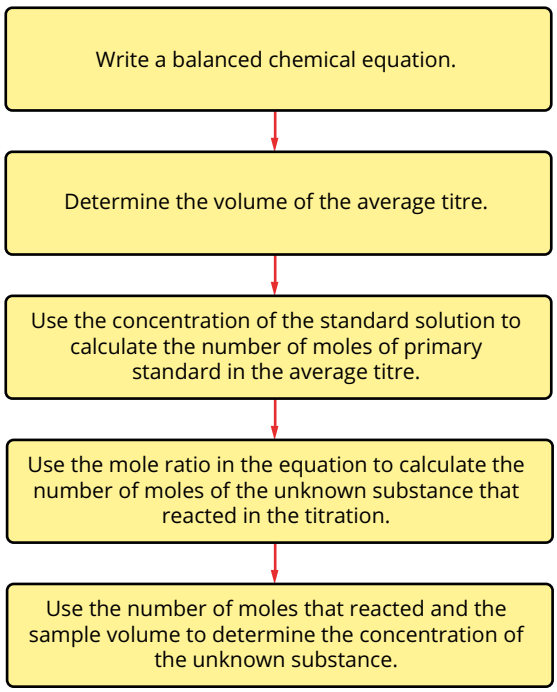


FIGURE 4.2.3 This flow chart summarises the steps in the calculation of the concentration of an unknown substance using the data from a titration in which the standard solution was in the burette.

Worked example 4.2.1

SIMPLE TITRATIONS

The concentration of a solution of hydrochloric acid (HCl) was determined by titration with a standard solution of sodium hydroxide (NaOH).

A 25.00 mL aliquot of HCl was titrated with a 1.00 mol L^{-1} solution of NaOH. Titres of 25.05 mL, 22.10 mL, 22.05 mL and 22.00 mL were required to reach the end point.

Calculate the concentration of the hydrochloric acid solution.

Thinking	Working
Construct a balanced chemical equation for the reaction.	An acid is reacting with a metal hydroxide, or base, so the products will be a salt and water: $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
Determine the volume of the average titre.	The titre of 25.05 mL is discarded as it is not concordant (i.e. it is not within a range of 0.10 mL from highest to lowest of the other titre volumes). $\text{average titre} = \frac{22.10 + 22.05 + 22.00}{3}$ $= 22.05\ \text{mL}$
Calculate the number of moles of the standard solution that was required to reach the end point.	$n(NaOH) = cV$ $= 1.00 \times 0.02205$ $= 0.02205\ \text{mol}$
Use the mole ratio in the equation to calculate the number of moles of the unknown substance that would have reacted with the given number of moles of the standard solution.	$\text{mole ratio} = \frac{n(HCl)}{n(NaOH)} = \frac{1}{1}$ $n(HCl) = n(NaOH)$ $= 0.02205\ \text{mol}$
Determine the concentration of the unknown substance.	$c(HCl) = \frac{n}{V}$ $= \frac{0.02205}{0.02500}$ $= 0.882\ \text{mol}\ L^{-1}$
Express your answer to the appropriate number of significant figures.	The final result is rounded off to 3 significant figures corresponding to the smallest number of significant figures in the original data. Four significant figures are used in the earlier steps of the calculation to avoid rounding off errors. Concentration of HCl = 0.882 mol L^{-1}

➤ Try yourself 4.2.1

SIMPLE TITRATIONS

The concentration of a solution of barium hydroxide ($Ba(OH)_2$) was determined by titration with a standard solution of hydrochloric acid (HCl).

A 10.00 mL aliquot of $Ba(OH)_2$ solution was titrated with a 0.125 mol L^{-1} solution of HCl. Titres of 17.23 mL, 17.28 mL, 17.40 mL and 17.21 mL of HCl were required to reach the end point.

Calculate the concentration of the barium hydroxide solution.

Titrations that involve dilution

It is often necessary to dilute a solution before carrying out a titration in order to obtain concentrations that are more convenient to use. This will result in titres that are within the volume range of the burette.

Suppose you want to perform an acid–base titration to find the concentration of hydrochloric acid in concrete cleaner. The concrete cleaner is so concentrated that it has to be accurately diluted before the titration. The following additional data is recorded:

- the volume of the aliquot of undiluted concrete cleaner
- the volume of diluted solution that is prepared.

The data obtained from such a titration is summarised in Table 4.2.4.

TABLE 4.2.4 Data from a titration involving diluted concrete cleaner

Volume of undiluted concrete cleaner	25.00 mL
Volume of diluted concrete cleaner	250.0 mL
Volume of titre of diluted concrete cleaner	19.84 mL
Concentration of standard Na_2CO_3 solution	0.4480 mol L^{-1}
Volume of aliquot of Na_2CO_3 solution	20.00 mL

In this titration, 25.00 mL of concrete cleaner was diluted to 250.0 mL in a volumetric flask prior to taking a sample for titration. This means the **dilution factor** is $\frac{250.0}{25.00} = 10.00$. The undiluted concrete cleaner will be 10.00 times more concentrated than the concentration of the aliquot. This will be taken into account in the calculations.

The steps required to calculate the concentration of undiluted concrete cleaner are summarised in the flow chart shown in Figure 4.2.4.

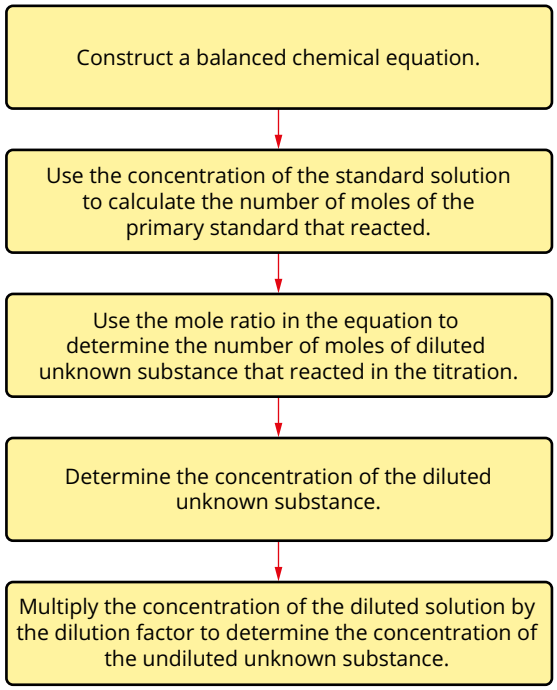


FIGURE 4.2.4 This flow chart shows the steps used in the calculation of the concentration of an unknown substance that has been diluted for use in a titration.

Worked example 4.2.2

TITRATION THAT INVOLVES DILUTION

A commercial concrete cleaner contains hydrochloric acid (HCl). A 25.00 mL volume of cleaner was diluted to 250.0 mL in a volumetric flask.

A 20.00 mL aliquot of 0.4480 mol L^{-1} sodium carbonate solution was placed in a conical flask. Methyl orange indicator was added and the solution was titrated with the diluted cleaner. The indicator changed permanently from yellow to pink when 19.84 mL of the cleaner was added.

Calculate the concentration of hydrochloric acid in the concrete cleaner.

Thinking	Working
Construct a balanced chemical equation.	A dilute acid is reacting with a metal carbonate so the products will be a salt, water and carbon dioxide gas: $2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$
Using the concentration of the standard solution, calculate the number of moles of the known substance that reacted in the titration. Remember that volume must be expressed in litres.	$n(Na_2CO_3) = cV$ $= 0.4480 \times 0.02000$ $= 0.008960\ mol$
Use the mole ratio in the equation to calculate the number of moles of the diluted unknown solution that reacted in the titration.	$\frac{n(HCl)}{n(Na_2CO_3)} = \frac{2}{1}$ $n(HCl) = \frac{2}{1} \times n(Na_2CO_3)$ $= \frac{2}{1} \times 0.008960$ $= 0.01792\ mol$
Calculate the concentration of diluted unknown solution reacting in the titration.	$V(\text{diluted HCl}) = 0.01984\ L$ $c(HCl) = \frac{n}{V}$ $= \frac{0.01792}{0.01984}$ $= 0.9032\ mol\ L^{-1}$
Multiply by the dilution factor to determine the concentration of undiluted concrete cleaner.	$\text{Dilution factor} = \frac{250.0}{25.00} = 10.00$ So undiluted $c(HCl)$ = diluted $c(HCl) \times 10.00$ $= 0.9032 \times 10.00$ $= 9.032\ mol\ L^{-1}$

➤ Try yourself 4.2.2

TITRATION THAT INVOLVES DILUTION

A commercial concrete cleaner contains hydrochloric acid (HCl). A 10.00 mL volume of cleaner was diluted to 250.0 mL in a volumetric flask.

A 20.00 mL aliquot of 0.2406 mol L^{-1} sodium carbonate solution was placed in a conical flask. Methyl orange indicator was added and the solution was titrated with the diluted cleaner. The indicator changed permanently from yellow to pink when 18.68 mL of the cleaner was added.

Calculate the concentration of hydrochloric acid in the concrete cleaner.



Uncertainties

The accuracy with which the volumes of the aliquot and titre are measured in volumetric analysis depends on the calibration of the equipment used. Often uncertainties are indicated on the equipment being used. However, if no **uncertainty** is indicated, the accepted uncertainty is always half the smallest division. For digital instruments, the absolute uncertainty is equal to the smallest decimal place displayed. Balance uncertainties depend on the number of decimal points. There are always errors associated with measurements of quantities such as mass and volume made during experimental work. These are some typical uncertainties associated with volumetric analysis:

- 20 mL pipette: ±0.03 mL
- 50 mL burette: ±0.05 mL for each reading
- 250 mL volumetric flask: ±0.3 mL
- 100 g capacity top loading balance: ±0.001 g
- 60 g capacity analytical balance: ±0.0001 g.

Other graduated laboratory glassware provides less precise measures:

- 50 mL measuring cylinder: ±0.1 mL
- 50 mL graduated beaker: ±5 mL.

Precision and accuracy

Every measurement in a **quantitative analysis** is subject to some form of error. Therefore, a calculation that makes use of these measurements will produce a result in which the errors have accumulated.

If repeated measurements of the same quantity yield values that are in close agreement, then the measurement is said to be **precise**. For example, a titration is generally repeated until at least three titres are obtained that are within narrowly specified limits. These are called concordant titres. Repeated measurement of the titres increases the precision of the result and minimises errors that may have affected one titre more than others.

If the average of a set of measurements of a quantity is very close to the true or accepted value of the quantity, then the measurement is said to be **accurate**. Figure 4.2.5 compares accuracy and precision.

Accuracy is the ability to obtain the correct measurement. To obtain accurate results, you must minimise systematic errors.

Precision is the ability to consistently obtain the same measurement. To obtain precise results, you must minimise random errors.

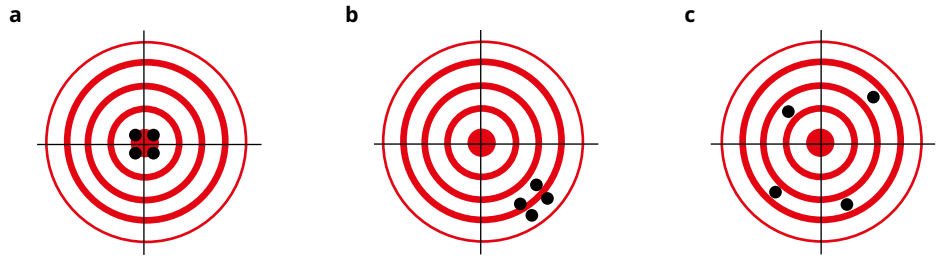


FIGURE 4.2.5 The holes in the targets illustrate the difference between accuracy and precision. Target (a) shows good accuracy and good precision. Target (b) illustrates poor accuracy but good precision, and target (c) shows both poor accuracy and poor precision. Analytical chemists aim to produce results that are both precise and accurate.

You can see that it is possible for a result to be precise but inaccurate.

Methods used for accurate quantitative analysis should be designed to minimise errors. Where errors cannot be avoided, any discussion of results should refer to the level of inaccuracy that may have accumulated. This requires an understanding of the different types of errors.

Types of errors

Mistakes

Mistakes are avoidable errors. Mistakes made during acid–base titrations could include:

- misreading the numbers on a scale
- mistakenly using a pipette of incorrect volume
- spilling a portion of a sample.

The effects of incorrectly rinsing volumetric glassware are detailed in Table 4.2.5.

TABLE 4.2.5 Rinsing glassware for volumetric analysis

Glassware	Correct	Incorrect
burette pipette	The final rinse of a burette or pipette should be with the acid or base they are about to be filled with.	Rinsing with water will dilute the acid or base solution.
volumetric flask titration flask (conical flask)	Volumetric and titration flasks should only be rinsed with deionised water.	Rinsing with acidic or basic solutions will introduce unmeasured amounts of acids or bases into the flask that can react and affect results.

A measurement that involves a mistake must be rejected and not included in any calculations or averaged with other measurements of the same quantity. Mistakes are not generally referred to as errors.

Systematic errors

A **systematic error** produces a constant bias in a measurement that cannot be eliminated by repeating the measurement. Systematic errors that affect an acid–base titration could include:

- a faulty balance
- a 20.0 mL pipette that delivers 20.2 mL
- an unsuitable indicator being used.

Whatever the cause, the resulting error is in the same direction for every measurement and the average will be either higher or lower than the true value.

Systematic errors are eliminated or minimised through calibration of apparatus and the careful design of a procedure. If the error cannot be eliminated, an effort should be made to determine its size so that the error can be taken into account in calculations.

Random errors

Random errors follow no regular pattern. The measurement is sometimes too large and sometimes too small. Random errors in volumetric analysis could include:

- inherent uncertainty in the last value after the decimal place in the measurement of the mass of a primary standard on an analytical balance
- difficulty in judging where the meniscus sits on the line when measuring a volume using a pipette
- difficulty in judging the fraction between two 0.1 mL scale markings on a burette.

The effects of random errors can be reduced by taking multiple measurements of the same quantity, then calculating an average. In volumetric analysis, the average of three concordant titres is used to reduce random error.

4.2 Review

SUMMARY

- Volumetric analysis is an analytical technique for determining the concentration of a solution by titrating it against a solution of known concentration (a standard solution) and volume.
- Volumetric flasks, pipettes and burettes are accurately calibrated pieces of glassware used in volumetric analysis.
- The point during a titration at which the reactants are present in equivalent amounts, as indicated by the coefficients in the equation for the reaction, is called the equivalence point.
- The end point is the point at which the indicator changes colour.
- Indicators used in acid–base titrations must have a sharp end point.
- The end point in an acid–base titration must be at or close to the equivalence point.
- Three concordant titres are usually obtained during volumetric analysis. Concordant titres lie within 0.10 mL from highest to lowest of each other.
- The concentration of acidic or basic solutions can be determined by volumetric analysis.
- Dilution of the unknown solution is sometimes required to obtain manageable titre volumes.
- The mole ratio in a balanced chemical equation allows the number of moles of a species in the equation to be calculated from the number of moles of any other species.
- All quantitative measurements involve an error and have an uncertainty associated with them.
- Accuracy refers to how closely a measurement agrees with the true value.
- Precision refers to how closely a set of measurements are to each other.
- A systematic error produces a constant bias in a measurement, which cannot be eliminated by repeating the measurement.
- A random error has an equal chance of being greater or lower than the true value.

KEY QUESTIONS

Retrieval

1 A solution of sodium hydroxide (NaOH) was standardised by titrating it using 25.00 mL aliquots of a standard solution of potassium hydrogen phthalate. The concentration of ethanoic acid (CH_3COOH) in vinegar was then found by diluting a 10.00 mL aliquot of vinegar into a volumetric flask. 20.00 mL aliquots of the diluted vinegar were then taken from the volumetric flask and titrated with the standardised NaOH solution.

a Name the solution that would have been made directly from a primary standard.

b Determine the solution that should be used to rinse the following pieces of equipment.

i 10.00 mL pipette

ii volumetric flask used to dilute vinegar

iii burette

2 Identify which of the following would be concordant titres: 15.42 mL, 16.22 mL, 16.26 mL, 17.01 mL and 16.18 mL. Explain your decision.

Comprehension

3 Explain the use of each of the following pieces of equipment.

a burette

b pipette

c standard flask

Analysis

4 The following titres were obtained when a solution of sulfuric acid (H_2SO_4) was titrated against a standard solution of potassium hydroxide.

Trial	1	2	3	4	5
Titre (mL)	26.28	25.46	25.38	25.62	25.42

Calculate the average volume of H_2SO_4 that would be used in volumetric calculations.

5 A 20.00 mL aliquot of sulfuric acid solution is neutralised by the addition of 22.98 mL of 1.34 mol L^{-1} potassium hydroxide solution. The equation for the reaction is:

$$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$$

Calculate the concentration of the sulfuric acid solution.

continued over page

4.2 Review *continued*

6 The concentration of ethanoic acid (CH_3COOH) in vinegar was determined by titration with a standardised solution of sodium hydroxide (NaOH). A 25.00 mL aliquot of vinegar required 21.56 mL of 0.995 mol L^{-1} NaOH to reach the end point.

- **a** Construct an equation for the reaction between ethanoic acid and sodium hydroxide.
- **b** Calculate the number of moles of NaOH used in the titration.
- **c** Calculate the number of moles of ethanoic acid that reacted.
- **d** Calculate the concentration of ethanoic acid in the vinegar.

7 A commercial concrete cleaner contains hydrochloric acid. A 25.00 mL volume of cleaner was diluted to 250.0 mL in a volumetric flask. A 25.00 mL aliquot of 0.5000 mol L^{-1} sodium carbonate solution was placed in a conical flask. Methyl orange indicator was added and the solution was titrated with the diluted cleaner. The indicator changed permanently from yellow to pink when 23.92 mL of the diluted cleaner had been added.

The equation for the reaction is:

$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + 2H_2O(l)$

Calculate the concentration of hydrochloric acid in the concrete cleaner.

Volumetric analysis



Research and planning

Aim

- To determine the concentration of ethanoic acid in samples of white vinegar using a standard solution as a reference.
- To gain an understanding of the techniques of volumetric analysis.
- To recognise the end point in an acid–base titration using an indicator.

Rationale (scientific background to the experiment)

The sour taste of vinegar is due to the presence of ethanoic acid (CH_3COOH). Ethanoic acid is a weak acid that is only partially ionised in water:

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

The concentration of ethanoic acid in a particular sample of vinegar can be determined by neutralising the vinegar with a base such as sodium hydroxide of known concentration. The more sodium hydroxide that is required for the reaction, the more ethanoic acid is present in the vinegar.

Timing

60 minutes

Materials

- 25 mL white vinegar samples—at least three varieties of vinegar
- 250 mL 0.1 mol L^{-1} sodium hydroxide (NaOH) solution
- phenolphthalein indicator
- 250 mL deionised water
- 3 × 100 mL conical flask
- 1 × 200 mL volumetric (standard) flask
- 1 × 20 mL pipette
- 1 × pipette filler
- burette, bosshead, retort stand and clamp
- funnel
- white tile
- dropping pipette

Safety

Pre-lab safety information		
Material used	**Hazard**	**Control**
white vinegar	may irritate eyes	wear skin and eye protection
sodium hydroxide (NaOH)	irritating to skin and eyes	avoid contact; wear skin and eye protection
phenolphthalein indicator	harmful if ingested and may irritate skin and eyes	avoid contact; wear skin and eye protection
Please indicate that you have understood the information in the safety table. Name (print): _____ I understand the safety information (signature): _____		

Method

Risk assessment

Assessment of risks includes chemical hazards and physical hazards. Before you commence this practical activity, you must conduct a risk assessment. Complete the template in your skills and assessment book or download it from your eBook.

1. Record the brand name of the bottle of vinegar you are analysing in the Analysing section.
2. Dilute the vinegar by pipetting 20.00 mL into a 200 mL standard flask. Half fill the flask with deionised water and shake it well to mix the solution. Add more water then use the dropping pipette until the bottom of the meniscus is level with the calibration line of the flask. Mix thoroughly.
3. Rinse the burette with sodium hydroxide solution. Fill the rinsed burette with fresh standard sodium hydroxide solution. Record the initial burette reading to two decimal places in Table 1.
4. Place a 20.00 mL aliquot of the diluted vinegar into a 100 mL conical flask. Add three drops of phenolphthalein indicator.
5. Place the conical flask containing diluted vinegar on a white tile beneath the burette and titrate the sodium hydroxide against the vinegar solution, swirling the flask continuously. Stop when the indicator changes to a pink colour, which persists for a minute.
6. Record the final burette reading to two decimal places in Table 1.
7. Repeat the titration (steps 4 to 6) until three concordant titres for the sodium hydroxide have been obtained.
8. Repeat steps 1 to 6 for three different brands of vinegar. This step may be done by different groups and class results compared.
9. When cleaning up, thoroughly rinse the burette with water, followed by a small volume of diluted vinegar, and more water. Traces of sodium hydroxide solution left in the burette may cause taps to become 'frozen' in place.

Variables

i. Independent: the brand of vinegar, and hence the concentration of ethanoic acid.

ii. Dependent: the volume of the standard solution (NaOH) used.

iii. Controlled: the concentration of the standard solution (NaOH), the volume of the vinegar used, the water that is used for cleaning and dilution, and the indicator used.

Analysing

Raw data

Brand name of vinegar _____

Concentration of the standardised sodium hydroxide (to ~4 decimal places) _____

1 Create a table for the titre volumes of each sample for each brand of vinegar (Table 1).

TABLE 1 Results showing titre volumes of standard solution (NaOH)

Brand of vinegar	Initial burette reading (mL)	Final burette reading (mL)	Titre (mL)
Titre 1			
Titre 2			
Titre 3			
Titre 4			

Processed data

2 Construct an equation that represents the reaction that occurs between ethanoic acid and sodium hydroxide.

3 Calculate the average titre of the sodium hydroxide solution used during the titrations.

4 Calculate the number of moles of sodium hydroxide present in the average titre of sodium hydroxide solution.

5 Calculate the number of moles of ethanoic acid present in each 20.00 mL aliquot of diluted vinegar.

6 Calculate the concentration of ethanoic acid (in moles per litre) in the diluted sample of vinegar.

Reflect and check that your data analysis demonstrates these characteristics

- ☐ Effective investigation of phenomena is demonstrated by the collection of sufficient and relevant raw data.
- ☐ Accurate application of algorithms, visual and graphical representations of data is demonstrated by appropriate processing and presentation of data to aid the analysis and interpretation of data.

Analysis

7 Determine the concentration of ethanoic acid (in moles per litre) in the undiluted sample of vinegar.

8 Deduce the percentage by mass (%*m*/*v*) of ethanoic acid in the undiluted vinegar.

9 Identify the value of the systematic error that occurs in each of the samples.

10 Explain any random errors that may have occurred in your experiments.

Reflect and check that your analysis demonstrates these characteristics

- ☐ Systematic and effective analysis of evidence is demonstrated by a thorough and appropriate error analysis.
- ☐ Systematic and effective analysis of evidence is demonstrated by a thorough identification of relevant trends, patterns and relationships.
- ☐ Insightful and valid interpretation of evidence is demonstrated by drawing a valid and defensible conclusion based on the analysis.

Interpreting and communicating

Conclusion

1 **a** Detemine what conclusions can be inferred from the analysis of your results.

b Explain the evidence that leads you to these conclusions.

Evaluation

2 Assess your analysis and conclusion. Identify whether the experiment provided an effective and efficient method of determining the concentration of ethanoic acid in each brand of vinegar. Explain your evaluation.

Improvements

3 Critique the experiment. If you were to repeat the experiment, identify the steps that you would do differently. Discuss the following points in your answer:

a Analyse how you would change the methodology to help improve the accuracy of the results.

b Evaluate how accurately you performed the tasks and the skills that you need to improve on in your technique.

c Explain how the collection of data could be improved or uncertainty reduced.

Reflect and check that your evaluation demonstrates these characteristics

- ☐ Critical evaluation of processes is demonstrated by a discussion of the reliability and validity of the experimental process supported by evidence such as the quality of the data (as quantified in the error analysis).
- ☐ Critical evaluation of the conclusion is demonstrated by a discussion of the veracity of the conclusions with respect to the error analysis and limitations or sufficiency of the data.
- ☐ Insightful evaluation of processes and conclusions is demonstrated by a suggestion of improvements or extensions to the experiment which are logically derived from the analysis of the evidence.

Chapter review

WS 3.1.9 WS 3.1.10 S.A.T. IA1

04

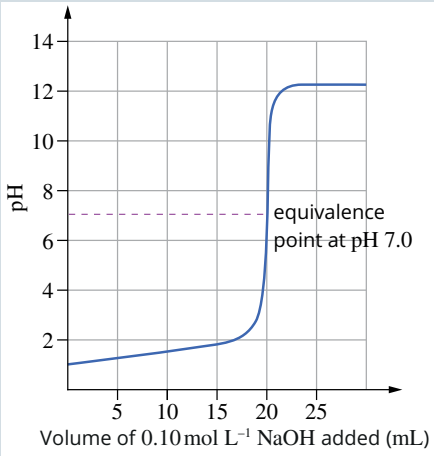
KEY TERMS

accurate
aliquot
average titre
burette
concordant titres
dilution factor
mistake
parallax error
pipette
precise
primary standard
quantitative analysis
random error
standard solution
systematic error
titre
uncertainty
volumetric analysis
volumetric flask

KEY QUESTIONS

Retrieval

1 The titration curve in the graph below shows the change in pH as a solution of 0.10 mol L^{-1} sodium hydroxide (NaOH) is added to a 20.00 mL solution of 0.10 mol L^{-1} hydrochloric acid (HCl).



The titration is repeated using a 0.20 mol L^{-1} sodium hydroxide solution. Select the correct statement about the second titration.

A The equivalence point occurs when 10 mL of NaOH is added and the pH is then 7.0.
B The equivalence point occurs when 40 mL of NaOH is added and the pH is then 7.0.
C The equivalence point occurs when 10 mL of NaOH is added and the pH is then greater than 7.0.
D The equivalence point occurs when 40 mL of NaOH is added and the pH is then greater than 7.0.

2 Sodium borate ($Na_2B_4O_7.10H_2O$) is used as a primary standard in volumetric analysis. Some properties of sodium borate are listed below. Identify which one of these properties is not important in the use of sodium borate as a primary standard.

A It is highly soluble in water.
B Its purity is greater than 99.5%.
C It is a soft, white, crystalline solid.
D It has a molar mass of 381 g mol^{-1}.

3 Determine which of the following indicators could be used in a titration in which the equivalence point is between pH 7.0 and 13.0.

	Indicator	pH range over which colour changes
I	methyl orange	3.1–4.4
II	methyl red	4.4–6.2
III	bromothymol blue	6.0–7.6
IV	phenolphthalein	8.3–10.0

A I only
B III only
C IV only
D I and II only

4 A standard solution of hydrochloric acid (HCl) is titrated four times against some sodium hydroxide (NaOH). The following titres were obtained: 21.05 mL, 20.75 mL, 20.65 mL and 20.75 mL.
The average titre is then calculated and used to determine the concentration of the NaOH. Select the correct value for the average titre.

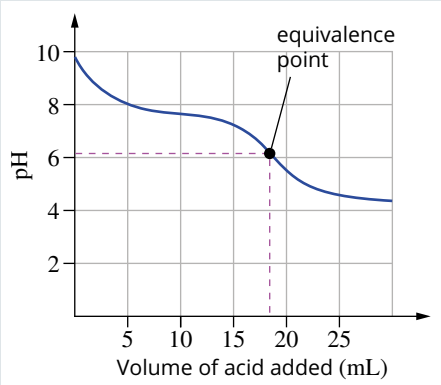
A 20.65 mL
B 20.72 mL
C 20.75 mL
D 20.80 mL

5 Select from the following list of characteristics of different chemical reactions the ones that would enable a reaction suitable for an acid–base titration.

A a fast reaction rate
B a slow reaction rate
C a large change in pH near the equivalence point
D a large equilibrium constant for the acid–base reaction

6 The concentration of battery acid can be determined by titrating a sample of it with a standard solution of a suitable base. Battery acid is sulfuric acid. Name a primary standard that would be suitable to use to make a standard solution for a successful volumetric analysis.

7 The graph shows the pH change occurring during an acid–base titration. Select a solution, at a concentration of 0.01 mol L^{-1}, that is most likely to be present in the conical flask for this titration.



8 A student wishes to determine the concentration of hydrochloric acid using sodium carbonate. List the steps required to accurately determine the concentration of hydrochloric acid using volumetric analysis.

Comprehension

9 Determine the concentration of a standard solution of hydrated oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) prepared by dissolving 25.21 g of hydrated oxalic acid in 250.0 mL of deionised water.

10 Determine the mass of sodium carbonate (Na_2CO_3) required to make a 500 mL standard solution of 0.400 mol L^{-1} Na_2CO_3.

11 Determine the volume of 0.200 mol L^{-1} KOH that is required to react with 30.0 mL of 0.100 mol L^{-1} HNO_3.

12 20.0 mL of a 1.00 mol L^{-1} solution of hydrochloric acid (HCl) reacts with 16.0 mL of a 1.00 mol L^{-1} solution of potassium carbonate (K_2CO_3).

- **a** Calculate the number of moles of HCl involved in the reaction.
- **b** Calculate the number of moles of K_2CO_3 involved in the reaction.
- **c** Identify the reactant that is in excess.
- **d** Calculate by how many moles this reactant is in excess.

13 A student performs two titrations:

- A 20.00 mL solution of a weak base is titrated with a 0.10 mol L^{-1} solution of HCl.
- A 20.00 mL solution of a strong base of the same concentration is also titrated with a 0.10 mol L^{-1} solution of HCl.

Explain the difference between the two titrations by discussing the pH of the initial base used in each titration.

Analysis

14 15.0 mL of a 2.00 mol L^{-1} solution of lithium hydroxide (LiOH) is added to 25.0 mL of a 0.400 mol L^{-1} solution of nitric acid (HNO_3). The equation for the reaction that occurs is:

$$HNO_3(aq) + LiOH(aq) \rightarrow LiNO_3(aq) + H_2O(l)$$

- **a** Determine which reactant is the limiting reactant.
- **b** Determine the mass of lithium nitrate ($LiNO_3$) that the reaction mixture will contain when the reaction is complete.

15 When a student prepared a 250.0 mL standard solution of sodium carbonate, the student added too much deionised water to the volumetric flask so that the solution level was above the graduation mark on the neck of the flask. Predict the effect of the student's mistake on the titration.

16 A standard solution of potassium carbonate (K_2CO_3) is made by adding 1.227 g of K_2CO_3 to a 250.0 mL volumetric flask and filling to the mark with water. 20.00 mL aliquots are taken and titrated against a sulfuric acid solution using methyl orange indicator. The average titre was 22.56 mL of sulfuric acid.

- **a** Construct the equation for the reaction.
- **b** Calculate the concentration of the K_2CO_3 solution.
- **c** Calculate the concentration of the sulfuric acid solution.

17 A chemistry student is required to determine accurately the concentration of a solution of hydrochloric acid. First the student makes up 250.00 mL of a standard solution of sodium carbonate (Na_2CO_3). This solution contains 1.358 g of Na_2CO_3. Next, the student takes a 20.00 mL aliquot of this standard solution and titrates it against the hydrochloric acid. An average titre of 20.24 mL of hydrochloric acid was required to reach the end point.

- **a** Construct a balanced equation for the reaction involving the titration.
- **b** Determine the concentration of the sodium carbonate solution.
- **c** Deduce the concentration of the hydrochloric acid as indicated by the student's results.
- **d** If sulfuric acid of the same concentration as the hydrochloric acid was used instead of the hydrochloric acid, predict the effect this would have had on the volume of acid required for the titration.

18 1.104 g of sodium carbonate (Na_2CO_3) is dissolved in water in a 250.00 mL volumetric flask. 20.00 mL aliquots of this solution were titrated with nitric acid (HNO_3). An average titre of 23.47 mL was found.

- **a** Determine the concentration of the Na_2CO_3 solution.
- **b** Calculate the concentration of the nitric acid.

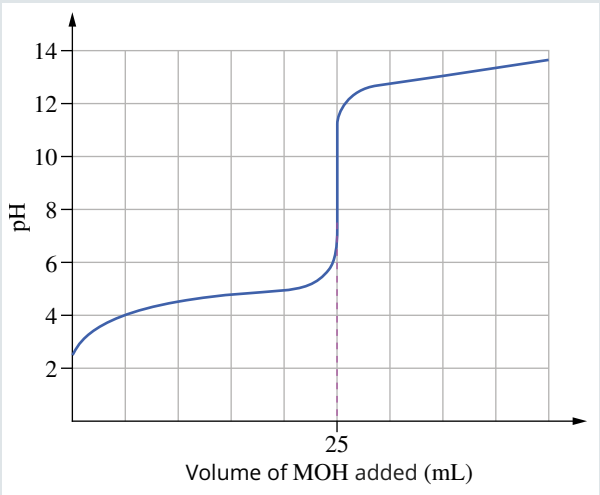
19 A student titrated an aliquot of standard sodium carbonate solution with hydrochloric acid in a burette. Deduce whether the concentration determined for the hydrochloric acid would be higher, lower or unchanged compared to the actual value if the following apparatus had been washed with water, but not dried, directly before use.

a pipette

b conical flask

c burette

20 HA is a monoprotic acid and MOH is a base. The titration curve shown is obtained when 20.0 mL of 0.100 mol L^{-1} HA is titrated with MOH.



a Determine if HA is a strong acid or a weak acid. Explain your reasoning.

b Methyl orange changes colour in the pH range 3.1 to 4.4, while phenolphthalein changes colour in the pH range pH 8.3 to pH 10.0. Select the indicator that would be the most suitable to use for this titration. Explain your reasoning.

c Determine the concentration of the base, MOH.

Knowledge utilisation

21 A manufacturer wants to know the exact concentration of hydrochloric acid in the concrete cleaner it produces.

a Determine the substance that you would use to make a standard solution for use in this titration and discuss why have you chosen this substance.

b Describe how would you prepare this standard solution for volumetric analysis.

c Explain how each piece of glassware used in a titration should be rinsed to ensure you obtain accurate and precise results.

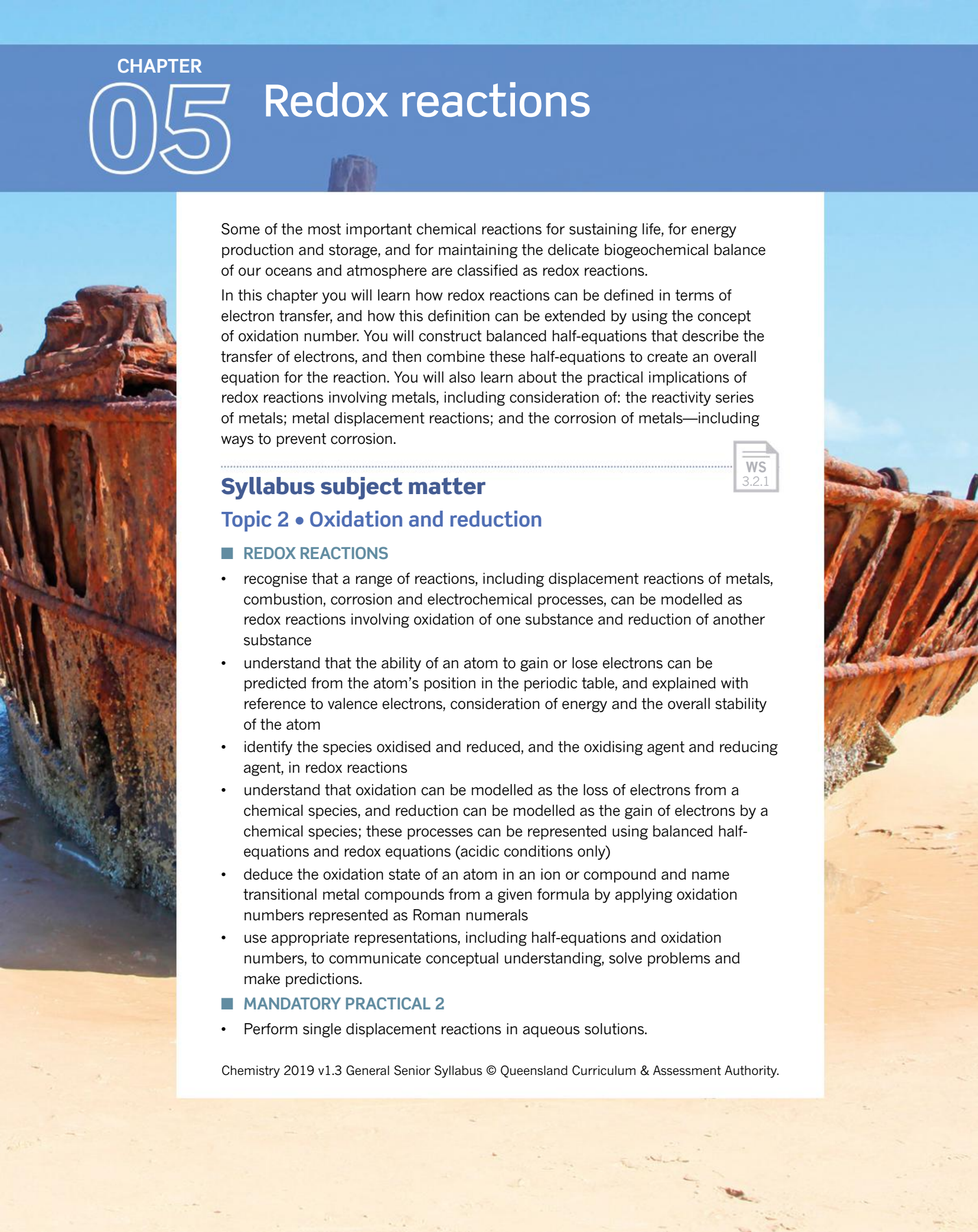
d A 25.00 mL sample of the concrete cleaner was diluted to 250.0 mL in a volumetric flask. A 25.00 mL aliquot of 0.5000 mol L^{-1} potassium carbonate solution was placed in a conical flask. Methyl orange indicator was added and the solution was titrated with the diluted cleaner. The indicator changed permanently from yellow to pink when 18.44 mL of the diluted cleaner had been added. Calculate the concentration of hydrochloric acid in the concrete cleaner.

e Determine whether the concentration calculated would be different if you used a standard solution of another base.



CHAPTER

05 Redox reactions



Some of the most important chemical reactions for sustaining life, for energy production and storage, and for maintaining the delicate biogeochemical balance of our oceans and atmosphere are classified as redox reactions.

In this chapter you will learn how redox reactions can be defined in terms of electron transfer, and how this definition can be extended by using the concept of oxidation number. You will construct balanced half-equations that describe the transfer of electrons, and then combine these half-equations to create an overall equation for the reaction. You will also learn about the practical implications of redox reactions involving metals, including consideration of: the reactivity series of metals; metal displacement reactions; and the corrosion of metals—including ways to prevent corrosion.

WS 3.2.1

Syllabus subject matter

Topic 2 • Oxidation and reduction

REDOX REACTIONS

- recognise that a range of reactions, including displacement reactions of metals, combustion, corrosion and electrochemical processes, can be modelled as redox reactions involving oxidation of one substance and reduction of another substance
- understand that the ability of an atom to gain or lose electrons can be predicted from the atom's position in the periodic table, and explained with reference to valence electrons, consideration of energy and the overall stability of the atom
- identify the species oxidised and reduced, and the oxidising agent and reducing agent, in redox reactions
- understand that oxidation can be modelled as the loss of electrons from a chemical species, and reduction can be modelled as the gain of electrons by a chemical species; these processes can be represented using balanced half-equations and redox equations (acidic conditions only)
- deduce the oxidation state of an atom in an ion or compound and name transitional metal compounds from a given formula by applying oxidation numbers represented as Roman numerals
- use appropriate representations, including half-equations and oxidation numbers, to communicate conceptual understanding, solve problems and make predictions.

MANDATORY PRACTICAL 2

- Perform single displacement reactions in aqueous solutions.

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5.1 Introducing redox reactions



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- describe redox reactions in terms of electron transfer
- recall that oxidation involves loss of electrons and reduction involves gain of electrons
- represent simple redox reactions using half-equations
- identify oxidising and reducing agents for simple redox reactions
- understand the reactivity of metals and metal displacement reactions in terms of redox processes
- understand the causes and effects of corrosion in terms of redox processes.



FIGURE 5.1.1 Potassium burning in chlorine gas—a spectacular example of a redox reaction

Your everyday life depends on a large number of chemical reactions. Many of these are **redox reactions**. The term 'redox' is derived from the specific reduction and oxidation processes that, when combined, complete the overall redox reaction.

Redox reactions are occurring within you and around you all the time. From the respiration reactions that enable your cells to produce energy, and the combustion reactions that warm your home, to the reactions in the batteries that keep your mobile phone working. The spectacular reaction between potassium and chlorine gas shown in Figure 5.1.1 is also an example of a redox reaction.

REDOX REACTIONS—ELECTRON TRANSFER REACTIONS

Fundamentally, redox reactions involve a transfer of electrons from one chemical species to another. The atom, molecule or ion that loses electrons in a redox process is said to have undergone **oxidation**—oxidation involves loss of electrons. The atom, molecule or ion that gains electrons during a redox reaction is said to have undergone **reduction**—reduction involves a gain of electrons.

Early understandings of redox reactions

When chemistry evolved from the ancient study of alchemy, many of the reactions known to early chemists involved air. French chemist Antoine Lavoisier identified the reactive component of air and named it oxygen. As a result, reactions in which oxygen was a reactant were described as oxidation reactions. In air, the combustion of an element such as carbon, sulfur or iron produces an oxide:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$
$$S(s) + O_2(g) \rightarrow SO_2(g)$$
$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

Because elemental iron reacts readily with oxygen, iron is generally found in nature in ores containing minerals, such as haematite (Fe_2O_3) and magnetite (Fe_3O_4). The iron metal used extensively for construction has been extracted from iron ore in a blast furnace.

The extraction of iron from iron ore in a blast furnace can be represented by the equation:

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$

In this reaction, the iron(III) oxide has lost oxygen and the carbon monoxide has gained oxygen. The iron(III) oxide is described as having been **reduced** and the carbon monoxide is described as having been **oxidised**.

Origins of the words 'oxidation' and 'reduction'

Scientists first used the term 'oxidation' in the late 18th century after the work of Antoine Lavoisier. Lavoisier showed that the 'burning' of metals, such as mercury, involved a combination with oxygen.

The term 'reduction' was used long before this to describe the process of extracting metals from their ores. The word 'reduction' comes from the Latin *reduco*, meaning to restore.

The process of metal extraction was seen as restoring the metal from its compounds, such as iron from iron oxide or copper from copper(II) oxide. The reduction of copper(II) oxide to form copper powder occurs when copper(II) oxide is heated in the presence of hydrogen or methane gas, as shown in Figure 5.1.2. Some fine particles of copper escape with the gas, causing the green flame.

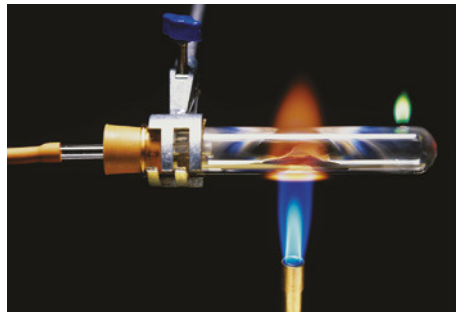


FIGURE 5.1.2 The reduction of copper(II) oxide to form copper powder occurs when it is heated in the presence of hydrogen or methane gas.

Transfer of electrons

Figure 5.1.3 shows that when a piece of magnesium ribbon is heated in a flame it burns with a brilliant white flame. Magnesium oxide powder is the product formed from this chemical reaction.



FIGURE 5.1.3 Magnesium ribbon burns brightly when heated in air to form a white powder, magnesium oxide.

This reaction can be represented by the equation:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

The reaction involves a loss and gain of electrons by the reactants, which can be represented by two **half-equations**.

Each magnesium atom loses two electrons to form a magnesium (Mg^{2+}) ion. The half-equation for this part of the overall reaction is written as shown. The electronic configurations are also shown:

$$\underset{2,8,2}{Mg(s)} \rightarrow \underset{2,8}{Mg^{2+}(s)} + 2e^-$$

Notice that when electrons are lost, they appear as products (on the right-hand side) in the half-equation.

At the same time, each oxygen atom in the oxygen molecule (O_2) gains two electrons (i.e. four electrons per oxygen molecule):

$$\underset{2,6}{O_2(g)} + 4e^- \rightarrow \underset{2,8}{2O^{2-}(s)}$$

Notice that when electrons are gained, they appear as reactants (on the left-hand side) in the half-equation. The electrons that are gained by the oxygen have come from the magnesium atoms.

Note that there is no overall loss of electrons, but a transfer of electrons from one atom to another. If an atom, ion or molecule loses electrons, there must be another atom, ion or molecule that gains electrons. Therefore, oxidation and reduction always occur simultaneously and cannot occur independently of one another.

Atoms also lose and gain electrons in many other reactions, and this transfer of electrons provides a widely used definition of oxidation and reduction.

The simple mnemonic 'OIL RIG' can be used to assist in remembering the differences between oxidation and reduction processes:

Oxidation
Is
Loss

Reduction
Is
Gain

> **Oxidation is defined as the loss of electrons.**
> **Reduction is defined as the gain of electrons.**

Electron transfer, electron configurations and the periodic table

The burning of magnesium described above involves metal magnesium atoms losing electrons and non-metallic oxygen atoms gaining electrons. You may recall from Units 1 and 2 that metals have relatively low electronegativity values and relatively low ionisation energies. This means that metal atoms have a relatively low tendency to draw valence electrons to themselves within chemical bonds and tend to lose valence electrons to other species in chemical reactions. In other words, metals tend to undergo oxidation during chemical reactions. Conversely, non-metals have relatively high electronegativity values and high electron affinity values. This means that non-metals

have a strong tendency to draw valence electrons to themselves in chemical bonds and tend to gain electrons from other species in chemical reactions. In other words, non-metals tend to undergo reduction during chemical reactions.

When a metal atom loses electrons, the atom becomes a stable cation with a stable electron configuration. In the case of the magnesium atom there are 12 electrons in total, with two electrons in the valence shell. The full electron configuration is 2,8,2. The loss of the two valence electrons leads to the formation of the Mg^{2+} ion, which has an electron configuration equivalent to that of the noble gas, neon (i.e. 2,8)—which we know is a very stable electron configuration.

When a non-metal atom gains electrons, the atom becomes a stable anion with a stable electron configuration. In the case of the oxygen atom, there are eight electrons in total with six electrons in the valence shell. The full electron configuration of oxygen is 2,6 and the valence shell can readily accommodate (or accept) two more electrons. The gain of two valence electrons forms the O^{2-} ion which also has the stable electron configuration of neon (i.e. 2,8).

When atoms undergo redox processes the number of electrons transferred is determined by the electron configurations of the atoms involved. Electrons are lost or gained to achieve a stable electron configuration. For main group elements this means that the position of the element in the periodic table can be used to predict how many electrons will be lost or gained.

Figure 5.1.4 shows the stable ions for a range of main group elements. We can see that **main group metals** lose enough electrons to achieve the same number and arrangement of electrons as the noble gas immediately preceding it in the periodic table. Conversely, main group non-metal elements will gain enough electrons to achieve the same number and arrangement of electrons as the noble gas immediately following it in the periodic table.

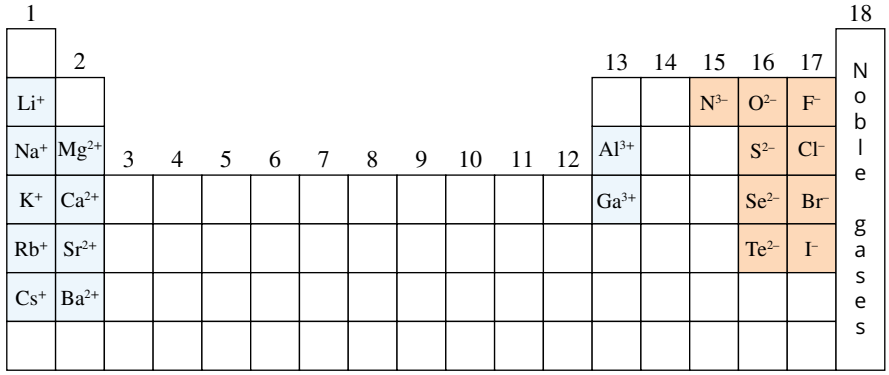


FIGURE 5.1.4 Predicting ionic charges using the periodic table

Other examples of redox reactions

Many redox reactions do not involve a reaction with oxygen. The reaction between potassium and chlorine shown in Figure 5.1.1 on page 118 is an example:

$$2K(s) + Cl_2(g) \rightarrow 2KCl(s)$$

Oxidation half-equation: $K(s) \rightarrow K^+(s) + e^-$

Reduction half-equation: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$

Another example is the reaction between copper and liquid sulfur:

$$Cu(s) + S(l) \rightarrow CuS(s)$$

Oxidation half-equation: $Cu(s) \rightarrow Cu^{2+}(s) + 2e^-$

Reduction half-equation: $S(l) + 2e^- \rightarrow S^{2-}(s)$

You will note that in each of the above chemical equations the charge on each of the atoms changes during the chemical reaction. A change in electrical charge on atoms, ions or molecules is one way that chemical reactions can be identified as redox reactions.

Worked example 5.1.1

UNDERSTANDING SIMPLE OXIDATION AND REDUCTION REACTIONS

Construct the oxidation and reduction half-equations for the reaction with the overall equation:

$$2Li(s) + Br_2(l) \rightarrow 2LiBr(s)$$

Thinking	Working
Identify the ions in the product.	LiBr is made up of Li^+ and Br^- ions.
Construct the half-equation for the oxidation of the reactant that forms positive ions and balance the equation with electrons.	$Li(s) \rightarrow Li^+(s) + e^-$
Construct the half-equation for the reduction of the reactant that forms negative ions and balance the equation with electrons.	$Br_2(l) + 2e^- \rightarrow 2Br^-(s)$

➤ Try yourself 5.1.1

UNDERSTANDING SIMPLE OXIDATION AND REDUCTION REACTIONS

Construct the oxidation and reduction half-equations for the reaction with the overall equation:

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

Oxidising agents and reducing agents

Just as an employment agent enables a client to become employed, an **oxidising agent** or **oxidant** enables or causes another chemical to be oxidised. Similarly, a **reducing agent**, or **reductant**, enables or causes another chemical to be reduced. Redox reactions always involve an oxidising agent and a reducing agent that react together.

In the reaction between magnesium and oxygen shown in Figure 5.1.5, magnesium is being oxidised by oxygen. So, oxygen is the oxidising agent. In turn, oxygen is gaining electrons from magnesium. It is being reduced by the magnesium, so magnesium is the reducing agent.

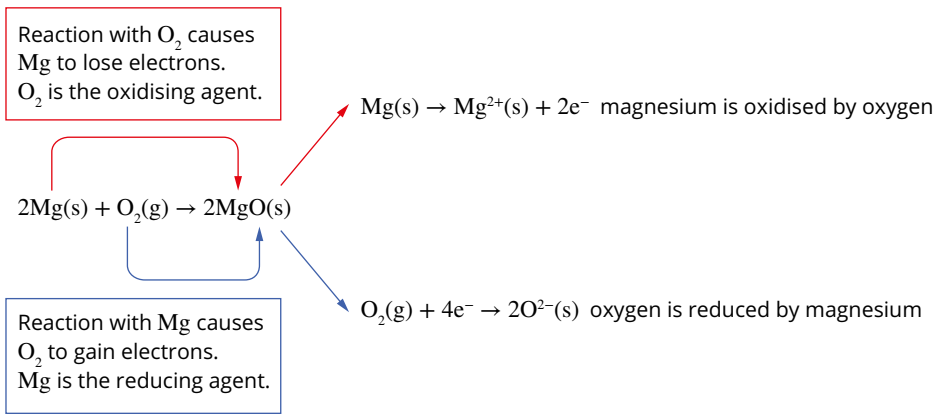


FIGURE 5.1.5 In the reaction between magnesium and oxygen, magnesium is the reducing agent and oxygen is the oxidising agent.

Since metals tend to lose electrons, they act as reducing agents. Conversely, since non-metals tend to gain electrons, they act as oxidising agents.

Figure 5.1.6 on page 122 summarises the list of redox terms introduced in this module.

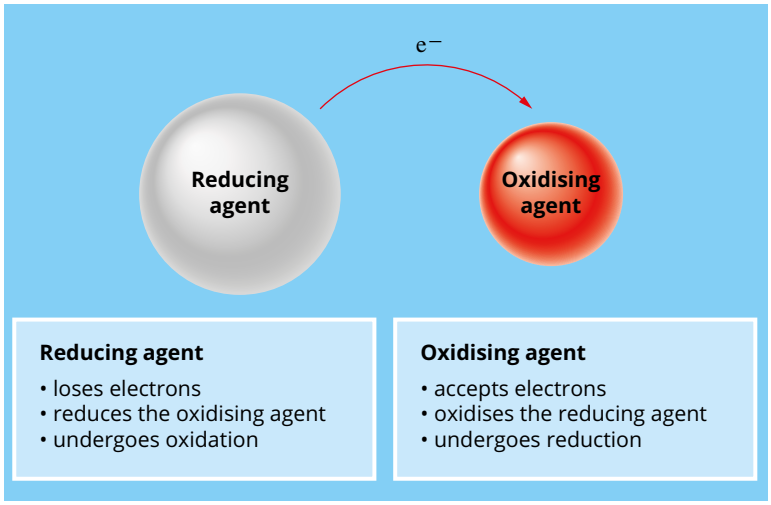


FIGURE 5.1.6 Summary of redox reaction terms

Balancing simple redox equations

Half-equations enable you to see the detail of what is happening in a redox reaction. Like other chemical equations, half-equations must be balanced so there is the same number of atoms of each element on each side of the arrow. Similarly, charge must also be balanced. Half-equations and full redox equations should indicate the states of all the species in the reaction as well.

Reducing agents cause another chemical to be reduced. In the reaction, they are oxidised.

Oxidising agents cause another chemical to be oxidised. In the reaction, they are reduced.

Worked example 5.1.2

WRITING SIMPLE HALF-EQUATIONS

When sodium metal reacts with fluorine gas (F_2), solid sodium fluoride is formed. The oxidation and reduction reactions can be represented by two half-equations.

Construct these half-equations and identify the substances that are oxidised and reduced.

Thinking	Working
Identify one reactant and the product it forms and represent them on each side of an equation. Balance the equation for the element.	$F_2(g) \rightarrow 2F^-(s)$
Add electrons to balance the equation for charge.	$F_2(g) + 2e^- \rightarrow 2F^-(s)$
To decide whether the reactant is oxidised or reduced, remember that oxidation is loss of electrons and reduction is gain of electrons.	Electrons are gained, so this is reduction. The $F_2(g)$ is being reduced.
Identify the second reactant and the product it forms, and represent them on each side of an equation. Balance the equation for the element.	$Na(s) \rightarrow Na^+(s)$
Add electrons to balance the equation for charge.	$Na(s) \rightarrow Na^+(s) + e^-$
To decide whether the reactant is oxidised or reduced, remember that oxidation is loss of electrons and reduction is gain of electrons.	Electrons are lost, so this is oxidation. The Na(s) is being oxidised.

➤ Try yourself 5.1.2

WRITING SIMPLE HALF-EQUATIONS

When a piece of copper metal is placed into a silver nitrate solution, silver metal is formed and the solution gradually turns blue, indicating the presence of copper(II) ions in the solution. The oxidation and reduction reactions can be represented by two half-equations.

Construct these half-equations and identify the substances that are oxidised and reduced.

Writing an overall redox equation

When writing equations for redox reactions, the two half-equations are normally written first and then added together to obtain an overall equation.

An overall equation does not show any electrons transferred; all the electrons lost in the oxidation reaction are gained in the reduction reaction. One, or perhaps both, of the half-equations may need to be multiplied by a factor to ensure that the electrons balance and can be cancelled out in the overall equation.

Consider the reaction of sodium and chlorine gas. In this reaction, each Na atom is oxidised and loses one electron. Each Cl_2 molecule is reduced and gains two electrons:

$$Na(s) \rightarrow Na^+(s) + e^-$$
$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$$

Two Na atoms must therefore be oxidised to provide the electrons required by each chlorine molecule that is reduced. To write an overall equation for this reaction, the half-equation involving the oxidation of Na is multiplied by a factor of two before combining it with the half-equation for reduction of Cl_2:

$$2Na(s) \rightarrow 2Na^+(s) + 2e^-$$

You can now write the two half-equations and add them to find the overall equation:

$$2Na(s) \rightarrow 2Na^+ + 2e^-$$
$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$$

When the electrons have been cancelled, the overall equation is:

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

When writing an overall redox equation from two half-equations, you need to balance the number of electrons.

Worked example 5.1.3

BALANCING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Sodium metal is oxidised by oxygen gas in air to form solid sodium oxide. Construct the half-equations for the reaction and hence construct the balanced overall equation.	
Thinking	**Working**
Identify one reactant and the product it forms, and represent them on each side of the equation. Balance the equation for the element.	$O_2(g) \rightarrow 2O^{2-}(s)$
Add electrons to balance the equation for charge.	$O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$
Identify the second reactant and the product it forms, and represent them on each side of the equation. Balance the equation for the element.	$Na(s) \rightarrow Na^+(s)$
Add electrons to balance the equation for charge.	$Na(s) \rightarrow Na^+(s) + e^-$
Multiply one equation by a suitable factor to ensure that the number of electrons is balanced. In this case we multiply the oxidation half-equation by four since the reduction of oxygen requires four electrons so the oxidation of sodium must supply four electrons.	$(Na(s) \rightarrow Na^+(s) + e^-) \times 4$ $4Na(s) \rightarrow 4Na^+(s) + 4e^-$
Add the oxidation and the reduction half-equations together, cancelling out electrons so that none are in the final equation. Combine ions to create the formula of the product.	$O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$ $4Na(s) \rightarrow 4Na^+(s) + 4e^-$ When the electrons have been cancelled, the overall equation is: $4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

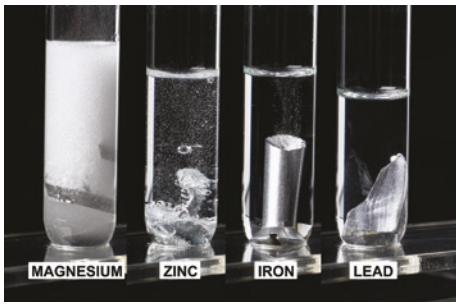


FIGURE 5.1.7 Some metals react with dilute acid to form a salt and hydrogen gas. The reaction between magnesium and dilute acid is extremely vigorous. The reaction between zinc and dilute acid is less vigorous. The reaction between iron and dilute acid is very slow. There is no reaction between lead and dilute acid. Based on this information, the order of metal reactivity from most reactive to least reactive is magnesium, zinc, iron and lead.

Element	Reactivity
K	most reactive
Na	
Li	
Ba	
Sr	
Ca	
Mg	
Al	
C*	
Mn	
Zn	
Cr	
Fe	
Cd	
Co	
Ni	
Sn	
Pb	
H_2*	
Sb	
Bi	
Cu	
Hg	
Ag	
Au	
Pt	least reactive

* Carbon (C) and hydrogen gas (H_2) added for comparison

FIGURE 5.1.8 Reactivity series of metals

➤ Try yourself 5.1.3

BALANCING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Aluminium metal is oxidised by oxygen gas in air to form solid aluminium oxide. Construct the half-equations for the reaction and hence construct the balanced overall equation.

THE REACTIVITY SERIES OF METALS

When metals undergo corrosion, some react quickly and vigorously with oxygen and water, and even more vigorously with acids. The reaction between other metals with oxygen is quite slow. Copper pipes oxidise slowly in the air, producing a brown-black copper oxide coating, while the reaction of magnesium ribbon in acid is more vigorous. These are both examples of redox reactions.

This module will examine the reactivity of different metals and describe how to write equations for reactions between metals and solutions of metal ions.

Reactivity of metals

Sodium, magnesium and iron are metals that are relatively easily oxidised. Sodium is oxidised so readily that it has to be stored under paraffin oil to prevent it from reacting with oxygen in the atmosphere. The oxidation of iron, which can eventually result in the formation of rust, can be an expensive problem.

Other metals do not corrode as readily. For example, platinum and gold are sufficiently inert and are found as pure elements in nature.

Figure 5.1.7 shows a comparison of four different metals reacting with dilute acid. By observing how readily metals react with oxygen, water, dilute acids and other metal salts, it is possible to determine an order of reactivity of metals.

The metals can be ranked in a list according to their reactivity, or ability to act as reducing agents. Figure 5.1.8 shows such a ranking, which is also known as a **reactivity series of metals**. Figure 5.1.9 shows the reduction half-equations for the metal cations as each cation gains electrons to form the corresponding metal.

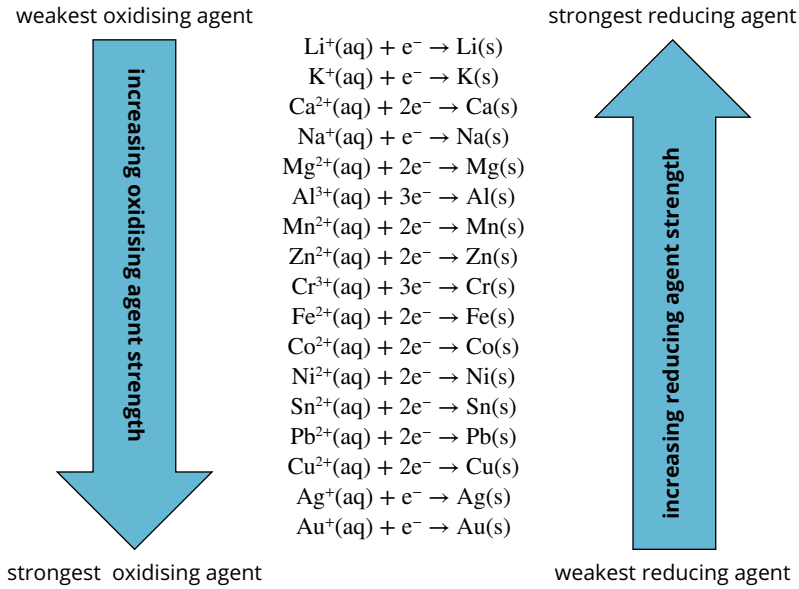


FIGURE 5.1.9 Reduction half-equations

The metals are listed on the right-hand side of the series, from the least reactive (Pt and Au) at the bottom to the most reactive (K and Na) at the top. The higher up the table a metal is placed, the more reactive it is. Remember that the most reactive metals are those that are oxidised most easily.

Metals, with their small number of valence electrons, generally act as reducing agents. A relatively small amount of energy is required to remove these valence electrons. In general, the lower the amount of energy required to remove the valence electrons, the more readily a metal will act as a reducing agent.

As you go down the reactivity series of metals in Figure 5.1.8:

- the metals, which are on the right-hand side, become less reactive. This means the metals higher in the series are easier to oxidise and therefore stronger reducing agents
- the metal cations, which are on the left-hand side, become increasingly easier to reduce and therefore more reactive. Cations lower in the series have a greater attraction for electrons so they are easier to reduce and are therefore relatively strong oxidising agents.

Metal displacement reactions

The order in which metals and their metal ions appear in the reactivity series enables you to predict which metals will **displace** other metals from solutions of their ions. Such reactions are known as **metal displacement reactions**.

A more reactive metal will be oxidised by, and donate its electrons to, the cation of a less reactive metal. The cation receives the electrons and is reduced. In other words, for a naturally occurring **spontaneous redox reaction** to occur, the metal ions of one metal must be below the other metal in the reactivity series, as shown in Figure 5.1.10. The more reactive metal acts as the reducing agent, and the metal ions of the other metal act as the oxidising agent.

When a strip of copper wire is placed in a solution of silver nitrate as shown in Figure 5.1.11, silver ions are reduced to silver atoms by copper atoms. The silver atoms are deposited as silver crystals. The copper atoms are oxidised to form a blue solution containing copper(II) ions. As a result of the reaction, copper(II) ions have displaced silver ions from the solution.

Silver ions have oxidised copper atoms, consistent with their order in the reactivity series, as shown in Figure 5.1.12. The overall redox reaction can be represented by the equation:

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

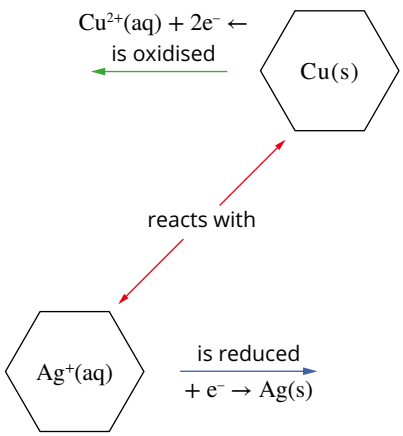


FIGURE 5.1.12 A spontaneous redox reaction occurs when copper is added to a solution of silver nitrate. Silver ions oxidise copper atoms.

A metal ion lower in the reactivity series (an oxidising agent) will react with a metal higher in the reactivity series (a reducing agent).

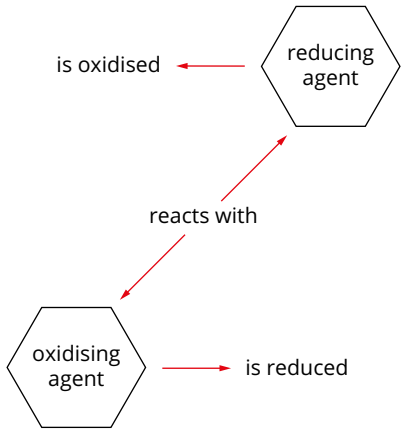


FIGURE 5.1.10 Predicting the reaction between an oxidising agent and a reducing agent

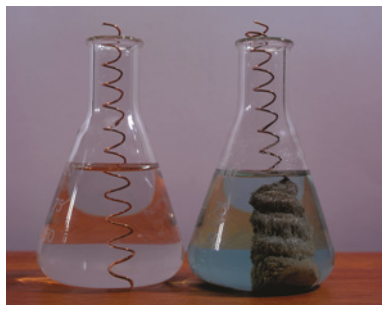


FIGURE 5.1.11 When a strip of copper wire is suspended in a solution of silver nitrate in the flask on the left, long crystals of silver metal start to form. In the flask on the right, the copper has displaced the silver from the solution.

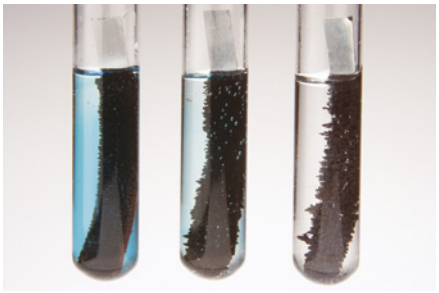


FIGURE 5.1.13 A brown deposit of copper metal is observed forming on the zinc and the blue copper(II) sulfate solution gradually becomes colourless as the concentration of Cu^{2+} ions decreases.

According to the reactivity series, a metal displacement reaction is predicted to occur when zinc is added to copper(II) sulfate solution, as shown in Figure 5.1.13.

Worked example 5.1.4

PREDICTING METAL DISPLACEMENT REACTIONS

Predict whether zinc will displace copper from a solution containing copper(II) ions and, if appropriate, construct the overall equation for the reaction.	
Thinking	**Working**
Locate the metal and the metal ions in the reactivity series.	Metals (reducing agents) are found on the right-hand side of the reactivity series and metal ions (oxidising agents) are found on the left-hand side of the reactivity series. $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$ $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $Co^{2+}(aq) + 2e^- \rightarrow Co(s)$ $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $2H^+(aq) + 2e^- \rightarrow H_2(g)$ $Sn^{4+}(aq) + 2e^- \rightarrow Sn(aq)$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Determine whether the metal is above (and to the left of) the metal ion in the table. If this is the case, there will be a reaction.	You can see from the reactivity series that Zn is on the right-hand side because it is a reducing agent and it is above Cu^{2+}, so there will be a reaction as shown in Figure 5.1.12.
Show the reduction reaction for the metal ion directly as it is written in the reactivity series, including states.	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Show the oxidation reaction for the metal from the reactivity series, writing the metal on the left-hand side of the arrow (as a reactant). Include states.	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
Combine the two half-equations, balancing electrons, to give the overall equation for the reaction.	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ --- $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

➤ Try yourself 5.1.4

PREDICTING METAL DISPLACEMENT REACTIONS

Predict whether copper will displace silver from a solution containing silver ions and, if appropriate, construct the overall equation for the reaction.

CORROSION

The reactions that occur when metals corrode are redox reactions. The costs associated with corroding metals are substantial, especially since iron, which is particularly prone to corrosion in the presence of water and oxygen, is so widely used as a structural material for buildings, bridges, gas and water pipes and ships. The effect of corrosion in water pipes is evident in the pumping system shown in Figure 5.1.14.



FIGURE 5.1.14 Corrosion is causing water to leak in these pipes in a pumping system.

In Australia, about $50 billion (approximately 3% of gross domestic product) is spent each year in an effort to prevent metals from corroding and replacing metal that has corroded. In spite of such efforts, steel structures continue to corrode, eventually producing the familiar orange-brown flakes known as rust, although corrosion prevention methods can slow down the rate of corrosion considerably.

This module will give you an opportunity to consider corrosion in terms of the causes and effects of an issue that relates to redox chemistry. In doing so, you will look at the redox reactions involved in corrosion both in the presence of water and in the absence of water.

Dry corrosion

Direct reaction with oxygen in the air to form a metal oxide is known as **direct corrosion** or **dry corrosion**. Sodium is so reactive that it must be stored under oil to prevent contact with oxygen. The following equation represents the dry corrosion of sodium:

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

Dry corrosion of aluminium forms a tough, impervious coating of aluminium oxide (Al_2O_3), which protects the metal underneath from further contact with oxygen. The aluminium window frame in Figure 5.1.15 is lightweight and corrosion resistant. Therefore it is an excellent material in situations where maintenance would be difficult.

Iron is much less reactive than sodium or aluminium; the rate of dry corrosion of iron is slow at room temperatures. When iron does corrode, it forms a coating that flakes off readily, leaving the metal underneath exposed to further corrosion.



FIGURE 5.1.15 An aluminium window frame is resistant to corrosion and is a useful material in situations where maintenance would be difficult.

Wet corrosion

The presence of moisture accelerates the corrosion of iron. This process is known as **wet corrosion**. The best-known example of wet corrosion is the formation of rust as a flaky, brown-red coating on iron.

Wet corrosion can occur in moist air or by direct immersion in water. Several factors affect the rate at which wet corrosion occurs. Consider the observations represented in Figure 5.1.16.



FIGURE 5.1.16 Wet corrosion. (a) A piece of steel wool (iron) does not corrode on supermarket shelves. However, once it becomes wet through use, it corrodes quickly. (b) An iron barbecue grill that has been coated with grease shows little sign of corrosion, even after being exposed to the rain for some time. (c) Rust in a car generally starts inside door frames, under mudguards, or in places where the paint has been chipped. (d) Shipwrecks corrode rapidly and will eventually disintegrate. (e) Corrosion occurs more rapidly in cities with a pollution problem, particularly where the pollutants include acidic oxides such as nitrogen dioxide and sulfur dioxide.

Each of these observations provides information about the factors that influence the rate of wet corrosion of iron. In general, corrosion is accelerated by:

- the presence of water
- impurities such as salt and acidic pollutants that dissolve in the water.

However, corrosion can be reduced when the iron is alloyed with certain other materials or when it has a protective coating. You will see this later when the methods of prevention of corrosion are discussed.

The wet corrosion process

Rust is a hydrated oxide of iron with the formula $Fe_2O_3 \cdot xH_2O$. There can be one to three water molecules associated with the iron oxide in its structure. An understanding of the steps involved in corrosion helps scientists to identify methods of corrosion prevention.

Step 1: Iron is oxidised to form Fe^{2+} ions at one region on the iron surface:

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

At the same time at another region on the surface, using the electrons produced by the oxidation process, oxygen is reduced in the presence of water to hydroxide ions:

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

The overall equation for step 1 is:

$$2Fe(s) + O_2(aq) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq)$$

Step 2: The formation of a precipitate of iron(II) hydroxide:

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$$

Steps 1 and 2 of the wet corrosion process are summarised in Figure 5.1.17.

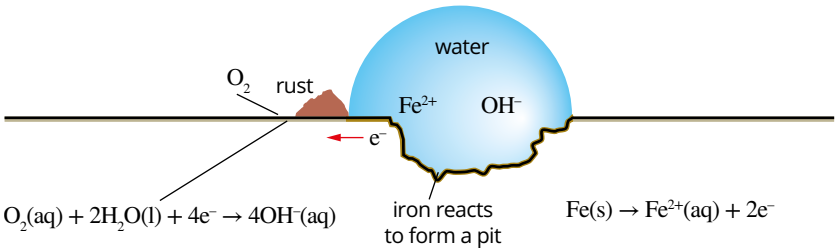


FIGURE 5.1.17 During wet corrosion, electrons are transferred through the iron from the area where oxidation occurs to the area where reduction occurs. Ions flow through the water droplets.

Step 3: Further oxidation of iron(II) hydroxide occurs in the presence of oxygen and water to produce iron(III) hydroxide, a red-brown precipitate:

$$4Fe(OH)_2(s) + O_2(aq) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$$

Step 4: In air, the iron(III) hydroxide loses water to form hydrated iron(III) oxide ($Fe_2O_3 \cdot xH_2O$), which is known as rust.

The porous rust easily flakes off the surface of the iron, exposing the iron underneath to further oxidation.

The wet corrosion of iron is accelerated if the water contains dissolved ions. This is particularly evident in coastal areas where iron objects are exposed to seawater. The presence of dissolved ions in the water increases its conductivity, which results in an increase in the rate of iron corrosion.

Prevention of corrosion

There are several ways to protect iron and steel structures against corrosion. These depend on the environment in which the structure is located, the design and intended use of the structure, and the relative costs of various protection measures.

The simplest way to protect against corrosion relies on the creation of a barrier between the iron and oxygen and water to provide a surface protection. Other methods are based on an understanding of the electrochemical nature of corrosion.

Surface protection

Surface protection involves covering the surface of the iron to prevent contact with oxygen and moisture. Materials such as paint and plastic can be used for this purpose. Moving parts, such as a bicycle chain, can be coated with oil or grease to reduce friction and prevent contact with oxygen and moisture.

Iron can also be protected by alloying with small quantities of metals such as chromium, nickel, manganese or molybdenum to produce stainless steel. The atoms of the metals used to make the **alloy** are all bonded into the metallic lattice. These metals oxidise slightly in air, but the oxide coating produced is continuous and unreactive. This oxide layer protects the metal from further oxidation.

Iron and steel can also be coated with thin layers of less reactive metals in a process known as **electroplating**. The 'tin' cans used to package food are made from steel plated with tin. Tin is a much less reactive metal than iron and does not corrode greatly in the atmosphere. In addition to the tin coating, cans used for food, such as the ones shown in Figure 5.1.18, have a plastic liner to prevent contact between the food and any metal oxides that may be present.



FIGURE 5.1.18 These food cans are made from steel that has been plated with tin to prevent them from corroding.

Electrochemical protection

Cathodic protection involves the use of a low-voltage, direct current (DC) power supply to give the iron being protected a negative charge. Because the iron is receiving electrons, oxidation is inhibited. Recall that oxidation is the loss of electrons.

The iron becomes the site of the reduction reaction, and is called the **cathode**. This method, represented in Figure 5.1.19, is used to protect large-scale steel structures such as wharves and pipelines. A single DC source operating at 4.2V and 2.5A will protect many kilometres of pipeline.

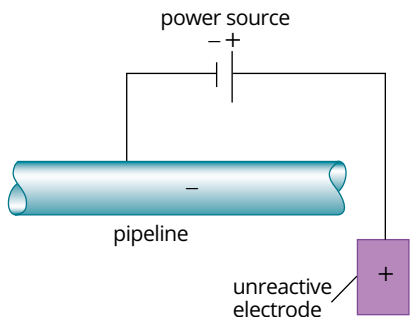


FIGURE 5.1.19 A pipeline carrying natural gas can be protected from corrosion if a direct current source is connected at intervals to give the pipe a negative charge.

Sacrificial protection also involves the iron acting as the cathode. A more easily oxidised metal, such as zinc, forms a region called the **anode** and is 'sacrificed' in order to protect the iron from corrosion. The more reactive metal loses electrons and forms metal cations in preference to the iron.

Iron that has been coated in zinc is known as galvanised iron and is used widely for roofs and sheds, as shown in Figure 5.1.20a. Galvanised iron is an example of sacrificial protection. When the zinc coating is scratched, the iron is still protected because the zinc loses electrons more readily than the iron. The diagram in Figure 5.1.20b depicts this process. The zinc slowly corrodes but the iron is protected for years.

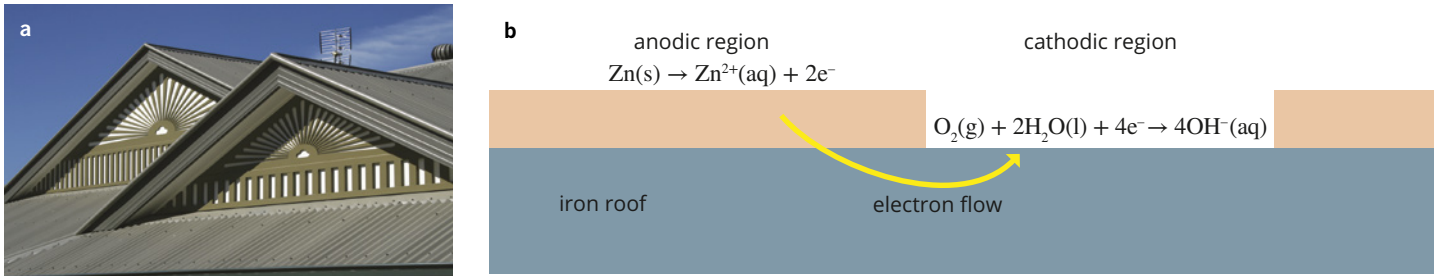


FIGURE 5.1.20 (a) A galvanised iron roof is a common sight in Australia. The zinc coating is oxidised in preference to the iron, protecting the structural role of the iron (b) Diagram showing cathodic and anodic regions.

Underground steel pipelines, bridge pillars and the steel hulls of ships can be protected by connecting them to blocks or plates of zinc, or other more reactive metals such as magnesium, as shown in Figure 5.1.21. Because these metals are more easily oxidised than iron, they lose electrons, which are transferred to the iron where reduction of oxygen and water occurs. The reactive metals, which are called **sacrificial anodes**, are eventually consumed and must therefore be replaced, but this is less expensive than replacing the steel structures that are being protected.



FIGURE 5.1.21 These aluminium sacrificial anodes are attached to the underwater steel structures of offshore gas platforms to protect them against corrosion.

PA 3.2.1

5.1 Review

SUMMARY

- Redox reactions are electron transfer reactions; one or more reactant substances lose electrons which are accepted by other reactants.
- The loss of electrons by a reactant is known as oxidation; the gain of electrons by a reactant is known as reduction.
- The loss and gain of electrons by reactants occurs simultaneously, so oxidation and reduction processes cannot occur independently of one another.
- Reduction processes and oxidation processes can each be represented via half-equations; the sum of the reduction and oxidation half-equations is used to generate the full redox equation.
- Oxidising agents cause the oxidation of another substance—they are themselves reduced in redox reactions; reducing agents cause the reduction of other substances—they are themselves oxidised in redox reactions.
- The relative reactivity of metals is represented in the metal reactivity series.
  - The metal reactivity series lists half-equations involving metals and their corresponding cations.
  - The half-equations involving stronger oxidising agents (the ones more easily reduced) appear lower in the reactivity series than those involving weaker oxidising agents.
  - The reactivity series can be used to predict whether a redox reaction is likely to occur.
- Metal displacement reactions involve the transfer of electrons from a more reactive metal to the positive ions of a less reactive metal in solution.
- Some metals readily corrode via oxidation processes. These processes can be characterised as 'dry corrosion' or 'wet corrosion'.
  - Dry corrosion refers to the oxidation of a metal by oxygen gas.
  - Wet corrosion involves both oxygen gas and water.
- Corrosion of metals can be prevented in a number of ways including:
  - surface protection (via paints, plastics and electroplating methods); or by
  - electrochemical protection (via cathodic protection or the use of sacrificial anodes).

KEY QUESTIONS

Retrieval

1 Define the following terms.
- **a** oxidation
- **b** reduction
- **c** redox reaction

2 Describe:
- **a** an oxidising agent
- **b** a reducing agent.

3 Use Figure 5.1.8 on page 124 to list the following in terms of increasing reducing strength: Mg, Ag, Ni, Sn, Li and Cu

4 State the difference between wet corrosion and dry corrosion.

5 Identify each of the following half-equations as involving either oxidation or reduction.
- **a** $Na(s) \rightarrow Na^+(aq) + e^-$
- **b** $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$
- **c** $S(s) + 2e^- \rightarrow S^{2-}(aq)$
- **d** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Comprehension

6 Summarise redox reactions by using the following terms to complete the sentences: gains, loses, I_2, I^-, reduced, oxidised.

When a reducing agent, such as Fe, reacts with an oxidising agent, such as _____, an ionic compound is formed. The reducing agent _____ electrons (is _____) and at the same time the oxidising agent _____ electrons (is _____). In this case, the products are Fe^{2+} and _____, which form FeI_2.

7 Explain why iron corrosion occurs more rapidly near coastal environments.

Analysis

8 Determine why underwater steel pillars often corrode more rapidly just beneath the surface of the water than above.

continued over page

5.1 Review *continued*

9 When a strip of magnesium metal is placed in a blue solution containing copper(II) ions ($Cu^{2+}(aq)$), crystals of copper appear and the solution soon becomes paler in colour.
- **a** Show that this reaction is a redox reaction by identifying the substance that is oxidised and the one that is reduced.
- **b** Construct a half-equation for the oxidation reaction.
- **c** Construct a half-equation for the reduction reaction.
- **d** Construct an overall redox equation.
- **e** Identify the oxidising agent and the reducing agent.
- **f** Explain why the solution loses some of its blue colour as a result of the reaction.

10 Refer to the reactivity series of metals on page 124 to predict whether the following reactions will spontaneously occur.
- **a** Silver metal is placed in a copper(II) nitrate solution.
- **b** A strip of aluminium is placed in a sodium chloride solution.
- **c** Magnesium is added to a solution of iron(II) sulfate.
- **d** Zinc is placed in a tin(II) sulfate solution.
- **e** A piece of tin is placed in a silver nitrate solution.
- **f** Lead(II) nitrate solution is poured into a beaker containing zinc granules.
- **g** Gold foil is added to a lead(II) nitrate solution.

11 Use the reactivity series of metals on page 124 to predict whether a reaction will occur in each of the following situations. Construct an overall equation for each reaction that you predict will occur.
- **a** Copper(II) sulfate solution is stored in an aluminium container.
- **b** Sodium chloride solution is stored in a copper container.
- **c** Silver nitrate solution is stored in a zinc container.

12 Balance the following half-equations and then classify each as an oxidation or a reduction reaction.
- **a** $Fe(s) \rightarrow Fe^{3+}(aq)$
- **b** $K(s) \rightarrow K^{+}(aq)$
- **c** $F_2(g) \rightarrow F^{-}(aq)$
- **d** $O_2(g) \rightarrow O^{2-}(aq)$

5.2 Identifying redox reactions

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- assign oxidation numbers to atoms in elements, compounds and polyatomic ions
- use oxidation numbers to determine whether a reaction is a redox reaction
- understand oxidation and reduction in terms of changes in oxidation numbers of atoms
- use oxidation numbers to identify oxidising and reducing agents
- use oxidation numbers to name ionic compounds involving transition metal ions
- use oxidation numbers to identify conjugate redox pairs.



How can we tell if a particular chemical reaction is in fact a redox reaction? In the reaction of magnesium (Mg(s)) with hydrochloric acid (HCl(aq)) we can see that charges on the Mg(s) and H^+(aq) ions change during the reaction. The net ionic equation for this reaction is:

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

The individual half-equations can be represented as:

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

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \text{ (reduction half-equation)}$$

Clearly there is a transfer of electrons from the magnesium metal to the H^+ ions, which changes the charge on both species. This change in charge is indicative of a redox reaction.

But what about a combustion reaction? For example, the combustion of methane (CH_4):

$$CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(l)$$

Or consider photosynthesis, which can be represented by this overall chemical equation:

$$6CO_2(g) + 6H_2O(l) \xrightarrow{\text{light}} C_6H_{12}O_6(s) + 6O_2(g)$$

Are these redox reactions? The substances represented in each of these equations are all molecular substances and have no net charge. We cannot say by simple inspection that there has been a change in charge of any of the atoms involved and we cannot readily determine if electron transfer has occurred. Therefore, we cannot easily determine if these reactions are redox reactions.

OXIDATION NUMBERS

It turns out that the combustion and photosynthesis reactions shown above are redox reactions and that a transfer of electrons has occurred between atoms of the reactant molecules. So the question remains; how can we tell if a chemical reaction is a redox reaction? And how can we tell which atom or molecule has been oxidised (and is therefore the reducing agent), and which atom or molecule has been reduced (and is therefore the oxidising agent)?

We do this by assigning **oxidation numbers** to atomic species or to individual atoms within molecular species. The oxidation number of an atom in a substance represents the charge that an atom would have if it was an ion.

The key to identifying whether a chemical reaction is a redox reaction is to determine if the oxidation number of any atoms change during the course of a reaction.

Rules for assigning oxidation numbers

If the oxidation number of a particular atom changes during a chemical reaction then we can say that the atom has undergone oxidation or reduction and that the reaction, overall, is a redox reaction.

Oxidation numbers are also referred to as **oxidation states**. The rules for assigning oxidation numbers (or states) to atoms in substances are outlined in Table 5.2.1. In the examples shown in the table, the oxidation number of an element is placed above its symbol. The plus or minus sign precedes the number and so distinguishes the oxidation number from the charge on an ion where the sign is generally placed after the number. For example, the oxide ion (O^{2-}) has a charge of 2– and an oxidation number of –2. While the values are the same in this instance, it is important to remember that oxidation states do not always indicate a charge on the species.

TABLE 5.2.1 Rules for determining oxidation numbers of elements in compounds

Rule	Examples
1 The oxidation number of a free element is zero.	$\overset{0}{Na}$, $\overset{0}{C}$, $\overset{0}{Cl_2}$, $\overset{0}{P_4}$
2 The oxidation number of a simple ion is equal to the charge on the ion.	$\overset{+1}{Na^+}$, $\overset{-1}{Cl^-}$, $\overset{+2}{Mg^{2+}}$, $\overset{-2}{O^{2-}}$, $\overset{+3}{Al^{3+}}$, $\overset{-3}{N^{3-}}$
3 In compounds, some elements have oxidation numbers that are regarded as fixed, except in a few exceptional circumstances. a Main group metals have an oxidation number equal to the charge on their ions. b Hydrogen has an oxidation number of +1 when it forms compounds with non-metals. Exception: In metal hydrides, the oxidation number of hydrogen is –1. c Oxygen usually has an oxidation number of –2. Exceptions: In compounds with fluorine, oxygen has a positive oxidation number. In peroxides, oxygen has an oxidation number of –1. d Halogens: The oxidation number of fluorine is –1 in all of its compounds. The oxidation number of the other halogens in their compounds (i.e. Cl, Br, I) is also –1 except where they are involved in compounds with O or another halogen above them in Group 17 in the periodic table.	ionic compounds: $\overset{+1}{K}Cl$, $\overset{+2}{Mg}SO_4$ compounds of H: $\overset{+1}{H_2}O$ metal hydrides: $Na\overset{-1}{H}$, $Ca\overset{-1}{H_2}$ compounds of O: $H_2\overset{-2}{O}$ compounds of O and F: $\overset{+2}{O}F_2$ peroxides: $H_2\overset{-1}{O_2}$, $Ba\overset{-1}{O_2}$ fluorine compounds: $\overset{+1}{H}\overset{-1}{F}$, $\overset{+2}{O}\overset{-1}{F_2}$ other halogen compounds: $\overset{+1}{H}\overset{-1}{Cl}$, $\overset{+1}{Cl_2}\overset{-2}{O}$, $\overset{+5}{Cl}\overset{-1}{F_5}$
4 The sum of the oxidation numbers of all atoms in a neutral compound is zero.	$\overset{+4}{C}\overset{-2}{O_2}$ Note that in CO_2, the oxidation number of each oxygen atom is written as –2; since the sum of all atoms must equal zero for a neutral compound then we can easily calculate that the oxidation number for the single C atom must be 4.
5 The sum of the oxidation numbers of all atoms in a polyatomic ion is equal to the charge on the ion.	$[\overset{+6}{S}\overset{-2}{O_4}]^{2-}$, $[\overset{-3}{N}\overset{+1}{H_4}]^+$
6 The most electronegative element is assigned the negative oxidation number.	$\overset{+2}{O}\overset{-1}{F_2}$, $\overset{+6}{S}\overset{-1}{F_6}$

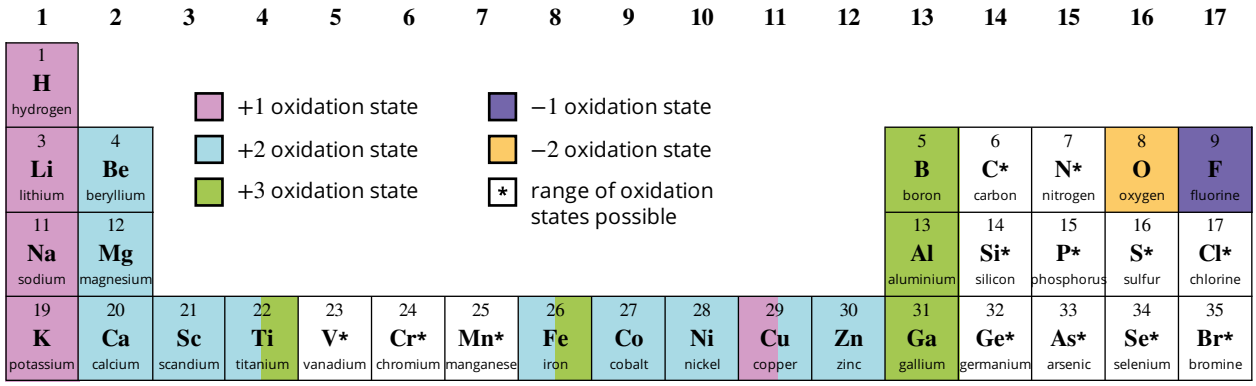
Oxidation numbers have no physical meaning and they do not indicate a formal charge nor are they representative of the physical or chemical properties of the substance. However, they are a useful tool for identifying which atoms have been oxidised and which atoms have been reduced.

If the oxidation number of an atom has increased after a chemical reaction, that atom has undergone oxidation.

If the oxidation number of an atom has decreased after a chemical reaction, that atom has undergone reduction.

Calculating oxidation numbers of atoms in compounds

The common oxidation states of the first 32 elements in their compounds are shown in the periodic table in Figure 5.2.1. Transition metals and some non-metals can have a range of oxidation states. These are usually calculated after applying the rules for all other elements in the compound.



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1 H hydrogen																
3 Li lithium	4 Be beryllium											5 B boron	6 C* carbon	7 N* nitrogen	8 O oxygen	9 F fluorine
11 Na sodium	12 Mg magnesium											13 Al aluminium	14 Si* silicon	15 P* phosphorus	16 S* sulfur	17 Cl* chlorine
19 K potassium	20 Ca calcium	21 Sc scandium	22 Ti titanium	23 V* vanadium	24 Cr* chromium	25 Mn* manganese	26 Fe iron	27 Co cobalt	28 Ni nickel	29 Cu copper	30 Zn zinc	31 Ga gallium	32 Ge* germanium	33 As* arsenic	34 Se* selenium	35 Br* bromine

FIGURE 5.2.1 Part of the periodic table showing the most common oxidation states of some elements.

For a compound containing several elements, you can use algebra and the rules given in Table 5.2.1 to calculate the oxidation number of an element.

Worked example 5.2.1

CALCULATING OXIDATION NUMBERS

Use the rules in Table 5.2.1 on page 134 to determine the oxidation number of each element in potassium perchlorate ($KClO_4$).

Thinking	Working
Identify an element that has a set value.	K is a main group metal in group 1. Applying rule 3a, the oxidation number of potassium is +1.
Identify any other elements that have set values.	According to rule 3c, oxygen has an oxidation number of −2 unless attached to fluorine or in a peroxide.
Use algebra to work out the oxidation number of other elements.	Let the oxidation number of chlorine in $KClO_4$ be x. Solve the sum of the oxidation numbers for x: $+1 + x + (4 \times -2) = 0$ $+1 + x - 8 = 0$ $x - 7 = 0$ $x = +7$
Show oxidation numbers above the elements in the formula.	$\overset{+1}{K}\overset{+7}{Cl}\overset{-2}{O_4}$ Note that the oxidation number of oxygen is written as −2 (not as −8), even though there are four oxygen atoms in the formula. Confirming rule 4 from Table 5.2.1 we can see that the sum of oxidation numbers of all atoms in the compound is zero (i.e. $1 + 7 + 4 \times -2 = 0$).

➤ Try yourself 5.2.1

CALCULATING OXIDATION NUMBERS

Use the rules in Table 5.2.1 on page 134 to determine the oxidation number of each element in sodium nitrate ($NaNO_3$).

USING OXIDATION NUMBERS

The oxidation number concept is a valuable tool that can be used to:

- identify whether a chemical reaction is a redox reaction (remember, if there is no change of oxidation number for all atoms involved in the reaction, excluding spectator ions, then the reaction is not a redox reaction)
- determine which substance is the oxidising agent and which is the reducing agent
- name ionic compounds involving cations derived from transition metals
- identify conjugate redox pairs.

Using oxidation numbers to identify oxidising and reducing agents

We have already noted that a change in oxidation number of an atom after a chemical reaction indicates that the reaction is a redox reaction. We also know that:

- an increase in oxidation number of an atom means that the atom has been oxidised; and
- a decrease in oxidation number of an atom means that the atom has been reduced.

Finally, we also know that an oxidising agent is itself reduced, and that a reducing agent is itself oxidised. We can therefore use this knowledge to assist in determining which reactant is the oxidising agent and which reactant is the reducing agent.

At the beginning of this chapter, you were alerted to a number of everyday processes that are redox reactions. Combustion reactions, where fuel is burned in order to produce heat while giving off CO_2 and water, are examples of redox reactions that are very important in our society. The equation for the burning of carbon in excess oxygen is:

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

At first glance, the reaction may not seem like a redox reaction because none of the species are ionic compounds so it is not clear which reactant is losing or gaining electrons. By using oxidation numbers, we can identify both an oxidation process and a reduction process for the reaction:

$$\overset{0}{C}(s) + \overset{0}{O_2}(g) \rightarrow \overset{+4-2}{CO_2}(g)$$

The carbon is oxidised because its oxidation number increases from 0 to +4, and the oxygen is reduced because its oxidation number decreases from 0 to −2. Furthermore, since the carbon is oxidised, it is identified as the reducing agent—it has enabled, or caused, the reduction of oxygen. Similarly, since oxygen has been reduced, it is identified as the oxidising agent—it has enabled, or caused, the oxidation of carbon.

In this way, the use of oxidation numbers allows you to look at a chemical reaction and determine whether it is a redox reaction and then, more specifically, to determine which reactant is the oxidising agent and which is the reducing agent.

Worked example 5.2.2

USING OXIDATION NUMBERS TO IDENTIFY OXIDISING AND REDUCING AGENTS

Determine whether the following is a redox reaction and (if so) identify the oxidising and reducing agents:

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

Thinking	Working
Determine the oxidation numbers for each element in the equation.	$\overset{-4+1}{C}H_4(g) + \overset{0}{2O_2}(g) \rightarrow \overset{+4-2}{C}O_2(g) + 2\overset{+1\ -2}{H_2O}(l)$
Assess if the oxidation number of any element has changed. If so, identify if it has increased (oxidation) or decreased (reduction).	The oxidation number of C has increased from –4 to +4, so the carbon in CH_4 has been oxidised. The oxidation number of O has decreased from 0 to –2, so oxygen has been reduced. The oxidation number for H has remained unchanged, so hydrogen has not undergone oxidation or reduction.
The compound or element containing the atom that has been oxidised is designated as the reducing agent. The compound or element containing the atom that has been reduced is designated as the oxidising agent.	CH_4 is identified as the reducing agent (it caused the reduction of O_2) and O_2 has been identified as the oxidising agent (it caused the oxidation of CH_4).

➤ Try yourself 5.2.2

USING OXIDATION NUMBERS TO IDENTIFY OXIDISING AND REDUCING AGENTS

Determine whether the following is a redox reaction and (if so) identify the oxidising and reducing agents:

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l)$$

Using oxidation numbers to name ionic compounds

As you learnt in Units 1 and 2, **transition elements** can form ions with a number of different charges. This means that many transition metals have variable oxidation numbers (or oxidation states). For example, there are two compounds that can be called iron chloride: $FeCl_2$ and $FeCl_3$.

Using the rules in Table 5.2.1 on page 134, you can see that the chloride ion has an oxidation number of –1. In $FeCl_2$ this means the oxidation number of iron is +2, whereas in $FeCl_3$ the oxidation number is +3.

To distinguish between the two iron chlorides, we insert Roman numerals to represent the appropriate oxidation number in the name:

- $FeCl_2$ is more correctly named iron(II) chloride
- $FeCl_3$ is more correctly named iron(III) chloride.

> For elements that can have variable oxidation states, the use of a Roman numeral in the name indicates the specific oxidation state of the element.

Using oxidation numbers to identify conjugate redox pairs

When a half-equation is written for an oxidation reaction, the reactant, a reducing agent, loses electrons. The product is an oxidising agent. We refer to the reactant and the product that it forms as a **conjugate redox pair**.

For example, consider the half-equation for the oxidation of zinc:

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

Zinc metal (Zn) is a reducing agent and forms $Zn^{2+}(aq)$, which is an oxidising agent. Zn(s) and $Zn^{2+}(aq)$ form a conjugate redox pair $Zn(s)/Zn^{2+}(aq)$.

In the $Zn(s)/Zn^{2+}(aq)$ conjugate redox pair, the oxidation number of zinc increases from 0 to +2. The increase in the oxidation number of zinc indicates that it is an oxidation half-reaction.

For the reduction half-equation, the reactant is an oxidising agent and will gain electrons. The product formed is a reducing agent. Therefore, another conjugate redox pair is present in the redox reaction.

When listing conjugate redox pairs, it is best to include the states of both the oxidising and reducing agent.

For example, consider the half-equation for the reduction of $Ag^+(aq)$:

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

$Ag^+(aq)$ is an oxidising agent and forms Ag(s), which is a reducing agent. $Ag^+(aq)$ and Ag(s) are also a conjugate redox pair. In this case, the oxidation number of silver decreases from +1 to 0, indicating that this is a reduction half-equation.

The relationship between changes in oxidation numbers and conjugate redox pairs can be seen by following the colour-coding in the equation in Figure 5.2.2. One conjugate redox pair is red and the other one is blue.

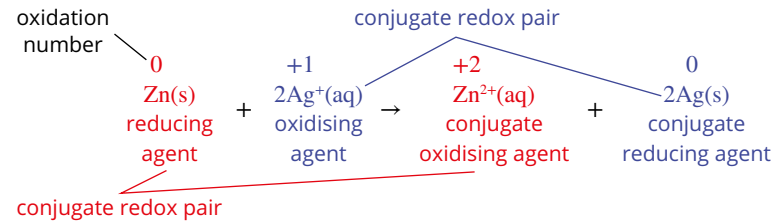


FIGURE 5.2.2 The change in oxidation numbers seen in conjugate redox pairs. For each redox reaction, there are two conjugate redox pairs.

5.2 Review

SUMMARY

- Oxidation numbers are calculated according to a set of rules, including:
  - free elements have an oxidation number of 0
  - in ionic compounds composed of simple ions, the oxidation number is equal to the charge on the ion
  - hydrogen in a compound usually has an oxidation number of +1
  - oxygen in a compound usually has an oxidation number of −2
  - the sum of the oxidation numbers in a neutral compound is 0
  - the sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion.
- An increase in the oxidation number of an element in a reaction indicates oxidation has occurred.
- A decrease in the oxidation number of an element in a reaction indicates reduction has occurred.
- For oxidation to occur, there must be a corresponding reduction.
- If there is no change in the oxidation number of any atoms involved in the equation for a particular reaction, then that reaction is not a redox reaction.
- The oxidation number (or oxidation state) is used to name ionic compounds containing transition metal ions. (N.B. the Roman numeral representation of the oxidation number is used.)
- A conjugate redox pair consists of an oxidising agent (a reactant) and the reducing agent (a product) that is formed when the oxidising agent gains electrons. In a redox reaction, if a conjugate redox pair consists of an oxidising agent (the reactant) and the reducing agent that is the product formed when the oxidising agent gains electrons, then the oxidation number of the oxidising agent (the reactant) decreases.
- In a redox reaction, if a conjugate redox pair consists of a reducing agent (a reactant) and the oxidising agent that is the product fomed when the reducing agent loses electrons, then the oxidation number of the reducing agent (the reactant) increases.
- Figure 5.2.3 summarises the redox terms that you need to understand from this module.

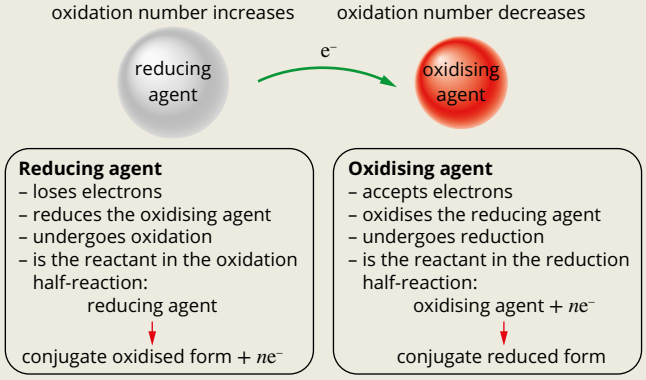


FIGURE 5.2.3 Summary of redox reaction terms

KEY QUESTIONS

Retrieval

1 Define the oxidation number of an atom in a substance.

2 State the oxidation number of:
- **a** an element
- **b** a monatomic ion.

3 Deduce the correct missing term by completing the following statements using either 'decreases' or 'increases'.
- **a** If the oxidation number of an atom _____ after a chemical reaction, that atom has undergone oxidation.
- **b** If the oxidation number of an atom _____ after a chemical reaction, that atom has undergone reduction.

4 Determine the oxidation state of the transition metal ion in the following ionic compounds.
- **a** copper(I) chloride (CuCl)
- **b** iron(III) nitrate ($Fe(NO_3)_3$)
- **c** chromium(III) oxide (Cr_2O_3)

5 Determine which one or more of the following substances contain manganese in the +6 oxidation state: $MnCl_2$, $MnCl_3$, MnO_2, $KMnO_4$, K_2MnO_4.

Comprehension

6 Calculate the oxidation numbers of each element in the following compounds or ions.
- **a** CaO
- **b** $CaCl_2$
- **c** HSO_4^-
- **d** MnO_4^-
- **e** F_2
- **f** SO_3^{2-}
- **g** $NaNO_3$
- **h** $K_2Cr_2O_7$

7 Indicate the correct conjugate redox pairs for each redox reaction by completing the following table.

Redox reaction	Conjugate redox pair (oxidation process)	Conjugate redox pair (reduction process)
$Na(s) + Ag^+(aq) \rightarrow Na^+(aq) + Ag(s)$		
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$		
$2K(s) + Cl_2(g) \rightarrow 2K^+(s) + 2Cl^-(s)$		

Analysis

8 Calculate the oxidation number of carbon in the following.
- **a** CO
- **b** CO_2
- **c** CH_4
- **d** C (graphite)
- **e** HCO_3^-

9 Compare oxidation numbers of atoms on both sides of the following equations to identify the oxidising agents and reducing agents.
- **a** $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$
- **b** $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
- **c** $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$
- **d** $2Fe^{2+}(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$

10 Each of the following half-equations have a mistake in them. For each half-equation determine what the error is and then state the correct half-equation.
- **a** $Ag(s) + e^- \rightarrow Ag^+(aq)$
- **b** $Cu(s) + e^- \rightarrow Cu^{2+}(aq) + 3e^-$
- **c** $Zn(aq) \rightarrow Zn^{2+}(s) + 2e^-$
- **d** $I_2(aq) + e^- \rightarrow I^-(aq)$
- **e** $Na^+(aq) - e^- \rightarrow Na(s)$

11 The element vanadium can exist in five oxidation states. Arrange V^{2+}, V, VO_2^+, V^{3+} and VO^{2+} in order of increasing oxidation state.

5.3 Balancing complex redox reactions using half-equations



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- balance half-equations for complex redox reactions
- balance overall redox equations for complex reactions.



FIGURE 5.3.1 The 'elephant's toothpaste' demonstration involves a redox reaction in which hydrogen peroxide is both the reducing agent and the oxidising agent.

Not all oxidation and reduction half-equations involve simple ions and their elements. Many interesting redox reactions, such as the 'elephant's toothpaste' reaction shown in Figure 5.3.1, can be quite complicated. For example, they often contain numerous reactants and products, have large stoichiometric coefficients, and typically involve polyatomic ions and other reactants and products that have oxygen and hydrogen in their formulas. The overall balanced equation for this example is $H_2O_2(aq) + H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$. Determining the individual half-equations for reactions like this can be quite complex. In this reaction, a solid potassium iodide catalyst is added to a hydrogen peroxide solution. Red colouring has been added for effect.

In this module you will learn how to balance complex redox equations in a few short steps.

BALANCING REDOX EQUATIONS FOR COMPLEX REACTIONS

The methods used for balancing chemical equations may break down when dealing with complex redox equations. Consider the following unbalanced chemical equations:

$$Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) \rightarrow Cr^{3+}(aq) + Fe^{3+}(aq)$$
$$As_4O_6(s) + MnO_4^-(aq) \rightarrow AsO_4^{3-}(aq) + Mn^{2+}(aq)$$

Attempting to balance these equations using the approaches outlined in Units 1 and 2 would not would be suitable. For a start, it is not immediately obvious if either of these reactions is a redox reaction; and if they are, it's not clear which substances are undergoing oxidation and which substances are undergoing reduction.

The first of these equations is particularly interesting as the element oxygen does not even appear on the right-hand side of the equation despite being present on the left-hand side. Finally, both of these equations contain complex, polyatomic, oxyanions, which usually require special attention when balancing equations.

For these reasons, there is a different approach to balancing complex chemical equations using a combination of assigning oxidation numbers and using half-equations. While you have some experience in balancing simple half-equations you need to be able to tackle more complex half-equations before attempting to balance full redox equations.

You will first learn how to balance more complex half-equations and then you will learn how to balance full redox equations. In both cases only reactions in acidic conditions are considered.

Steps for balancing complex half-equations (acidic conditions)

Half-equations that involve atoms or simple ions can be written quite easily. For example, knowing that magnesium metal is oxidised to form Mg^{2+} ions in solution, you can readily show the half-equation as:

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

However, half-equations involving polyatomic ions are usually less obvious. The anaesthetic nitrous oxide or laughing gas (N_2O) can be prepared by the reduction of nitrate ions in an acidic solution:

$$2NO_3^-(aq) + 10H^+(aq) + 8e^- \rightarrow N_2O(g) + 5H_2O(l)$$

Such equations can be deduced from the following steps. The reduction of nitrate ions will be used to illustrate this process.

1 Balance all elements except oxygen and hydrogen in the half-equation. Since the compound of N on the right-hand side is N_2O, we need two NO_3^- ions on the left-hand side:

$$2NO_3^- \rightarrow N_2O$$

2 Balance the oxygen atoms by adding H_2O molecules to one side of the half-equation. Since there are now six O atoms on the left-hand side, we need to put five H_2O molecules on the right-hand side to balance the O atoms:

$$2NO_3^- \rightarrow N_2O + 5H_2O$$

3 Balance the hydrogen atoms by adding H^+ ions to one side of the half-equation. Since there are now 10 H atoms on the right-hand side, we need to put 10 H^+ ions on the left-hand side:

$$2NO_3^- + 10H^+ \rightarrow N_2O + 5H_2O$$

4 Balance the charge on both sides of the half-equation by adding electrons (e^-) to the side with the greater positive charge. In this case, the total charge on the left-hand side is $(2 \times -1) + (10 \times +1) = +8$. The total charge on the right-hand side is zero. Make the charges equal by adding eight electrons to the left-hand side:

$$2NO_3^- + 10H^+ + 8e^- \rightarrow N_2O + 5H_2O$$

The total charge on both sides is now equal and the total number (and type) of atoms is also equal. This half-equation is now balanced.

5 Indicate whether each substance exists as a dissolved solute or as a solid, liquid or gas by inserting the appropriate label:

$$2NO_3^-(aq) + 10H^+(aq) + 8e^- \rightarrow N_2O(g) + 5H_2O(l)$$

It is important to note that half-equations and full redox equations must be fully balanced, as shown in Figure 5.3.2. The number of each element must be equal on each side, just as with any other chemical equation. In addition, the total charge on each side of the equation must also be equal. We should also note that the charges being equal does not mean they must be zero.

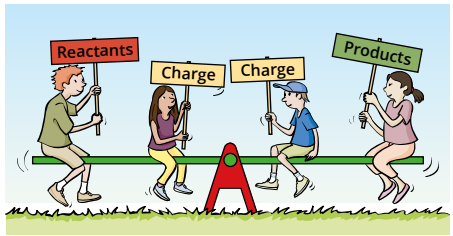


FIGURE 5.3.2 In balanced half-equations and overall redox equations, the number of atoms of each element is equal on both sides and the total charge on each side is equal.

Steps for balancing full redox equations (acidic conditions)

The steps we use to balance chemical equations for complex redox reactions are outlined below. The five steps for balancing half-equations have been included in Step 3 below.

Balancing complex redox equations is best demonstrated via examples; the unbalanced equations introduced at the beginning of this module are used as examples below.

1 Calculate oxidation numbers of each atom to determine which (if any) atoms are undergoing oxidation and which atoms are undergoing reduction. (If no atoms change their oxidation number then the reaction is not a redox reaction and the use of the half-equation approach is not valid.)

2 Split the chemical equation into two unbalanced half-equations, one containing the reactants and products for the oxidation process and one containing the reactants and products for the reduction process.

3 Construct and balance each half-equation. They must be both mass-balanced and charge-balanced.
   - i Balance all atoms except O and H first.
   - ii Balance O atoms by adding H_2O to one side of the half-equation.
   - iii Balance H atoms by adding H^+ ions to one side of the equation.
   - iv Balance the charge on both sides of the half-equation by adding electrons (e^-) to the side with the greater positive charge.
   - v Indicate whether each substance exists as a dissolved solute or as a solid, liquid or gas.

The steps for balancing complex redox half-equations must be carried out in sequence for the process to work.

4 Add the two half-equations together to obtain the final balanced redox equation.
   i Electrons cannot appear in the final redox equation. If there are unequal numbers of electrons in the half-equations, multiply each half-equation by whole numbers to ensure that the electrons lost in the oxidation half-equation equal the electrons gained in the reduction half-equation.
   ii Simplify the redox equation by cancelling any species that occurs on both sides.
   iii Check that you have the same number of each type of atom on each side and check that the total charge on the left-hand side is the same as the total charge on the right-hand side.

To balance the following equation we need to follow the steps outlined above.

$$Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) \rightarrow Cr^{3+}(aq) + Fe^{3+}(aq)$$

Step 1: Calculating the oxidation numbers for each atom using the rules in Table 5.2.1 gives the following for the left-hand side (LHS) and the right-hand side (RHS) of the equation:

LHS: Cr = +6 (rule 5); O = –2 (rule 3c); Fe = +2 (rule 2)

RHS: Cr = +3 (rule 2); Fe = +3 (rule 2)

The Fe atom has increased its oxidation number and has therefore undergone oxidation; Cr has decreased its oxidation number and has therefore undergone reduction.

Step 2: Split the reaction into unbalanced oxidation and reduction half-equations:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) \text{ (unbalanced oxidation half-equation)}$$

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq) \text{ (unbalanced reduction half-equation)}$$

Step 3: Complete and balance each half-equation. Balance elements other than O and H first, then add H_2O and H^+ to balance the O and H atoms. Finally, add electrons (e^-) to balance charge.

For the oxidation half-equation the Fe atoms are already balanced and no O or H atoms are present so we only need to add one electron to the RHS:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

We take the same approach with the reduction half-equation. There are two Cr atoms on the LHS so we need to place a 2 in front of Cr^{3+} on the RHS:

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$$

We note that there are seven O atoms on the LHS so we must place seven H_2O on the RHS:

$$Cr_2O_7^{2}–(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

This results in 14 H atoms on the RHS so we place 14 H^+ ions on the LHS:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

The total charge on the LHS is +12. The total charge on the RHS is +6. We therefore place six electrons on the LHS:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

Step 4: We now add the two half-equations together to obtain the full redox equation. First, however, we note that there are uneven numbers of electrons appearing in both half-equations. We therefore need to multiply each half-equation by appropriate factors to ensure that there is an equal number of electrons lost in the oxidation half-equation as there is gained in the reduction half-equation. We do this by multiplying the oxidation half-equation by six; this gives six electrons on the RHS of this half-equation to match the six electrons on the LHS of the reduction half-equation. When we add these two half-equations together, the electrons will cancel:



$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$$

This equation is now both mass-balanced and charge-balanced.

Worked example 5.3.1

BALANCING COMPLEX REDOX EQUATIONS (ACIDIC CONDITIONS)

Balance the following equation using half-equations.

$$As_4O_6(s) + MnO_4^-(aq) \rightarrow AsO_4^{3-}(aq) + Mn^{2+}(aq)$$

Thinking	Working
Step 1. Calculate the oxidation numbers for each atom in the chemical equation (using the rules in Table 5.2.1 on page 134). Determine which atoms are undergoing oxidation and which are undergoing reduction.	$\overset{+3}{As}_4\overset{-2}{O}_6(s) + \overset{+7}{Mn}\overset{-2}{O}_4^-(aq) \rightarrow \overset{+5}{As}\overset{-2}{O}_4^{3-}(aq) + \overset{+2}{Mn}^{2+}(aq)$ The oxidation number of As has increased from +3 to +5, so the arsenic in As_4O_6 has been oxidised. The oxidation number of Mn in MnO_4^- has decreased from +7 to +2, so manganese has been reduced. The oxidation number for O has remained unchanged, so oxygen has not undergone oxidation or reduction.
Step 2. Split the reaction into two unbalanced half-equations, one containing the reactants and products for the oxidation process and one containing the reactants and products for the reduction process.	$As_4O_6(s) \rightarrow AsO_4^{3-}(aq)$ (unbalanced oxidation half-equation) $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$ (unbalanced reduction half-equation)
Step 3. Formulate and balance each half-equation. They must be both mass-balanced and charge-balanced. Balance elements other than O and H first, then add H_2O and H^+ to balance the O and H atoms. Finally, add electrons (e^-) to balance charge.	For the oxidation half-equation, four As atoms appear on the LHS so we place a '4' in front of AsO_4^{3-} on the RHS: $As_4O_6(s) \rightarrow 4AsO_4^{3-}(aq)$ This gives 16 O atoms on the RHS. We therefore add $10H_2O$ to the LHS to balance O atoms (there are already six O atoms on the LHS): $As_4O_6(s) + 10H_2O(l) \rightarrow 4AsO_4^{3-}(aq)$ This gives 20 H atoms on the LHS. We therefore add $20H^+$ to the RHS: $As_4O_6(s) + 10H_2O(l) \rightarrow 4AsO_4^{3-}(aq) + 20H^+(aq)$ The total charge on the LHS is zero. The total charge on the RHS = $4 \times -3 + 20 \times +1 = +8$. We therefore need to add $8e^-$ to the RHS: $As_4O_6(s) + 10H_2O(l) \rightarrow 4AsO_4^{3-}(aq) + 20H^+(aq) + 8e^-$ Taking the same approach with the reduction half-equation, we note the Mn atoms are already balanced. We need to place $4H_2O$ on the RHS to balance the O atoms. This gives eight H atoms on the RHS; we therefore place $8H^+$ on the LHS. We balance the charge by adding $5e^-$ to the LHS: $MnO_4^- + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
Step 4. Add the two half-equations together to obtain the final balanced redox equation.	We note that there are uneven numbers of electrons appearing in both half-equations. We therefore need to multiply each half-equation by appropriate factors to ensure that there is an equal number of electrons lost in the oxidation half-equation as there is gained in the reduction half-equation. We do this by multiplying the oxidation half-equation by five and the reduction half-equation by eight; thus giving a total of 40 electrons in each half-equation. When we add these two half-equations together, the electrons will cancel: $5As_4O_6(s) + 50H_2O(l) + 8MnO_4^-(aq) + 64H^+(aq) \rightarrow$ $20AsO_4^{3-}(aq) + 100H^+(aq) + 8Mn^{2+}(aq) + 32H_2O(l)$ This equation is now both mass-balanced and charge-balanced and simplifies to the following (after cancelling H_2O and H^+ ions on both sides): $5As_4O_6(s) + 18H_2O(l) + 8MnO_4^-(aq) \rightarrow 20AsO_4^{3-}(aq) + 36H^+(aq) + 8Mn^{2+}(aq)$

➤ Try yourself 5.3.1

BALANCING COMPLEX REDOX EQUATIONS (ACIDIC CONDITIONS)

Construct the balanced redox equation for the reaction between ethanol and the dichromate ion to produce ethanoic acid and the chromium(III) ion, as represented by the following unbalanced equation:

$$C_2H_6O(l) + Cr_2O_7^{2-}(aq) \rightarrow C_2H_4O_2(aq) + Cr^{3+}(aq)$$

5.3 Review

SUMMARY

- The following steps must be taken to balance redox half-equations under acidic conditions.
  1. Balance all atoms except oxygen and hydrogen.
  2. Balance the oxygen atoms by adding H_2O molecules to one side of the half-equation.
  3. Balance the hydrogen atoms by adding H^+ ions to one side of the half-equation.
  4. Balance the charge on both sides of the half-equation by adding electrons (e^-) to the side with the greater positive charge.
  5. Indicate whether each substance exists as a dissolved solute or as a solid, liquid or gas by inserting the appropriate label.
- To construct an overall equation, add the oxidation half-equation and the reduction half-equation, making sure that the number of electrons used in reduction equals the number of electrons released during oxidation.
- When combining oxidation and reduction half-equations under acidic conditions, any $H^+(aq)$ and $H_2O(l)$ that appear on both sides of the arrow should be cancelled down.

KEY QUESTIONS

Retrieval

1 Select the correct word to complete the following sentences.

a Electrons appear on the **left-hand/right-hand** side of a half-equation for oxidation half-equations.

b Electrons appear on the **left-hand/right-hand** side of a half-equation for reduction half-equations.

2 List the steps for balancing redox half-equations in acidic conditions.

Comprehension

3 Determine half-equations for the:

a reduction of MnO_2 to Mn^{2+}

b reduction of MnO_4^- to MnO_2

c reduction of SO_4^{2-} to H_2S

d oxidation of SO_2 to SO_4^{2-}

e oxidation of H_2S to S

f oxidation of SO_3^{2-} to SO_4^{2-}.

4 When zinc powder is sprinkled into an acidified solution of potassium dichromate ($K_2Cr_2O_7$), a reaction occurs that produces zinc ions and chromium(III) ions in solution. The potassium ions are spectator ions and the net reaction is between Zn(s) and $Cr_2O_7^{2-}(aq)$ ions.

a Determine the oxidation half-equation for the reaction.

b Determine the reduction half-equation for the reaction.

c Use your answers to parts **a** and **b** to construct a balanced equation for the overall reaction.

5 Construct the half-equations and the balanced overall equation for the reaction in which:

a a solution containing iron(II) ions is oxidised by an acidified solution containing dichromate ions ($Cr_2O_7^{2-}$). The products include iron(III) and chromium(III) ions

b a solution containing sulfite ions (SO_3^{2-}) reacts with an acidified solution of permanganate ions (MnO_4^-) to produce a colourless solution containing sulfate ions and manganese(II) ions

c manganese dioxide (MnO_2) reacts with concentrated hydrochloric acid to form chlorine gas and a solution containing manganese(II) ions.

Analysis

6 Classify each of the following as 'redox' or 'not redox'.

a $Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$

b $LiCl(aq) + AgNO_3(aq) \rightarrow LiNO_3(aq) + AgCl(s)$

c $AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + HNO_3(aq)$

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

e $H_2CO_3(aq) + Ca(NO_3)_2(aq) \rightarrow 2HNO_3(aq) + CaCO_3(s)$

7 As a result of a traffic accident, residents in a Gold Coast suburb had to be evacuated when toxic fumes leaked from a container of sodium dithionite ($Na_2S_2O_4$). The dithionite ion reacts with water according to the equation:

$2S_2O_4^{2-}(aq) + H_2O(l) \rightarrow S_2O_3^{2-}(aq) + 2HSO_3^-(aq)$

a State the oxidation number of the sulfur in the following ions.

i $S_2O_4^{2-}$

ii $S_2O_3^{2-}$

iii HSO_3^-

b Determine half-equations for the oxidation and reduction reactions that occur when sodium dithionite is mixed with water.

MANDATORY PRACTICAL 2

Simple displacement reactions



Research and planning

Aim

- To perform a series of single displacement reactions in aqueous solution.
- To determine a reactivity series based on the results of single displacement reactions.

Rationale (scientific background to the experiment)

By definition, reduction is a gain of electrons and oxidation is a loss of electrons. In single displacement reactions in aqueous solutions, the metal loses its electrons to the metal ion in solution. This is a redox reaction. The metal losing its electrons is the reductant and the metal gaining electrons is the oxidant.

Single displacement reactions only occur if the metal is more reactive than the metal ions in solution and as such will give away its electrons. A reactivity series can be developed based on this, with the more reactive metals, those more easily oxidised, sitting higher in the series than those less easily oxidised.

Timing

50 minutes

Materials

- 5 × small clean strips or pieces of each of the following metals: Mg, Zn, Ag, Cu
- 5 × iron nails (not galvanised)
- 5 × test tubes and test-tube rack
- 25 mL × 0.1 mol L^{-1} solutions of the following cations: Mg^{2+}, Zn^{2+}, Ag^{+}, Cu^{2+} and Fe^{2+} (The anions in these salts could be any of nitrates, sulfates or chlorides.)
- safety glasses

Safety

- Wear safety glasses and a laboratory coat.
- Take care to rinse off any aqueous solution that may spill on your body.

Method

Risk assessment

Assessment of risks include chemical hazards and physical hazards. Before you commence this practical activity, you must conduct a risk assessment. Complete the template in your skills and assessment book or download it from your eBook.

1 Examine the following table, which shows the possible combinations of metals and metal ion salt aqueous solutions.

Set up the five test tubes in the test-tube rack and add 5 mL of the first metal ion salt solution from the table to each.

2 Place a piece of each of the different metals in a different test tube and observe.

3 Record your findings in the results table.

4 Discard contents of all test tubes and set up again as in step 1, using the second metal ion salt aqueous solution from the table.

5 Repeat steps 2 and 3 using fresh metal samples.

6 Continue until all five solutions have been used.

Variables

i Independent: the combination of metal and metal ion salt aqueous solution used in the reaction.

ii Dependent: if a reaction occurs and the rate of the redox reaction.

iii Controlled: the amount of metal used, the volume and concentration of the metal ion salt aqueous solution used.

Analysing

Raw data

1 Create a table to illustrate whether reactions occurred between metal and metal ions in solution. Use your table to record if there is a reaction (✓) or no reaction (✘).

	Aqueous solution				
Metal	**Mg^{2+}**	**Zn^{2+}**	**Fe^{2+}**	**Ag^{+}**	**Cu^{2+}**
Mg					
Zn					
Fe					
Ag					
Cu					

Processed data

2 Using your results from question **1**, deduce which was the:

i most reactive metal

ii least reactive metal.

3 Determine half-equations for each reaction that occurred.

Reaction	Reduction half-equation	Oxidation half-equation

Reflect and check that your data analysis demonstrates these characteristics

- ☐ Effective investigation of phenomena is demonstrated by the collection of sufficient and relevant raw data.
- ☐ Accurate application of algorithms, visual and graphical representations of data is demonstrated by appropriate processing and presentation of data to aid the analysis and interpretation of data.

Analysis

4 Analyse your results table and create a reactivity series listing the reduction half-equations from the strongest oxidant at the top to the weakest oxidant at the bottom.

5 Compare and contrast the reactivity series you have created with Figure 5.1.8 on page 124. Identify why there might be differences between your table and the one in the textbook.

Reflect and check that your analysis demonstrates these characteristics

- ☐ Systematic and effective analysis of evidence is demonstrated by a thorough and appropriate error analysis.
- ☐ Systematic and effective analysis of evidence is demonstrated by a thorough identification of relevant trends, patterns and relationships.
- ☐ Insightful and valid interpretation of evidence is demonstrated by drawing a valid and defensible conclusion based on the analysis.

Interpreting and communicating

Conclusion

1 **a** From the analysis of your results, determine what conclusions can be inferred.

b Explain the evidence that leads you to these conclusions.

Evaluation

2 Assess your analysis and conclusions. Identify whether the experiment provided an effective and efficient method of determining the reactivity series of metals. Explain your evaluation.

Improvements

3 Critique the experiment. If you were to repeat the experiment, identify the steps that you would do differently. Discuss the following in your answer.

a Analyse how you would change the methodology to help improve the accuracy of the results.

b Evaluate how you performed the tasks and the skills that you need to improve on in your technique.

c Explain how the collection of data could be improved or uncertainty reduced.

Reflect and check that your evaluation demonstrates these characteristics

- ☐ Critical evaluation of processes is demonstrated by a discussion of the reliability and validity of the experimental process supported by evidence such as the quality of the data (as quantified in the error analysis).
- ☐ Critical evaluation of the conclusion is demonstrated by a discussion of the veracity of the conclusions with respect to the error analysis and limitations or sufficiency of the data.
- ☐ Insightful evaluation of processes and conclusions is demonstrated by a suggestion of improvements or extensions to the experiment which are logically derived from the analysis of the evidence.

Chapter review

05

KEY TERMS

alloy
anode
cathode
cathodic protection
conjugate redox pair
direct corrosion
displace
dry corrosion
electroplating
half-equation
main group metal
metal displacement reaction
oxidant
oxidation
oxidation number
oxidation state
oxidised
oxidising agent
reactivity series of metals
redox reaction
reduced
reducing agent
reductant
reduction
sacrificial anode
sacrificial protection
spontaneous redox reaction
transition element
wet corrosion

KEY QUESTIONS

Retrieval

1 List the overall steps for balancing full redox equations in acidic conditions.

2 State why oxidation and reduction must occur simultaneously in redox reactions.

3 State what process the metal atoms have undergone when pure metals are extracted from their oxide ores.

4 Determine whether each of the following statements is true or false.

a Group 1 and 2 metal ions, such as Na^+, are reducing agents because they tend to lose electrons.

b Group 17 molecules, such as I_2, can be oxidising agents or reducing agents.

c Non-metal ions, such as Cl^-, can be reducing agents because they can lose electrons.

d Metals, such as Cu, can be oxidising agents because they can gain electrons.

5 Deduce the correct missing terms by completing the following sentences that describe oxidation and reduction.

Oxidation and reduction occur together. Oxidation occurs when an atom _____ electrons to form a _____ ion, such as when a calcium atom, with an electronic configuration of 2, 8, 8, 2, _____ electrons to form a Ca^{2+} ion. Reduction occurs when an atom _____ electrons to form a _____ ion or when a cation _____ electrons to become a neutral atom. An example is when a bromine atom, with _____ electrons in its valence shell, _____ an electron to form a _____ ion.

6 List the following in terms of increasing reducing strength.

K, Cu, Sn, Mg, Zn.

Comprehension

7 Consider the following half-equations and the overall equation for the reaction between sodium metal and a solution of silver ions.

$$Na(s) \rightarrow Na^+(aq) + e^-$$
$$Ag^+(aq) + e^- \rightarrow Ag(s)$$
$$Na(s) + Ag^+(aq) \rightarrow Na^+(aq) + Ag(s)$$

Determine which one of the following sets of statements correctly describes this redox reaction.

A Na(s) is the reducing agent, $Ag^+(aq)$ is the oxidising agent, sodium metal is oxidised.

B Na(s) is the oxidising agent, $Ag^+(aq)$ is the reducing agent, sodium metal is reduced.

C Na(s) is the reducing agent, $Ag^+(aq)$ is the oxidising agent, sodium metal is reduced.

D $Na^+(aq)$ is the oxidising agent, Ag(s) is the reducing agent, sodium metal is oxidised.

8 Magnesium reacts with nickel(II) ions according to the following equation:

$$Mg(s) + Ni^{2+}(aq) \rightarrow Mg^{2+}(aq) + Ni(s)$$

Determine which one of the following is the correct set of conjugate redox pairs for this reaction.

A $Mg^{2+}(aq)/Mg(s)$ and $Ni^{2+}(aq)/Ni(s)$

B $Ni(s)/Mg^{2+}(aq)$ and $Ni^{2+}(aq)/Mg(s)$

C $Mg(s)/Ni(s)$ and $Ni^{2+}(aq)/Mg^{2+}(aq)$

D $Mg(s)/Ni^{2+}(aq)$ and $Ni(s)/Mg^{2+}(aq)$

9 Determine which one of the following alternatives describes what happens when sodium and oxygen react.

A Each sodium atom gains one electron.

B Each sodium atom loses one electron.

C Each oxygen atom gains one electron.

D Each oxygen atom loses one electron.

10 Determine which one of the following redox equations has not been balanced correctly.
- **A** $Zn^{2+}(aq) + Mg(s) \rightarrow Zn(s) + Mg^{2+}(aq)$
- **B** $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$
- **C** $Fe^{2+}(aq) + Zn(s) \rightarrow Fe(s) + Zn^{2+}(aq)$
- **D** $Ag^{+}(aq) + Cu(s) \rightarrow Ag(s) + Cu^{2+}(aq)$

11 Determine which one of the following factors does not increase the rate of corrosion of a metal object.
- **A** The presence of water with dissolved oxygen.
- **B** The presence of acidic pollutants dissolved in water.
- **C** The presence of impurities, such as salt, dissolved in water.
- **D** The presence of a coating of paint over the surface of the metal object.

12 Deep-sea divers sometimes report that the metal on vessels they find on the seabed does not appear to have corroded. Determine which one of the following might contribute to the lack of corrosion.
- **A** Deep-sea creatures eat iron oxide.
- **B** A lack of light prevents corrosion from occurring.
- **C** There is little oxygen dissolved in the water near the seabed.
- **D** The concentration of dissolved salt in the sea decreases with increasing depth.

13 Explain the term 'electrochemical protection' of iron.

14 Calculate the oxidation number of sulfur in each of the following compounds.
- **a** SO_2
- **b** H_2S
- **c** H_2SO_4
- **d** SO_3
- **e** Na_2SO_3
- **f** $Na_2S_2O_3$

15 Show your understanding of oxidation numbers and elements by completing the following table.

Compound	Element	Oxidation number
$CaCO_3$	Ca	
HNO_3	O	
H_2O_2		−1
HCO_3^-		+4
HNO_3	N	
$KMnO_4$		+7
H_2S	S	
Cr_2O_3	Cr	
N_2O_4	N	

16 Copper bowls and trays can be decorated by etching patterns on them using concentrated nitric acid. The overall reaction is:
$Cu(s) + 4HNO_3\ (aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$
- **a** Determine what the oxidation number of copper is:
  - **i** before the reaction
  - **ii** after the reaction.
- **b** Determine the oxidation number of nitrogen:
  - **i** before the reaction
  - **ii** after the reaction.
- **c** Name the oxidising agent and reducing agent in this process.

17 Show your understanding of conjugate pairs by completing the following table, giving the conjugate redox pairs for each of the reactions.

Equation	Conjugate redox pair (oxidation)	Conjugate redox pair (reduction)
$Fe(s) + I_2(aq) \rightarrow FeI_2(aq)$		
$Mg(s) + FeCl_2(aq) \rightarrow MgCl_2(aq) + Fe(s)$		
$10Br^-(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Br_2(aq)$		
$Cu(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$		

18 Complete the summary below as you balance the half-equation for the reduction of NO_3^- to NO_2 in acidic solution:

$$NO_3^-(aq) \rightarrow NO_2(g)$$

Step	Task	How it's done	Half-equation
1	Balance nitrogens.		$NO_3^-(aq) \rightarrow NO_2(g)$
2	Balance oxygens by adding _____.	Add _____ H_2O molecule(s) to right-hand side of the equation.	
3	Balance hydrogens by adding _____.	Add _____ H^+ ion(s) to _____ of the equation.	
4	Balance charge by adding _____.	Charge on left-hand side = _____ Charge on right-hand side = _____ Add _____ e^- to the _____ of the equation.	
5	Add state symbols to give the final half-equation.	Give the appropriate states for each reactant and product in the equation.	

19 During each of the following analyses, redox reactions occurred. Construct half-equations for the oxidation and reduction reactions. Use these half-equations to construct an overall equation for each reaction.

- **a** Zinc was reduced by reacting it with a solution of Pb^{2+} ions. Lead metal was precipitated and Zn^{2+} ions were formed.
- **b** The amount of Fe^{2+} ions in iron tablets was determined by oxidising them to Fe^{3+} ions using an acidified solution of MnO_4^- ions. The MnO_4^- ions were reduced to Mn^{2+} ions during the reaction.
- **c** Sulfur dioxide (SO_2), a preservative in dried fruit, was determined by oxidation to SO_4^{2-} using a solution of I_2. Iodide (I^-) ions were produced.
- **d** An acidified solution of bleach, which contains OCl^- ions, was titrated against a solution of I^- ions. The reaction products included Cl^- and I_2.

20 In dry cells commonly used in torches, an electric current is produced from the reaction of zinc metal with solid manganese oxide (MnO_2). During this reaction, Zn^{2+} ions and solid Mn_2O_3 are formed. Show half-equations, and hence an overall equation, for the reaction.

21 The following equations are not balanced.

- **i** Identify the species that has been reduced and the species that has been oxidised.
- **ii** Show balanced half-equations for the oxidation and reduction reactions.
- **iii** Combine the half-equations to show a balanced overall equation.

- **a** $Ce^{4+}(aq) + H_2S(g) \rightarrow Ce^{3+}(aq) + S(s) + H^+(aq)$
- **b** $NO_3^-(aq) + H^+(aq) + Cu(s) \rightarrow NO(g) + H_2O(l) + Cu^{2+}(aq)$
- **c** $H_2O_2(aq) + Br^-(aq) + H^+(aq) \rightarrow Br_2(l) + H_2O(l)$
- **d** $MnO_2(s) + H^+(aq) + S(s) \rightarrow Mn^{2+}(aq) + H_2O(l) + SO_2(g)$

Analysis

22 Sort the following substances in order of increasing oxidation states of nitrogen.

NO, K_3N, N_2O_4, N_2O, $Ca(NO_3)_2$, N_2O_3, N_2

23 Consider the following products that are made during the wet corrosion of iron. Put them in the correct order in which they are made.

$Fe(OH)_3(s)$, $Fe_2O_3.xH_2O$, $Fe(OH)_2(s)$, $Fe^{2+}(aq)$, $OH^-(aq)$

24 Iron reacts with hydrochloric acid according to the ionic equation:

$$Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$$

- **a** Determine what has been oxidised in this reaction.
- **b** Determine what the product of oxidation is.
- **c** Construct the half-equation for the oxidation reaction.
- **d** Identify the oxidising agent.
- **e** Determine what has been reduced in this reaction and the product of reduction.
- **f** Construct the half-equation for the reduction reaction.
- **g** Identify the reducing agent.

25 Calcium metal that is exposed to the air forms an oxide coating.

- **a** Determine the formula of calcium oxide.
- **b** Deduce what has been oxidised in this reaction.
- **c** Show a half-equation for the oxidation reaction.
- **d** Determine what has been reduced in this reaction.
- **e** Show a balanced half-equation for the reduction reaction.
- **f** Show an overall equation for this redox reaction.
- **g** Deduce the correct missing terms by completing the following sentences.

Calcium has been _____ by _____ to calcium ions. The _____ has gained electrons from the _____. The oxygen has been _____ by _____ to oxide ions. The _____ has lost electrons to the _____.

26 In the following redox reactions, determine which species have been oxidised and which have been reduced.
- **a** $Cu^{2+}(aq) + Mg(s) \rightarrow Cu(s) + Mg^{2+}(aq)$
- **b** $Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
- **c** $PbO(s) + CO(g) \rightarrow Pb(s) + CO_2(g)$
- **d** $Ca(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$
- **e** $Pb^{2+}(aq) + Fe(s) \rightarrow Pb(s) + Fe^{2+}(aq)$

27 When zinc reacts with a solution of hydrochloric acid, hydrogen gas is produced.
- **a** Determine what has been oxidised in this reaction.
- **b** Construct the half-equation for the oxidation reaction.
- **c** Determine what has been reduced in this reaction.
- **d** Construct the half-equation for the reduction reaction.
- **e** Identify the oxidising agent.
- **f** Identify the reducing agent.
- **g** Construct the overall equation for this redox reaction.

28 An unknown metal is placed in solutions of aluminium nitrate and iron(II) sulfate. After a period of time, the metal is found to have reacted with the iron(II) sulfate solution, but not the aluminium nitrate solution. Determine a possible identity of the unknown metal.

29 Iron nails are placed into solutions of $CuSO_4$, $MgCl_2$, $Pb(NO_3)_2$ and $ZnCl_2$. Predict in which solutions you would expect a coating of another metal to appear on the nail. Explain your answer.

30 Determine why it is usually not necessary to protect structures made of copper from corrosion.

31 The iron in galvanised iron nails is protected from corrosion by a coating of zinc. Explain why a coating of tin instead of zinc would not be appropriate protection for iron nails.

32 Explain why steel garden furniture rusts more readily in coastal areas than it does inland.

33 Determine whether elements from the following groups would be more likely to be oxidised or reduced when they take part in chemical reactions with the other group.

Group A: sodium, calcium and magnesium

Group B: sulfur, oxygen and chlorine

34 Solid ammonium dichromate decomposes to form chromium(III) oxide, nitrogen gas and steam.
- **a** Calculate the oxidation numbers of chromium and nitrogen in the reactant ammonium dichromate ($(NH_4)_2Cr_2O_7$) and the products Cr_2O_3 and N_2. Identify which reactants have been reduced and oxidised.
- **b** Complete and balance the following half-equations.
  - **i** $NH_4^{+}(s) \rightarrow N_2(g)$
  - **ii** $Cr_2O_7^{2-}(s) \rightarrow Cr_2O_3(s)$
- **c** Identify each of the half-equations in part **b** as either reduction or oxidation processes and explain your answer in terms of oxidation numbers.
- **d** Construct the balanced overall equation for the reaction that occurs.
- **e** Identify the conjugate redox pairs for the reaction.

Knowledge utilisation

35 Create a concept map that shows the links between the following terms: redox reactions, oxidising agent, reducing agent, electrons, oxidation, reduction.

36 Predict which of the following food cans best protect its food contents. Support your decision by referring to the relative ease of oxidation.
- **A** an intact steel food can
- **B** a dented steel food can
- **C** an intact steel food can lined with zinc
- **D** a dented steel food can lined with zinc
- **E** an intact steel food can lined with tin
- **F** a dented steel food can lined with tin

CHAPTER

06 Galvanic cells as a source of energy

By the end of this chapter, you will know how galvanic cells generate electricity from chemical reactions. You will see how experimental data from galvanic cells can be used to compare the relative strengths of oxidising and reducing agents.

The relative strengths of oxidising and reducing agents are conveniently summarised in a table known as the electrochemical series. You can use the electrochemical series to predict the likelihood of individual redox reactions occurring, and to calculate the potential differences of different galvanic cells.

Finally, you will learn how different types of galvanic cells are used as a source of power for a range of uses.

Syllabus subject matter

Topic 2 • Oxidation and reduction

ELECTROCHEMICAL CELLS

- understand that electrochemical cells, including galvanic 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).

GALVANIC CELLS

- understand that galvanic cells, including fuel cells, generate an electrical potential difference from a spontaneous redox reaction which can be represented as cell diagrams including anode and cathode half-equations
- recognise that oxidation occurs at the negative electrode (anode) and reduction occurs at the positive electrode (cathode) and explain how two half-cells can be connected by a salt bridge to create a voltaic cell (examples of half-cells are Mg, Zn, Fe and Cu and their solutions of ions)
- describe, using a diagram, the essential components of a galvanic cell; including the oxidation and reduction half-cells, the positive and negative electrodes and their solutions of their ions, the flow of electrons and the movement of ions, and the salt bridge.

STANDARD ELECTRODE POTENTIAL

- determine the relative strength of oxidising and reducing agents by comparing standard electrode potentials
- recognise that cell potentials at standard conditions can be calculated from standard electrode potentials; these values can be used to compare cells constructed from different materials
- recognise the limitation associated with standard reduction potentials
- use appropriate mathematical representation to solve problems and make predictions about spontaneous reactions, including calculating cell potentials under standard conditions.



SCIENCE AS A HUMAN ENDEAVOUR

- **Breathalysers and measurement of blood alcohol levels:** The level of alcohol in the body can be measured by testing breath or blood alcohol concentrations.

MANDATORY PRACTICAL 3

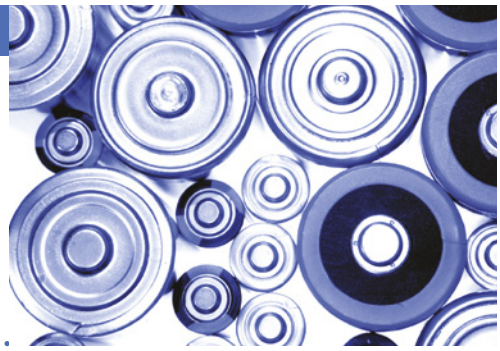
Construct a galvanic cell using two metal/metal-ion half-cells.

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6.1 Galvanic cells

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand that a galvanic cell uses a spontaneous redox reaction to convert chemical energy into electrical energy
- identify the key components of a galvanic cell and explain how the cell operates
- construct half-equations for the processes that occur within the compartments of a galvanic cell and use the half-equations to construct an overall equation for the cell reaction.



Electronic devices such as mobile phones, notebook computers, cameras and hearing aids all depend on small portable sources of electricity: cells and batteries (Figure 6.1.1). Portable energy in the form of cells and batteries enables you to operate electrical equipment without the restrictions of a power cord.

The demand for electronic devices has stimulated the production of a variety of cells, from tiny button cells for watches and calculators, to the huge batteries used to operate lighthouses. The energy provided by cells and batteries may be more expensive than energy from other sources, such as fossil fuels, but this cost is offset by their convenience.

In this module, you will learn how cells are constructed, and how they provide you with a source of electrical energy.



FIGURE 6.1.1 Your way of life depends on cells and batteries.

INTRODUCING GALVANIC CELLS

An **electrochemical cell** is a device in which chemical energy is converted into electrical energy, or vice versa. A **galvanic cell** (which is also known as a **voltaic cell**) is a type of electrochemical cell in which chemical energy is converted into electrical energy. The cells in your mobile phone and laptop are galvanic cells.

If we connect several cells in series to obtain a higher potential difference or 'voltage', the combination of cells is called a **battery**. The term 'battery' strictly only applies to a combination of cells, but it is in everyday use to describe cells as well.

Figure 6.1.2 shows how you can produce a galvanic cell from simple laboratory equipment.

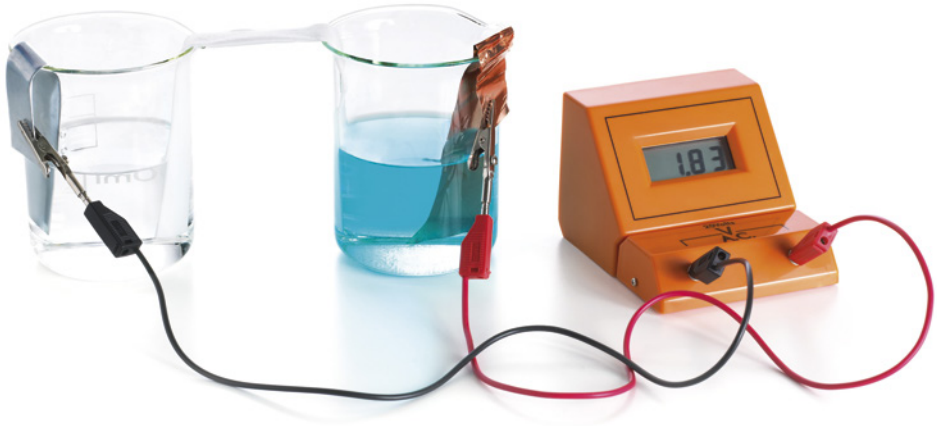


FIGURE 6.1.2 Construction of a galvanic cell from simple laboratory equipment

In Figure 6.1.3, you can see a diagram of a cell called the Daniell cell, named after the scientist who invented it in 1836, John Daniell. The cell produces an electric current that flows through the wire and light globe. This part of the cell is called the **external circuit**. The globe converts the electrical energy of the current into light and heat.

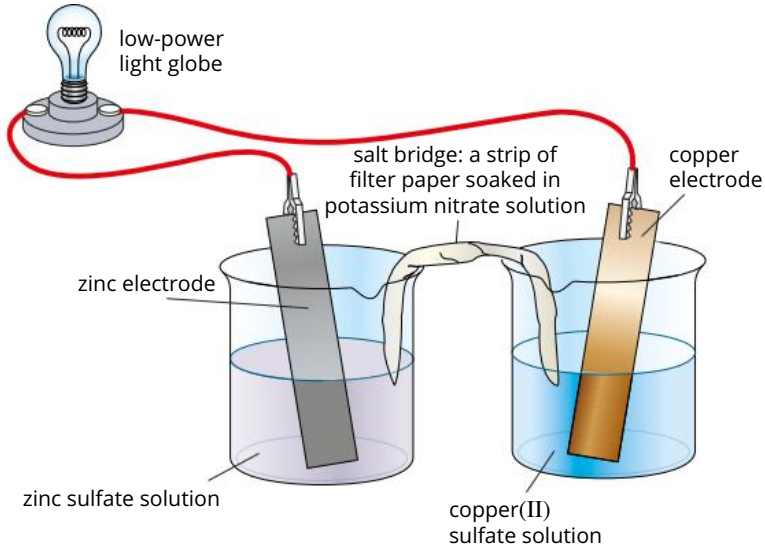


FIGURE 6.1.3 The Daniell cell is a type of galvanic cell.

The current flows because a chemical reaction is taking place in the cell. If you leave the cell with a light globe connected for several hours, you will see evidence of this reaction occurring: the zinc metal corrodes, the copper metal becomes covered with a furry dark brown deposit and the blue copper(II) sulfate solution loses some of its colour.

If you replace the light globe with a **galvanometer** (an instrument for detecting electric current), the galvanometer will indicate that electrons flow from the zinc **electrode** through the wire to the copper electrode. Current flows only if the two halves of the cell are connected by a **salt bridge**. A salt bridge is often made from filter paper soaked in a relatively unreactive **electrolyte**, such as a solution of potassium nitrate.

These observations lead to the following explanations about what is occurring in a galvanic cell.

- The reaction in the cell is a redox reaction, because electrons are being transferred.
- The zinc electrode corrodes because the zinc metal forms zinc ions in solution:

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

- The oxidation of the zinc metal releases electrons, which flow through the wire to the copper electrode.
- Electrons are accepted by copper(II) ions in the solution when the ions collide with the copper electrode. A reduction reaction occurs:

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

- The copper metal that is formed deposits on the electrode as a dark brown coating.

In this cell, there is a transformation of chemical energy to electrical energy. Figure 6.1.4 shows the processes that occur during the operation of the cell. The equation for the overall reaction is found by adding the two half-equations:

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

Note that when these half-equations are added together, there are the same number of electrons (two) on each side of the equation so the electrons are cancelled out and do not appear in the final equation.

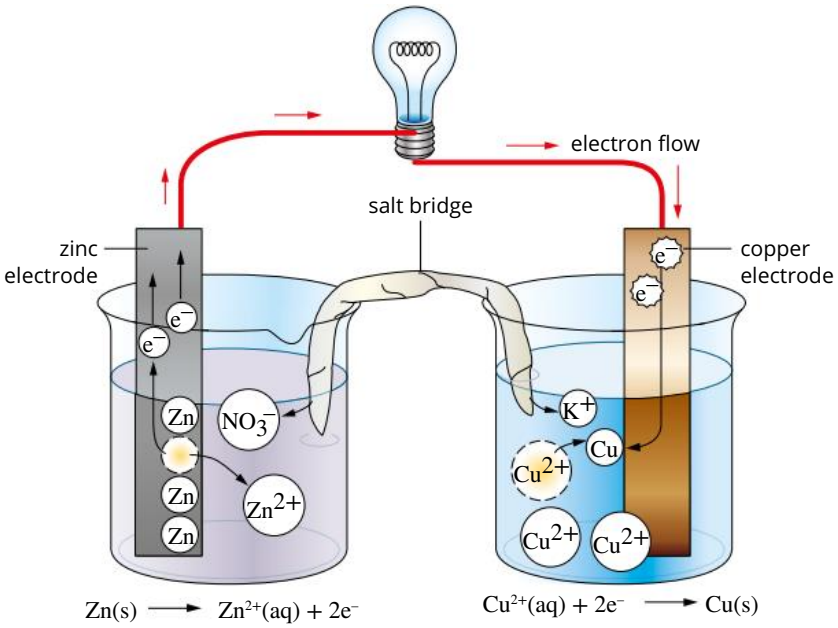


FIGURE 6.1.4 A representation of the electrode reactions in a Daniell cell. The salt bridge contains potassium nitrate solution.

This redox reaction is described as a **spontaneous reaction** because it occurs naturally.

Copper(II) ions act as the oxidising agent, or oxidant, and zinc metal acts as the reducing agent, or reductant.

ENERGY TRANSFORMATIONS IN DIRECT REACTIONS

You may have seen a similar reaction to the one that occurs in a Daniell cell if you have copper-plated a piece of metal, such as zinc. When zinc is immersed in an aqueous solution containing $Cu^{2+}(aq)$ ions, the metal becomes coated in dark brown copper. This can be seen in Figure 6.1.5. At the same time, thermal energy is produced, which escapes into the surrounding environment as heat.

The overall equation for this metal displacement reaction is:

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

This reaction is an example of a spontaneous exothermic reaction. If the reactants are allowed to come into direct contact with each other, their chemical energy is transformed directly to thermal energy. However, in a galvanic cell, the half-reactions occur in separate containers, and the electrons are transferred by the external circuit so that chemical energy is transformed into electrical energy.

The energy changes that occur in galvanic cells and when reactants undergo direct reaction are summarised in Figure 6.1.6.

HOW A GALVANIC CELL OPERATES

A galvanic cell is designed so that half-reactions occur in two separate compartments of the cell. Because the oxidising agent and reducing agent do not come into direct contact with each other, electrons can only be transferred through an external circuit connecting the negative and positive electrodes.

This flow of electrons creates an electric current. Therefore, the chemical energy of the reactants is transformed into electrical energy.

A chemical that causes another substance to be oxidised is called an oxidising agent and is itself reduced in a redox reaction.

Similarly, a chemical that causes another substance to be reduced is called a reducing agent.

Reducing agents are oxidised in redox reactions.



FIGURE 6.1.5 $Cu^{2+}(aq)$ ions in blue-coloured copper(II) sulfate solution reacting directly with a strip of zinc metal

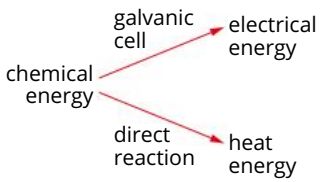


FIGURE 6.1.6 Energy transformations that occur when reactants are separated in a galvanic cell and when the reactants react directly

Half-cells

A galvanic cell can be regarded as consisting of two **half-cells**. Each half-cell contains an electrode in contact with a solution (Figure 6.1.7). In the Daniell cell, one half-cell contains Cu(s) and $Cu^{2+}(aq)$; the other contains Zn(s) and $Zn^{2+}(aq)$. The species present in each half-cell form a conjugate redox pair (an oxidising agent and its corresponding reduced form).

If one member of the conjugate pair in a half-cell is a metal, it is usually used as the electrode. Some redox pairs, such as $Cu^{2+}(aq)/Cu^{+}(aq)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$, do not involve solid metals. If no metal is present, an inert (unreactive) electrode, such as platinum or graphite, is used. This can be seen in Figure 6.1.7.

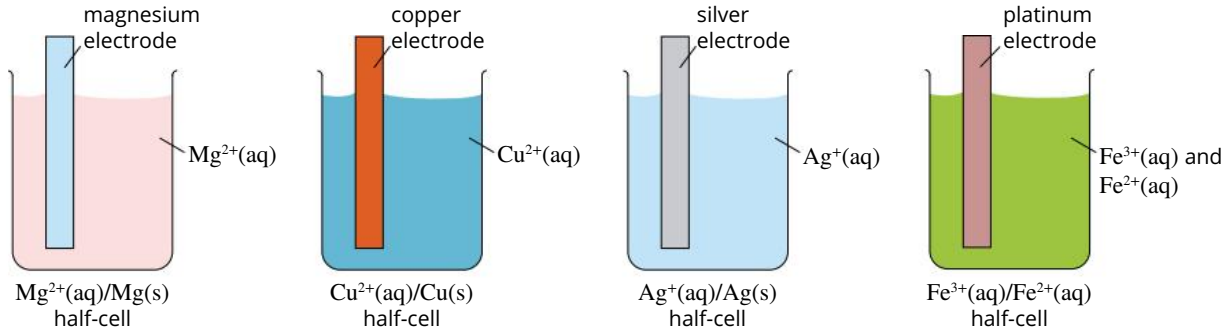


FIGURE 6.1.7 Typical half-cells. The $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell on the right does not contain a solid metal to act as an electrode, so an inert platinum electrode must be added.

In some half-cells, one of the conjugate pairs may be a gas. In such cases, a special 'gas electrode' like the one shown in Figure 6.1.8 for the $H^{+}(aq)/H_2(g)$ half-cell is used. Note that half-cells usually contain other species not involved in the reaction, such as spectator ions and the solvent.

The electrode at which oxidation occurs is called the anode. In a galvanic cell, the anode, where electrons are released, is described as the negative terminal. The electrode at which reduction occurs is called the cathode. The cathode, where electrons are gained, is the positive terminal in a galvanic cell.

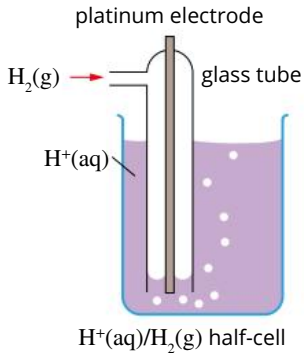


FIGURE 6.1.8 A $H^{+}(aq)/H_2(g)$ half-cell consists of a platinum rod in a solution of $H^{+}(aq)$ with H_2 gas bubbling through the solution.

The purpose of the salt bridge

The salt bridge contains ions that are free to move so that they can balance charges formed in the two half-cell compartments. *Cat*ions move towards the *cat*hode and *an*ions move towards the anode, as shown in Figure 6.1.9.

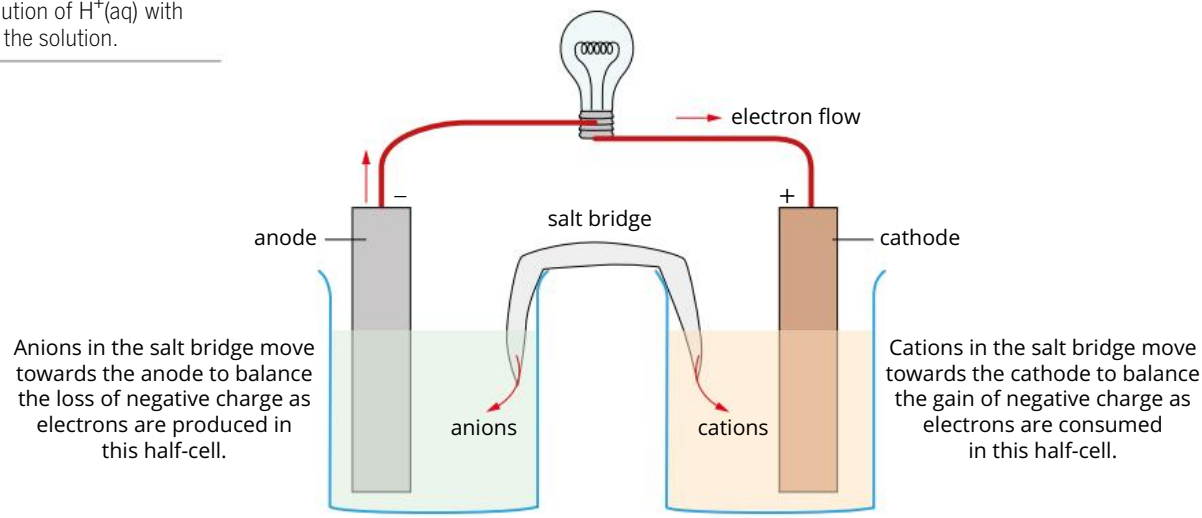


FIGURE 6.1.9 The movement of cations and anions in a salt bridge balances the charges produced and consumed in each half-cell, allowing the flow of electrons through the external circuit.

Without a salt bridge, the solution in one compartment in the galvanic cell would accumulate negative charge and the solution in the other compartment would

accumulate positive charge as the reaction proceeded. Such accumulation of charge would stop the reaction very quickly and, hence, prevent further reaction.

The salt bridge is also called the **internal circuit**.

> Cations in the salt bridge move towards the cathode and anions in the salt bridge move towards the anode.

WRITING HALF-CELL EQUATIONS

If a conjugate redox pair consists of an element and its corresponding ion, then the half-equation is relatively easy to write. For instance, knowing that a reduction reaction involves the conjugate redox pair of Zn^{2+} ions and Zn, you can quickly write the half-cell equation as:

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

Half-cell equations involving polyatomic ions may be more complex to write. The equation for the reduction reaction in a half-cell containing the dichromate ion ($Cr_2O_7^{2-}$) and Cr^{3+} ion redox pair is:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

You learnt to construct half-equations such as these in Chapter 5.

> In balanced half- and overall equations the:
> - number of atoms of each element is equal on both sides
> - total charge on each side is equal.

Writing an overall equation for a cell reaction

The half-equations for the oxidation and reduction reactions that occur in a cell can be added together to obtain an overall, or full, equation. An overall equation does not show any electrons; all the electrons lost in the oxidation reaction are gained in the reduction reaction. You may need to multiply one or both half-equations by a factor to ensure that the electrons balance and can be cancelled out in the overall equation.

> The number of electrons lost in the oxidation reaction must equal the number of electrons gained in the reduction reaction.

DRAWING AND LABELLING A DIAGRAM OF A GALVANIC CELL

If you know the reaction occurring in a galvanic cell, then you can draw a diagram of the cell identifying key features, such as the anode, cathode, electrode polarity, direction of electron flow and direction of the flow of ions.

For example, consider a cell with the cell reaction:

$$Cu(s) + Cl_2(g) \rightarrow Cu^{2+}(aq) + 2Cl^-(aq)$$

From this reaction, you can see that:

- copper metal is at the anode (because copper loses electrons—i.e. copper is oxidised—and oxidation occurs at the anode)
- chlorine gas is present at the cathode (because chlorine gains electrons—i.e. chlorine is reduced—and reduction occurs at the cathode).

As in all galvanic cells:

- electrons flow through the external circuit from the anode (negative) to the cathode (positive)
- anions flow in the internal circuit to the anode and cations flow towards the cathode.

This information is used to draw and label the diagram of the cell as shown in Figure 6.1.10.

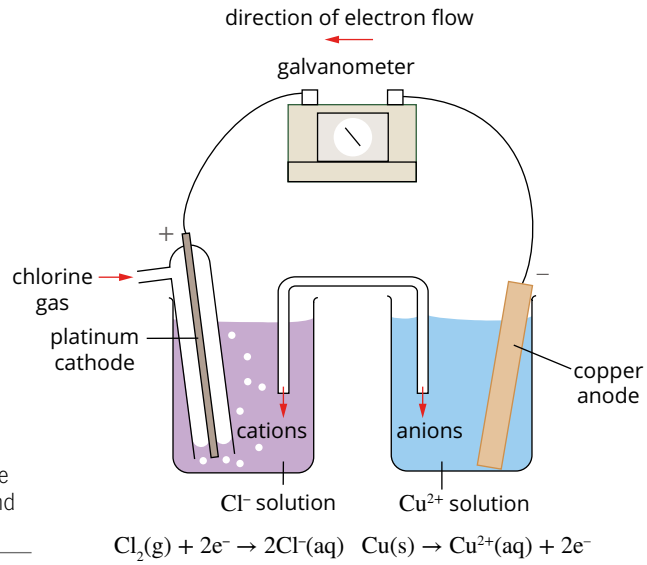


FIGURE 6.1.10 A diagram of the cell containing $Cl_2(g)/Cl^-(aq)$ and $Cu^{2+}(aq)/Cu(s)$ half-cells

6.1 Review

SUMMARY

- The reactions that occur in galvanic cells are spontaneous and exothermic.
- In a galvanic cell, chemical energy is converted directly into electrical energy in a redox reaction.
- A cell is made from two half-cells.
- Each half-cell contains a conjugate redox pair.
- An oxidation reaction occurs in one half-cell and a reduction reaction occurs in the other half-cell.
- The electrode in the half-cell in which oxidation occurs is called the anode; the electrode in the half-cell in which reduction occurs is called the cathode.
- In galvanic cells, the anode is negative and the cathode is positive.
- Electrons flow through the external circuit from the anode to the cathode.
- A salt bridge allows a cell to produce electricity by preventing the accumulation of charge. Cations in the salt bridge move towards the cathode and anions move towards the anode.
- If the reactants in a galvanic cell reaction are allowed to come into direct contact, chemical energy is converted into heat energy rather than electrical energy.
- These key concepts about a galvanic cell are summarised in Figure 6.1.11.

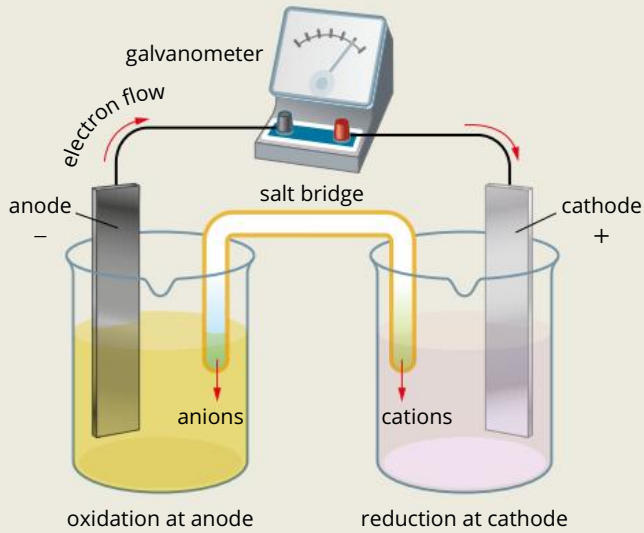


FIGURE 6.1.11 Key concepts about how a galvanic cell works

KEY QUESTIONS

Retrieval

1 State the meaning of the following terms.
- **a** galvanic cell
- **b** electrochemical cell
- **c** salt bridge
- **d** battery

2 Describe how to construct a galvanic cell.

3 Deduce the correct terms in bold by completing the following sentences.

In a galvanic cell, electrons move through the external circuit from the **positive/negative** terminal to the **positive/negative** terminal. Cations in the salt bridge move towards the **anode/cathode** and anions in the salt bridge move towards the **anode/cathode**.

Comprehension

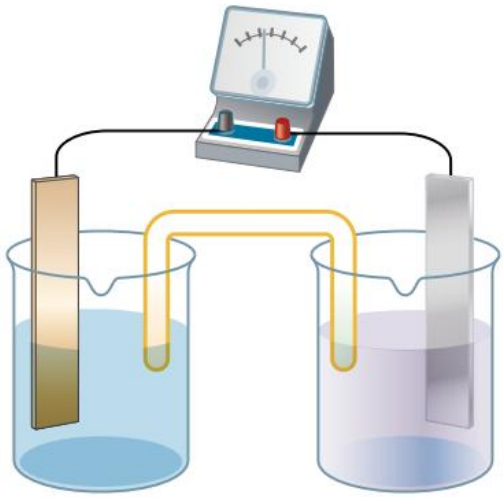
4 Draw labelled diagrams of the following half-cells.
- **a** $Ni^{2+}(aq)/Ni(s)$
- **b** $Sn^{4+}(aq)/Sn^{2+}(aq)$
- **c** $H^{+}(aq)/H_2(g)$

5 State the chemical symbol of a suitable material to use as the electrode in each of the following half-cells.
- **a** $Mg^{2+}(aq)/Mg(s)$
- **b** $Fe^{3+}(aq)/Fe^{2+}(aq)$
- **c** $Cl_2(g)/Cl^{-}(aq)$

6 Label the diagram of the galvanic cell below with the following terms.

- anode
- cathode
- positive electrode
- negative electrode
- reduction reaction
- oxidation reaction
- salt bridge

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



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

7 In a galvanic cell, the cathode is the positive terminal and the anode is the negative terminal. When a galvanic cell is in operation, the positively charged ions (cations) in the salt bridge move towards the cathode and the negatively charged ions (anions) in the salt bridge move towards the anode. Explain why the cations and anions move in these directions.

8 Describe how you would construct a half-cell with the following half-cell equations.

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

b $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

Analysis

9 The overall equation for the reaction that occurs in a cell made up of $Al^{3+}(aq)/Al(s)$ and $Sn^{2+}(aq)/Sn(s)$ half-cells is:

$$2Al(s) + 3Sn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Sn(s)$$

Deduce the half-equations for the reaction occurring at the:

a cathode

b anode.

10 Draw a diagram of the cell from question **9** and label the:

- half-equation for the reaction occurring in each half-cell
- anode and cathode
- direction of electron flow
- electrode polarities (which electrode is positive and which is negative)
- direction of anion and cation flow from the salt bridge.

11 The following reaction occurs within a galvanic cell:

$$Mg(s) + Cl_2(g) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

a Identify the half-cell that acts as the:

i anode of the cell

ii cathode of the cell.

b Compare the energy change that occurs in the cell with the energy change that occurs when magnesium and chlorine react directly.

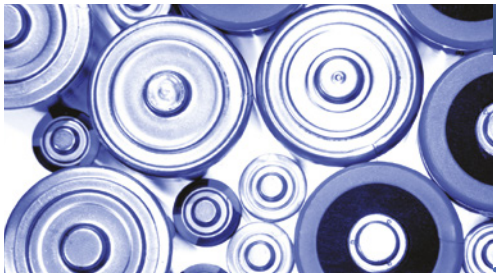
12 A cell is constructed from $Sn^{4+}(aq)/Sn^{2+}(aq)$ and $H^+(aq)/H_2(g)$ half-cells. If the $Sn^{4+}(aq)/Sn^{2+}(aq)$ half-cell is positive, determine the:

a half-cell that acts as the anode

b direction of movement of cations in the salt bridge

c overall equation for the cell reaction.

6.2 The electrochemical series



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand that the relative strength of oxidising and reducing agents can be compared using standard electrode potentials
- use standard electrode potentials to predict the reactions that will occur in different cells under standard conditions, including calculating their cell potentials.



FIGURE 6.2.1 Water dropped onto sodium metal. Sodium is highly reactive; the products are sodium hydroxide and hydrogen gas.

Metals vary in their reactivity. While platinum and gold are unreactive and widely used for jewellery, some other metals are very reactive. For example, sodium reacts so readily with oxygen and water, as shown in Figure 6.2.1, that it must be stored in paraffin oil.

Galvanic cells can help you compare the relative reactivity of metals. Galvanic cells can be constructed from various combinations of half-cells. The experimental data collected from these combinations allows chemists to determine the oxidising and reducing strengths of many different substances. This information is very useful, because it allows you to predict the products of various reactions, calculate the voltages of cells and develop more powerful and longer-lasting batteries.

RELATIVE OXIDISING AND REDUCING STRENGTHS

A half-cell contains a conjugate redox pair. The reactions that can occur in a half-cell can be written as reversible reactions, showing the relationship between the two chemicals in the redox pair. For example, the reaction in a:

- half-cell containing the $H^+(aq)/H_2(g)$ redox pair may be written as:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

- half-cell containing the $Zn^{2+}(aq)/Zn(s)$ redox pair may be written as:

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

Figure 6.2.2 shows a diagram of a cell constructed from $H^+(aq)/H_2(g)$ and $Zn^{2+}(aq)/Zn(s)$ half-cells.

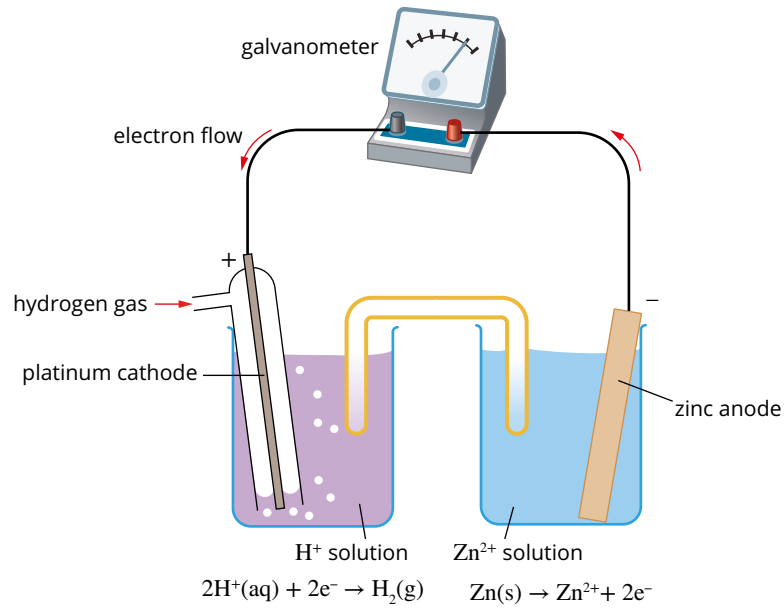


FIGURE 6.2.2 A diagram of a cell constructed from $H^+(aq)/H_2(g)$ and $Zn^{2+}(aq)/Zn(s)$ half-cells

Notice that in this cell the zinc electrode is negative. The reactions that are occurring are:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

Zn is oxidised to Zn^{2+} and H^+ is reduced to H_2. Zinc can be described as a reducing agent or reductant because it causes the reduction of H^+ to occur. The H^+ is described as an oxidising agent or oxidant because it causes the Zn to be oxidised to Zn^{2+}.

Because electrons flow from the Zn^{2+}/Zn half-cell to the H^+/H_2 half-cell, we can infer that:

- zinc is a stronger reducing agent than H_2
- H^+ is a stronger oxidising agent than Zn^{2+} ions.

In a galvanic cell, the stronger reducing agent is in the half-cell with the negative electrode (anode). The stronger oxidising agent is in the half-cell with the positive electrode (cathode).

POTENTIAL DIFFERENCE

A current flows in a galvanic cell because one half-cell has a greater tendency to push electrons into the external circuit than the other half-cell. Chemists say that a **potential difference** exists between the two half-cells. The potential difference of a cell is sometimes also called the **electromotive force**, or emf, and is commonly referred to as the voltage.

The potential difference of a cell, symbol *E*, has the unit of a **volt** (V) and is measured with a **voltmeter**.

Potential differences of cells are usually measured under the **standard conditions** of:

- a pressure of 1 bar (100 kPa)
- 1 mol L^{-1} concentration of solutions.

The potential difference of a cell under standard conditions is given the symbol E°. Potential differences are usually measured at 25°C.

Standard electrode potentials

It is impossible to measure the potential difference of an isolated half-cell because both oxidation and reduction must take place for a potential difference to exist. However, you can assign a standard half-cell potential (E°) to each half-cell by connecting the cells to a standard reference half-cell and measuring the voltage produced.

A hydrogen half-cell, $H^+(aq)/H_2(g)$, under standard conditions, is used for this purpose and its E° value is arbitrarily assigned as zero. This half-cell is known as the **standard hydrogen half-cell** or standard hydrogen electrode.

The **standard electrode potential** of other cells may then be measured by connecting them to the standard hydrogen half-cell, as shown in Figure 6.2.3 for the $Fe^{2+}(aq)/Fe(s)$ half-cell.

We can summarise the information obtained from this measurement shown in Figure 6.2.3 on page 162 as follows:

$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \quad E^\circ = -0.44\,V$$

The negative sign indicates that the electrode in the half-cell was negative when connected to the hydrogen half-cell. Since the electrode is negative, oxidation is occurring in the $Fe^{2+}(aq)/Fe(s)$ half-cell and the electrons that are produced from the iron electrode move towards the hydrogen half-cell. The value of –0.44 V is known as both the standard electrode potential and the **standard reduction potential**. The standard electrode potential gives a numerical measure of the tendency of a half-cell reaction to occur as a reduction reaction.

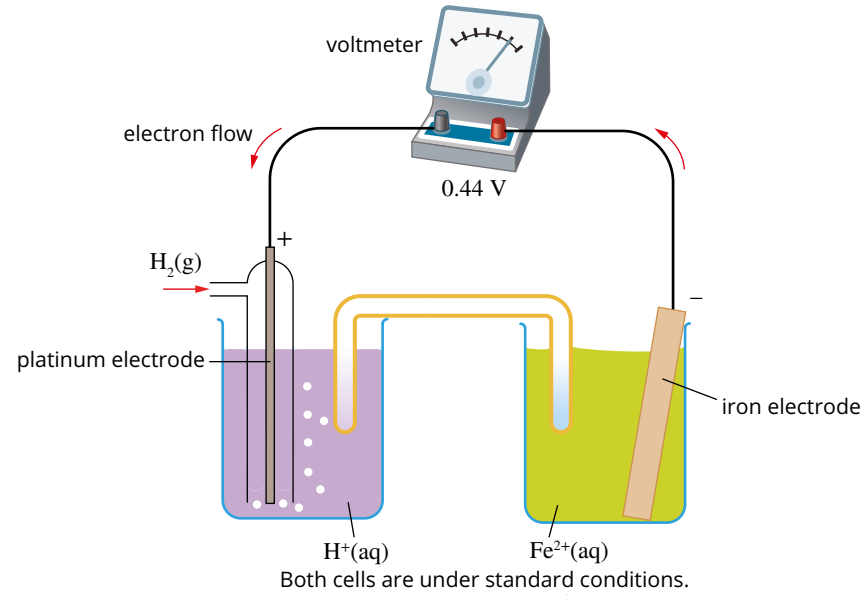


FIGURE 6.2.3 Measuring the standard half-cell potential of a $Fe^{2+}(aq)/Fe(s)$ half-cell. From the voltmeter reading and negative polarity of the iron electrode, the $E°$ of this half-cell is –0.44 V.

THE ELECTROCHEMICAL SERIES

By connecting the standard hydrogen electrode to different half-cells and measuring their standard reduction potentials, chemists have developed a table called the **electrochemical series** (Table 6.2.1). See also Table 2 in Appendix E.

Under non-standard conditions, the order of the half-cell reactions in the table may change.

Notice the value of 0.00 V given for the $H^+(aq)/H_2(g)$ half-equation. All other $E°$ values are relative to this arbitrary standard. The strongest oxidising agent, F_2, is at the bottom left of the table and the strongest reducing agent, Li, is at the top-right of the table.

In a galvanic cell, the stronger reducing agent is oxidised so it is in the half-cell with the negative electrode (anode). The stronger oxidising agent is reduced so it is in the half-cell with the positive electrode (cathode).

Strong reducing agents donate electrons more readily than weak ones.

Strong oxidising agents accept electrons more readily than weak ones.

Strong reducing agents have weak conjugate oxidising agents.

Strong oxidising agents have weak conjugate reducing agents.

Using the electrochemical series

The data in the electrochemical series shown in Table 6.2.1 is the result of the work of many scientists. This table is one of the most useful references for chemists. Two uses of the electrochemical series are described below.

Predicting cell reactions

You can use the electrochemical series to predict what will happen when two specific half-cells are combined to form a cell. The strongest oxidising agent in the cell will react with the strongest reducing agent.

Another way to predict the electrode reactions is to remember that the half-reaction that is lower in the electrochemical series goes forward and the higher one is reversed. As a consequence:

- a reduction reaction will occur in the half-cell with the higher $E°$ value, whereas an oxidation reaction will occur in the half-cell with the lower $E°$ value
- the positive electrode will be in the half-cell with the higher $E°$ value, whereas the negative electrode will be in the other half-cell.

TABLE 6.2.1 The electrochemical series. The strongest oxidising agents are at the bottom left of the table and the strongest reducing agents are at the top-right of the table.

Strength as oxidising agent	Oxidised species ⇌ reduced species	E° (Volts)	Strength as reducing agent
Very weak oxidising agents	$Li^+(aq) + e^- \rightleftharpoons Li(s)$	–3.04	Very strong reducing agents
	$K^+(aq) + e^- \rightleftharpoons K(s)$	–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	
Increasing strength as oxidising agents	$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.15	Increasing strength as reducing agents
	$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+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	
	$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68	
	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+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	
	$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77	
Very strong oxidising agents	$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.89	Very weak reducing agents

The equation for the overall cell reaction is found by adding the two half-equations. Worked example 6.2.1 shows you how to use the electrochemical series to predict a cell reaction.

Worked example 6.2.1

PREDICTING THE OPERATION OF A GALVANIC CELL

A cell is made from $Ag^+(aq)/Ag(s)$ and $Fe^{2+}(aq)/Fe(s)$ half-cells under standard conditions and 25°C. Use the electrochemical series to predict the overall cell reaction, identify the anode and cathode, and determine the direction of electron flow.

Thinking	Working
Identify the two relevant half-equations in the electrochemical series.	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ $E° = -0.44\,V$ $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $E° = +0.80\,V$
Identify the strongest oxidising agent (the species on the left of the series with the most positive $E°$ value) and the strongest reducing agent (the species on the right of the series with the most negative $E°$ value).	Because Ag^+ is lower on the left side of the table than Fe^{2+}, it is the stronger oxidising agent. Fe, being higher on the right side of the table than Ag, is a stronger reducing agent.
Construct the two half-equations that will occur. The strongest oxidising agent will react with the strongest reducing agent. (Hint: The reduction equation has the most positive $E°$ value and the oxidation equation has the most negative $E°$ value.)	Reduction: $Ag^+(aq) + e^- \rightarrow Ag(s)$ Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ Because this is the oxidation reaction, the equation in the electrochemical series should be written in reverse.
Construct the overall cell equation.	Multiply the Ag^+/Ag half-cell equation by two so that the number of electrons in each half-equation is equal, and then add the two equations together: $[Ag^+(aq) + e^- \rightarrow Ag(s)] \times 2$ $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ $2Ag^+(aq) + Fe(s) \rightarrow 2Ag(s) + Fe^{2+}(aq)$
Identify the anode and the cathode in this cell. The anode is the electrode at which oxidation occurs. The cathode is the electrode at which reduction occurs.	The silver electrode will be the cathode and the iron electrode will be the anode.
Determine the polarities of the electrodes and the direction of electron flow in the cell. The anode is negative; the cathode is positive.	Electrons flow from the negative electrode (anode) to the positive electrode (cathode) as shown in Figure 6.2.4.

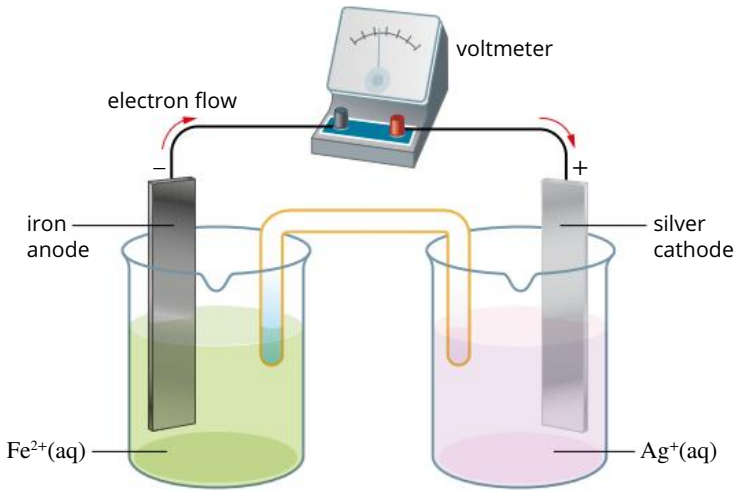


FIGURE 6.2.4 A diagram of the cell containing Fe^{2+}/Fe and Ag^+/Ag half-cells

➤ Try yourself 6.2.1

PREDICTING THE OPERATION OF A GALVANIC CELL

A cell is made from $Sn^{2+}(aq)/Sn(s)$ and $Ni^{2+}(aq)/Ni(s)$ half-cells under standard conditions and at 25°C. Use the electrochemical series to predict the overall cell reaction, identify the anode and cathode, and determine the direction of electron flow.

Calculating the voltage of a cell

The maximum potential difference of a cell under standard conditions is the difference between the $E°$ values of its two half-cells. It is defined as follows:

cell potential difference = $E°$ of half-cell containing the oxidising agent – $E°$ of half-cell containing the reducing agent

An easy way to remember this for galvanic cells is:

cell potential difference = more positive half-cell $E°$ – less positive half-cell $E°$

For example, the maximum cell voltage of a cell constructed from $Ag^+(aq)/Ag(s)$ and $Fe^{2+}(aq)/Fe(s)$ half-cells under standard conditions can be calculated as follows:

cell potential difference = more positive half-cell $E°$ – less positive half-cell $E°$

$= E°(Ag^+(aq)/Ag(s)) - E°(Fe^{2+}(aq)/Fe(s))$

$= +0.80 - (-0.44)$

$= 1.24\text{V}$

Different values for the cell voltage are obtained under non-standard conditions.

As a galvanic cell discharges, the cell voltage eventually drops to zero and the cell is referred to as 'flat'. Equilibrium has then been reached.

i The easiest way to calculate the cell potential difference is to remember:
cell potential difference = more positive half-cell $E°$ – less positive half-cell $E°$

Worked example 6.2.2

CALCULATING THE VOLTAGE OF A GALVANIC CELL

Calculate the maximum cell voltage of a cell made from $Mg^{2+}(aq)/Mg(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cells under standard conditions and 25°C.

Thinking	Working
Identify the two relevant half-equations in the electrochemical series.	$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $E° = -2.36$ V $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $E° = +0.77$ V
Calculate the cell potential using the formula: cell potential difference = more positive half-cell $E°$ – less positive half-cell $E°$	cell potential difference $= +0.77 - (-2.36)$ $= 3.13$ V

➤ Try yourself 6.2.2

CALCULATING THE VOLTAGE OF A GALVANIC CELL

Calculate the maximum cell voltage of a cell made from $Cl_2(g)/Cl^-(aq)$ and $Br_2(l)/Br^-(aq)$ half-cells under standard conditions and 25°C.

WS 3.2.3 WS 3.2.4

6.2 Review

SUMMARY

- The standard hydrogen half-cell is used as the standard reference half-cell; its value is arbitrarily assigned as zero.
- The standard electrode potential or standard reduction potential ($E°$) of a half-cell is measured by connecting the half-cell to a standard hydrogen half-cell and measuring the voltage produced.
- The standard electrode potential gives a numerical measure of the tendency of a half-cell reaction to occur as a reduction reaction.
- Standard electrode potentials are used as the basis of the electrochemical series.
- In the electrochemical series, half-reactions are listed in order so that the strongest oxidising agent is at the bottom left of the series (with the most positive $E°$ value) and the strongest reducing agent is at the top-right (with the most negative $E°$ value).
- The electrochemical series is valid for standard conditions; that is, gas pressures of 1 bar and solution concentrations of 1 mol L^{-1}. Standard electrode potentials are usually measured at 25°C.
- The relative strengths of oxidising and reducing agents can be determined by comparing standard electrode potentials, and these can be used to predict half-cell and overall cell reactions.
- The maximum potential difference of a cell under standard conditions can be calculated from standard electrode potentials:

  cell potential difference = $E°$ of half-cell containing the oxidising agent – $E°$ of half-cell containing the reducing agent

  or, more simply:

  cell potential difference = more positive half-cell $E°$ – less positive half-cell $E°$
- For a spontaneous reaction to occur, an oxidising agent (on the left of the electrochemical series) must react with a reducing agent (on the right) that is higher in the series.

KEY QUESTIONS

Retrieval

1 State the meaning of the following terms.
- **a** potential difference
- **b** standard conditions
- **c** standard electrode potential

2 Deduce the correct terms in bold by completing the following sentences.

In a galvanic cell, the stronger reducing agent is in the half-cell with the **negative/positive** electrode. This electrode is the **anode/cathode**. The stronger oxidising agent is in the half-cell with the **negative/positive** electrode. This electrode is the **anode/cathode**.

Comprehension

3 Describe how the standard electrode potential ($E°$) of a half-cell is measured using a standard hydrogen electrode. In your answer, describe how the sign of the electrode potential is determined.

Analysis

4 A galvanic cell was constructed from $Al^{3+}(aq)/Al(s)$ and $Pb^{2+}(aq)/Pb(s)$ half-cells. Use the electrochemical series (Table 2 in Appendix E) to predict the:
- **a** oxidation and reduction half-equations
- **b** overall cell reaction
- **c** identity of the anode and cathode.

5 Draw a diagram of a cell formed from $Cl_2(g)/Cl^-(aq)$ and $Sn^{2+}(aq)/Sn(s)$ half-cells. Using the electrochemical series (Table 2 in Appendix E), label the diagram to show the:
- **a** half-cell reactions
- **b** anode and cathode
- **c** direction of electron flow
- **d** electrode polarities (which electrode is positive and which is negative)
- **e** directions of flow of the anions and cations in the salt bridge
- **f** overall reaction.

6 For the following half-cells

i $Fe^{3+}(aq)/Fe^{2+}(aq)$ and $H^+(aq)/H_2(g)$

ii $Cl_2(g)/Cl^-(aq)$ and $Pb^{2+}(aq)/Pb(s)$

use the electrochemical series (Table 2 in Appendix E) to predict the:

a half-cell reactions

b anode and cathode

c direction of electron flow

d electrode polarities (which electrode is positive and which is negative)

e directions of flow of the anions and cations in the salt bridge

f overall reaction.

7 Calculate the potential difference for cells constructed from the following standard half-cells.

a $Ag^+(aq)/Ag(aq)$ and $H^+(aq)/H_2(g)$

b $Br_2(l)/Br^-(aq)$ and $Fe^{2+}(aq)/Fe(s)$

8 A standard cell has the following cell reaction:

$$2H^+(aq) + 2Cr^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + H_2(g)$$

If the voltage of this cell is 0.40 V, determine the E^o for the following half-reaction:

$$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$$

9 A cell constructed from standard $Ti^{3+}(aq)/Ti^{2+}(aq)$ and $Br_2(l)/Br^-(aq)$ half-cells has a potential difference of 1.46 V. If the electrode in the $Ti^{3+}(aq)/Ti^{2+}(aq)$ half-cell is negative, use the electrochecmical series (Table 2 in Appendix E) to calculate the standard electrode potential of a $Ti^{3+}(aq)/Ti^{2+}(aq)$ half-cell.

10 A cell is constructed from standard $Ni^{2+}(aq)/Ni(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cells.

a Identify the strongest oxidising agent in the cell.

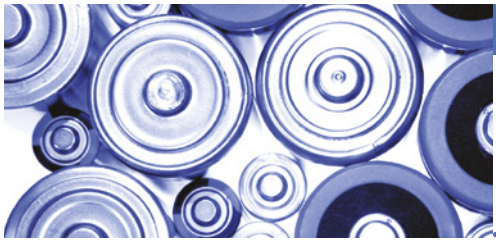
b Identify the strongest reducing agent in the cell.

c Describe the direction of flow of cations and anions in the salt bridge.

11 Consider the galvanic cells made from standard half-cells as listed below. Rank the cells in order of their voltage, from highest to lowest.

- $Ag^+(aq)/Ag(s)$ and $Cl_2(g)/Cl^-(aq)$
- $Fe^{2+}(aq)/Fe(s)$ and $Ag^+(aq)/Ag(s)$
- $Fe^{2+}(aq)/Fe(s)$ and $Cl_2(g)/Cl^-(aq)$

6.3 Predicting direct redox reactions



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- predict whether a redox reaction will occur when chemicals are directly mixed
- recognise the limitations associated with the use of standard reduction potentials to predict whether a redox reaction will be observed.

The electrochemical series provides us with a ranking of the relative strengths of oxidising and reducing agents.

In this module, you will see that you can apply your understanding of the electrochemical series to predict the likelihood of a redox reaction taking place when different chemicals are combined.

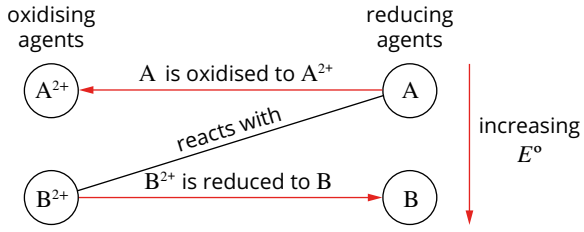
PREDICTING REACTIONS

If the contents of the half-cells of a galvanic cell were mixed, the reactants would react directly. Energy would be released as heat rather than as electrical energy. Reactions that occur in galvanic cells or when chemicals are directly mixed are described as naturally occurring reactions, or spontaneous reactions.

In the last module, you saw that in a galvanic cell the strongest oxidising agent in the cell reacts with the strongest reducing agent. In other words, the half-reaction with the more positive E° value in the electrochemical series occurs in the forward direction (as reduction), and the reaction with the more negative E° value occurs in the reverse direction (as oxidation).

This principle applies equally to redox reactions that occur when reactants are mixed directly.

As shown in Figure 6.3.1, for a spontaneous reaction to occur, an oxidising agent (on the left of the electrochemical series) must react with a reducing agent (on the right) that has a more negative E° value in the electrochemical series.



A reacts with B^{2+}.

No reaction occurs for the other combinations: A and B, A^{2+} and B^{2+}, A^{2+} and A, B and B^{2+}, A^{2+} and B.

FIGURE 6.3.1 Oxidising agents only react significantly with reducing agents that have more negative E° values in the electrochemical series.

With half-equations arranged in order of increasing oxidising agent strength, you can predict that a spontaneous reaction will occur by looking for substances that are arranged in a top-right/bottom-left position.

Worked example 6.3.1

PREDICTING DIRECT REDOX REACTIONS

Consider the following equations that appear in the order shown in the electrochemical series.

$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $\quad E^\circ = -2.36\,V$

$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $\quad E^\circ = -0.24\,V$

$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$ $\quad E^\circ = +1.08\,V$

Use the electrochemical series to predict the effect of mixing:

a $Br_2(l)$ and $Mg^{2+}(aq)$

b $Mg^{2+}(aq)$ and $Ni(s)$

c $Ni^{2+}(aq)$ and $Mg(s)$.

Thinking	Working
Identify the two relevant half-equations in the electrochemical series. Predict whether or not a reaction occurs. A chemical species on the left of the electrochemical series (an oxidising agent) reacts with a chemical species on the right (a reducing agent) that has a half-reaction with a more negative E°. Construct the overall equation.	**a** $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $\quad E^\circ = -2.36\,V$ $Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$ $\quad E^\circ = +1.08\,V$ No reaction occurs because both $Br_2(aq)$ and $Mg^{2+}(aq)$ are oxidising agents. **b** $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $\quad E^\circ = -2.36\,V$ $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $\quad E^\circ = -0.24\,V$ No reaction occurs because the half-reaction involving the oxidising agent, Mg^{2+}, has a more negative E° than that of the reducing agent, Ni, in the electrochemical series. **c** $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $\quad E^\circ = -2.36\,V$ $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $\quad E^\circ = -0.24\,V$ A reaction occurs because the half-reaction involving the oxidising agent, Ni^{2+}, has a more positive E° than that of the reducing agent, Mg, in the electrochemical series. The lower half-equation in the series occurs in the forward direction: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ The higher half-equation occurs in the reverse direction: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ The overall reaction equation is found by adding the half-equations: $Ni^{2+}(aq) + Mg(s) \rightarrow Ni(s) + Mg^{2+}(aq)$

➤ Try yourself 6.3.1

PREDICTING DIRECT REDOX REACTIONS

Consider the following equations that appear in the order shown in the electrochemical series:

$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$ $\quad E^\circ = -0.13\,V$

$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$ $\quad E^\circ = +0.54\,V$

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $\quad E^\circ = +1.36\,V$

Use the electrochemical series to predict the effect of mixing:

a $I_2(s)$ and $Pb^{2+}(aq)$

b $Cl^-(aq)$ and $I_2(s)$

c $I_2(s)$ and $Pb(s)$.

Limitations of predictions

The standard half-cell potentials given in the electrochemical series are measured under standard conditions. As you would expect, half-cell potentials can vary under other conditions.

When conditions are very different from standard conditions, the order of half-reactions in the electrochemical series may also be different, and predictions of reactions based on the standard half-cell potentials may not be reliable.

It is also important to remember that the electrochemical series gives no information about the rate at which reactions occur.

6.3 Review

SUMMARY

- The relative strength of oxidising and reducing agents can be determined by comparing standard electrode potentials, and these can be used to predict the tendency of a reaction to occur, both in galvanic cells and in direct reactions.
- For a spontaneous reaction to occur, an oxidising agent (on the left of the electrochemical series) must react with a reducing agent (on the right) that has a more negative E°.
- Overall equations for redox reactions can be obtained by adding half-equations.
- When reactants react in a galvanic cell, chemical energy is transformed into electrical energy. However, when they react directly their chemical energy is transformed into heat energy.
- The standard half-cell potentials in the electrochemical series are measured under standard conditions. Under other conditions, the order of half-reactions may be different, and predictions based on the electrochemical series may not be reliable.

KEY QUESTIONS

Retrieval

1 Describe the conditions necessary for an oxidising agent to react with a reducing agent at standard conditions when the reactants are mixed directly.

Comprehension

2 When a strip of zinc metal is placed in a silver nitrate solution, a coating of silver metal forms on the surface of the strip.
- **a** Construct the overall equation for the reaction.
- **b** Describe the energy change that takes place in this reaction.

3 Explain why predictions of reactions based on the standard half-cell potentials do not always correspond with observations when the reactants are mixed.

4 Use the electrochemical series (Table 2 in Appendix E) to determine whether:
- **a** sodium is a stronger reducing agent than lithium
- **b** $Fe^{2+}(aq)$ is a stronger oxidising agent than $Ca^{2+}(aq)$
- **c** $Sn^{2+}(aq)$ can act as an oxidising agent and a reducing agent.

Analysis

5 Use the electrochemical series (Table 2 in Appendix E) to determine whether or not a reaction will occur when the following are mixed.
- **a** $Cl_2(g)$ and $Fe^{2+}(aq)$
- **b** $Br^-(aq)$ and $I_2(s)$
- **c** $Br^-(aq)$ and $Zn(s)$
- **d** $Fe^{2+}(aq)$ and $Zn(s)$

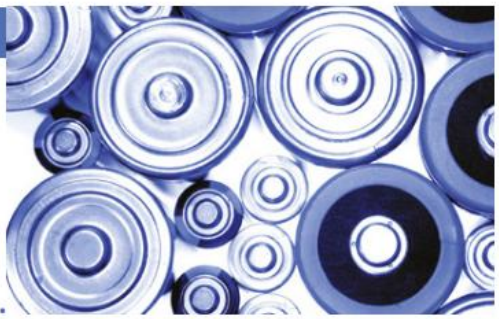
6 Using the electrochemical series (Table 2 in Appendix E), determine whether a reaction will occur in the following situations. If a reaction does occur, construct the overall equation for the reaction.
- **a** Chlorine gas is bubbled into a solution containing bromide ions.
- **b** Chlorine gas is bubbled into a solution containing iodide ions.
- **c** A bromine solution is added to a solution containing chloride ions.
- **d** A bromine solution is added to a solution containing iodide ions.

7 Iron nails are placed into $1\,mol\,L^{-1}$ solutions of $CuSO_4$, $MgCl_2$, $Pb(NO_3)_2$ and $ZnCl_2$. Use the electrochemical series (Table 2 in Appendix E) to identify in which solution(s) you would expect a coating of a metal other than iron to appear on the nail.

6.4 Everyday sources of power

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- distinguish between primary and secondary cells
- describe the energy transformations that take place when cells and batteries are recharged
- appreciate some of the different types of galvanic cells that are in widespread use, including their use for measuring blood alcohol concentrations.



The battery was invented by Alessandro Volta in 1800. Following World War II, an expanding range of electrical appliances became available that required small, high-capacity power sources. Today, more than two centuries after Volta's invention, cells and batteries are a common power source for many household and industrial applications.

Cells and batteries can be used as fixed energy storage systems, such as in solar energy systems, burglar alarms and smoke detectors. They are also used extensively in portable applications including mobile phones, watches, digital cameras and laptop computers. The portability of these devices relies on these sources of electrical energy.

Cells and batteries use spontaneous redox reactions as the source of energy. In this module, you will look at the two main types of cells in use and how chemical reactions in these cells are used to produce electricity for everyday applications.

The two basic types of cells are:

- **primary cells**, which are disposable and designed not to be recharged
- **secondary cells**, which are rechargeable and designed to be reused many times.

Both primary cells and secondary cells are types of galvanic cells.

PRIMARY CELLS

Common commercial **alkaline cells**, such as those you would usually use in a torch or a remote control, are **non-rechargeable cells**. Some non-rechargeable alkaline cells are shown in Figure 6.4.1. They 'go flat' when the cell reaction reaches equilibrium, and you have to buy a replacement.

Cells that cannot be recharged are called primary cells. In primary cells, the products slowly migrate away from the electrodes or are consumed by side reactions occurring in the cell, preventing the cells from being recharged.



FIGURE 6.4.1 Non-rechargeable alkaline cells are used to power many devices, including torches, smoke detectors and calculators. They are discarded once they go flat.

An example of a primary cell: the alkaline cell

The alkaline cell was developed in the late 1960s to meet a growing need for small, high capacity sources of power for portable electrical appliances.

Figure 6.4.2 on page 172 shows the construction of an alkaline cell and the reactions that occur in the cell. This cell is similar to the simple galvanic cells looked at earlier in this chapter, but has been designed so the two half-reactions occur in separate places within the one container. A potassium hydroxide electrolyte performs the same function as a salt bridge in the simple cells.

Alkaline cells are especially cost-effective in torches, flashguns and motorised toys, where high currents are needed intermittently. The cell produces about 1.5 V. Once the reaction in the cell reaches equilibrium the cell is 'flat' and cannot be used again.

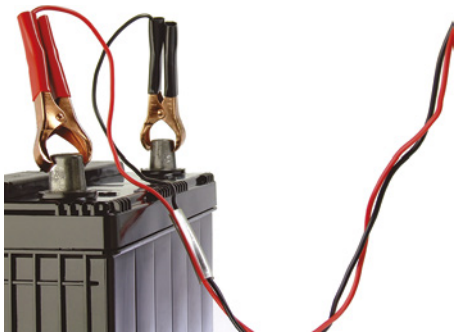
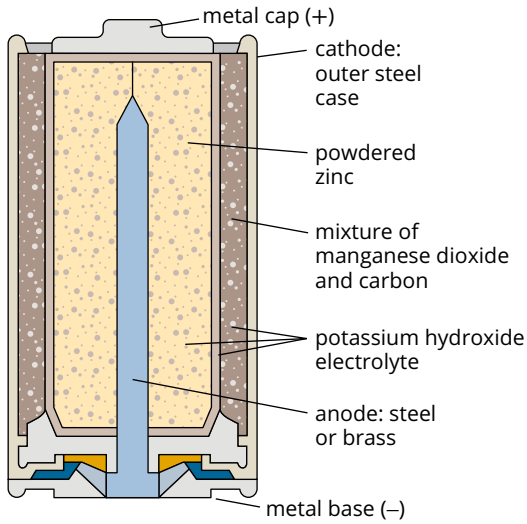


FIGURE 6.4.3 Charging a secondary battery involves connecting the positive terminal of a charger to the battery's positive electrode and the negative electrode of the charger to the battery's negative electrode.



At the anode (–):
$Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$

At the cathode (+):
$2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$

Overall reaction:
$Zn(s) + 2MnO_2(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + Mn_2O_3(s)$

FIGURE 6.4.2 Construction of an alkaline cell

> **i** Primary cells cannot be recharged, whereas secondary cells can be recharged by connecting them to an external source of electricity.

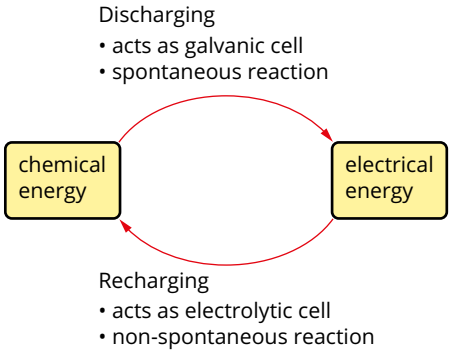


FIGURE 6.4.4 Energy transformations in secondary cells



FIGURE 6.4.5 Lead–acid batteries are secondary cells that are used to start cars, trucks and motorcycles.

SECONDARY CELLS

Rechargeable cells, such as **lithium-ion cells**, **lead-acid batteries** and **nickel–metal hydride cells**, are known as secondary cells or **accumulators**.

Rechargeable cells and batteries have become very popular and are found in mobile phones, laptop computers, cameras and portable power tools. They are also fundamental to the operation of cars, electric vehicles and solar power energy storage systems.

Most types of rechargeable cells can undergo many hundreds of recharges. To recharge a cell, the cell reaction must occur in reverse: the products of the reaction must be converted back into the original reactants. This is done by connecting the cell to a 'charger', a source of electrical energy, which has a potential difference a little greater than the potential difference of the cell. The positive terminal of the charger is connected to the cell's positive electrode and the negative electrode of the charger is connected to the cell's negative electrode (see Figure 6.4.3).

Electrical energy supplied by the charger is converted into chemical energy in the cell. In order for it to be possible to regenerate the reactants, the products formed in the cell during discharge must remain in contact with the electrodes in a convertible form.

The energy transformations in a secondary cell can be summarised as follows.

- When a secondary cell discharges, it acts as a galvanic cell, converting chemical energy into electrical energy.
- When the cell is recharged, it acts as a type of cell called an **electrolytic cell**. Electrical energy is transformed into chemical energy in an electrolytic cell. You will learn more about the operation of electrolytic cells in Chapter 7.

The energy transformations and redox processes that occur during the discharging and recharging of a secondary cell are summarised in Figure 6.4.4

Lead–acid batteries are the most widely used type of secondary cell. They are relatively cheap and reliable, provide high currents and have a long lifetime. Most people know the lead–acid battery simply as a car battery, as shown in Figure 6.4.5. It is used to start the car's engine and to operate the car's electrical accessories when the engine is not running. Once the engine starts, an alternator, which is run by the engine, provides electrical energy to operate the car's electrical system and recharge the battery.

Breathalysers and measurement of blood alcohol levels

Drinks such as wine, beer and vodka contain ethanol (CH_3CH_2OH). Ethanol acts as a depressant, slowing the functioning of the brain. When alcoholic drinks are consumed in excess, their intoxicating qualities can lead to antisocial behaviour and can damage a person's health.

The ethanol content of alcoholic drinks varies, as shown in Table 6.4.1.

TABLE 6.4.1 Typical ethanol contents of selected alcoholic beverages

Drink	Ethanol content (%v/v)
spirits (brandy, bourbon, gin, rum, vodka, whiskey etc.)	37
port, sherry	18
wines (including sparkling wines)	12
pre-mixed vodka-based drinks	9
alcoholic cider	10
beer	5.0
'light' beer	2.5

Regulations require that the ethanol content of alcoholic drinks be specified on their labels, since the content determines how much drink can be consumed without adverse effects.

Because ethanol slows down reaction time, it seriously affects a person's driving skills. It is estimated that alcohol has contributed to nearly 40% of all road accidents. Governments have responded by introducing penalties, such as fines and licence disqualification, for drivers whose blood alcohol concentration exceeds a certain level—typically 0.05% (m/v). Probationary or P-plate drivers are required to have a zero blood alcohol level.

The introduction of penalties, a policy of randomly testing motorists for blood alcohol level, and various advertising campaigns have all helped to increase public awareness of the link between alcohol consumption and road accidents.

Chemists were involved in the invention of the breathalyser, an instrument designed for police to use to estimate blood alcohol content, as shown in Figure 6.4.6. Rather than analysing samples of blood, this instrument measures the concentration of alcohol in a person's breath, which is closely related to the concentration of alcohol in their blood.

If this screening test indicates that a driver's blood is over 0.05% (m/v), more accurate measurements are taken either in a 'booze bus' or at a police station. These accurate measurements use instrumental techniques such as infrared spectroscopy or gas–liquid chromatography.



FIGURE 6.4.6 Breathalysers are used to analyse the blood alcohol content of motorists. Some breathalysers are a type of galvanic cell.

Most police departments use breathalysers based on galvanic cells, as shown in Figure 6.4.7. The breathalysers have platinum electrodes and, when the motorist exhales into the breathalyser, any ethanol present in the motorist's breath is oxidised to ethanoic acid by oxygen in the air.

The half-reactions are:

- at the anode:
  $CH_3CH_2OH(g) + H_2O(l) \rightarrow CH_3CO_2H(aq) + 4H^+(aq) + 4e^-$
- at the cathode:
  $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

The electric current produced by this reaction is measured and displayed as a measure of overall blood alcohol content.

The breathalyser is an example of a type of galvanic cell called a fuel cell. You will learn more about fuel cells in Chapter 12.

Review

1 Construct an overall equation for the reaction that occurs in a breathalyser.

2 Deduce the correct terms in bold by completing the following sentences.
In a breathalyser the electrode at which ethanol reacts is **positive/negative** and the ethanol acts as the **oxidising agent/reducing agent**. Cations in the electrolyte flow towards the **anode/cathode**. Electrons flow through the external circuit from the **anode/cathode** to the **anode/cathode**.

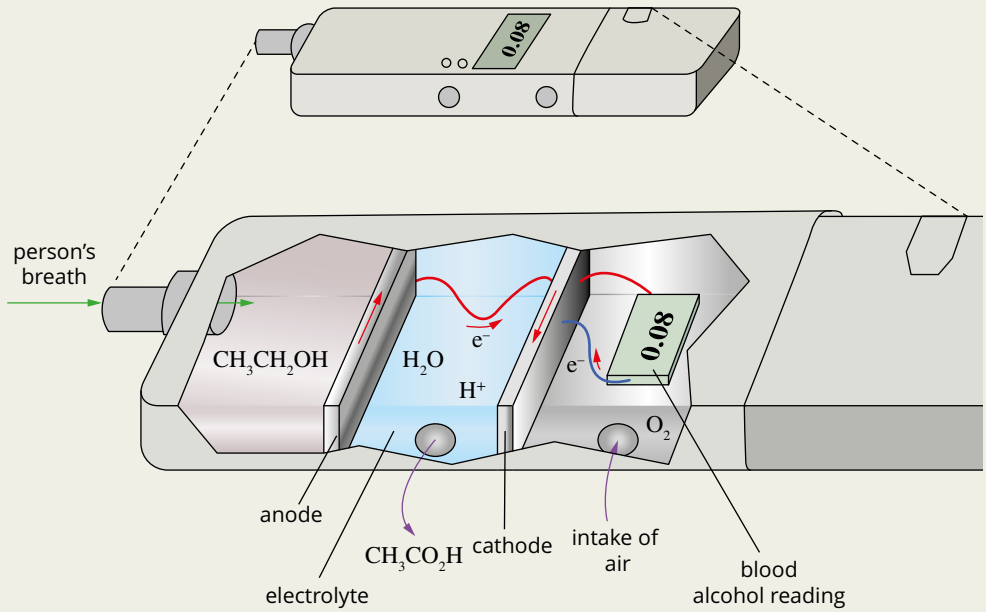


FIGURE 6.4.7 Construction of a breathalyser based on a galvanic cell

6.4 Review

SUMMARY

- Primary and secondary cells are examples of galvanic cells.
- Primary cells cannot be recharged.
- Secondary cells can be recharged by connecting them to an external source of electricity.
- For a cell to be rechargeable, the products of the discharge reaction have to remain in contact with the electrodes.
- During the recharging of a secondary cell, the cell reaction is reversed and the products of the cell reaction are converted back into the original reactants.
- When a secondary cell discharges and produces electrical energy, it acts as a galvanic cell; when it is recharged, it acts as an electrolytic cell.

KEY QUESTIONS

Retrieval

1 Describe the key difference between a primary cell and a secondary cell.

Comprehension

2 Identify whether the cells and batteries commonly used in the following appliances are primary or secondary cells.

a car
b calculator
c mobile phone
d torch

Analysis

3 Silver-zinc button cells are used in hearing aids and watches. In a silver–zinc button cell, the cell reaction is:

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

The zinc acts as the anode and the cell contains a potassium hydroxide electrolyte. Construct a half-equation for the reaction occurring at the:

a anode
b cathode.

4 Assess whether each of the following statements about cells and batteries is true or false.

a Primary cells are recharged once they become 'flat'.
b When a secondary cell is recharged, the cell reaction is the reverse of the reaction during discharging.
c When a phone battery is recharged, chemical energy is converted into electrical energy.
d In a secondary cell, the reactants and products of the cell reaction remain in contact with the electrodes.

5 Car batteries are secondary cells. The reaction that occurs in a car battery as it delivers electricity is represented by the equation:

$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

a State the formula of the chemical that is oxidised in this reaction.
b State the formula of the chemical that is reduced in this reaction.
c Determine the equation that occurs as a car battery is charging.
d Describe the energy transformation that occurs as a car battery is charging.

Constructing a galvanic cell and a table of standard electrode potentials

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Research and planning

Aim

- To construct a number of different galvanic cells.
- To identify the essential components of galvanic cells.
- To use the cells to determine the relative positions of various pairs of oxidising agents and reducing agents in the table of standard electrode potentials.

Rationale (scientific background to the experiment)

During the operation of a galvanic cell, the relative abilities of the chemical species in the half-cells to donate and accept electrons determine which electrode is positive and which is negative. The half-cell containing the stronger reducing agent will undergo an oxidation reaction; the electrode in this half-cell is the anode and will be negative. The other half-cell will contain the stronger oxidising agent and undergo a reduction reaction; the electrode in this half-cell is the cathode.

Timing

40 minutes

Materials

- 50 mL × 0.1 mol L^{-1} copper(II) nitrate solution, $Cu(NO_3)_2(aq)$
- 50 mL of an equal mixture of 0.1 mol L^{-1} iron(III) nitrate solution, $Fe(NO_3)_3(aq)$, and 0.1 mol L^{-1} iron(II) sulfate solution, $FeSO_4(aq)$
- 50 mL of an equal mixture of 0.05 mol L^{-1} iodine solution, $I_2(aq)$, and 0.1 mol L^{-1} potassium iodide solution, KI(aq)
- 50 mL × 0.1 mol L^{-1} zinc nitrate solution, $Zn(NO_3)_2(aq)$
- 50 mL × 0.1 mol L^{-1} potassium nitrate solution, $KNO_3(aq)$
- copper electrode
- zinc electrode
- 2 × carbon rods
- 5 × 100 mL beakers
- voltmeter
- 2 × wire leads with alligator clips
- 6 × strips of 2 cm × 15 cm chromatography paper or filter paper
- safety glasses and gloves



Safety

Pre-lab safety information		
Material used	**Hazard**	**Control**
0.1 mol L^{-1} copper(II) nitrate solution	for solid $Cu(NO_3)_2$: harmful if swallowed; irritant to eyes and skin	Wear safety glasses and a laboratory coat.
0.1 mol L^{-1} zinc nitrate solution	for solid $Zn(NO_3)_2$: harmful if swallowed; irritant to eyes, skin and respiratory system	Wear safety glasses and a laboratory coat.
0.05 mol L^{-1} iodine solution		Wear safety glasses and a laboratory coat.
0.1 mol L^{-1} potasium iodide solution		Wear safety glasses and a laboratory coat.
0.1 mol L^{-1} iron(III) nitrate solution	for solid $Fe(NO_3)_3$: harmful if swallowed	Wear safety glasses and a laboratory coat.
0.1 mol L^{-1} iron(II) sulfate solution	for solid $FeSO_4$: harmful if swallowed	Wear safety glasses and a laboratory coat.
0.1 mol L^{-1} potassium nitrate solution		Wear safety glasses and a laboratory coat.
Please indicate that you have understood the information in the safety table. Name (print): _____ I understand the safety information (signature): _____		

Method

Risk assessment

Assessment of risks include chemical hazards and physical hazards. Before you commence this practical activity, you must conduct a risk assessment. Complete the template in your Skills and Assessment Book or download it from your eBook.

1 Construct the following four half-cells:

Half-cell	Constituent parts
Cu^{2+}/Cu	100 mL beaker containing a copper electrode and 50 mL of copper(II) nitrate solution
Fe^{3+}/Fe^{2+}	100 mL beaker containing a carbon rod and 50 mL of iron(III) nitrate/iron(II) sulfate solution
I_2/I^-	100 mL beaker containing a carbon rod and 50 mL of iodine/potassium iodide solution
Zn^{2+}/Zn	100 mL beaker containing a zinc electrode and 50 mL of zinc nitrate solution

2 Make a salt bridge by folding a piece of filter paper and soaking it in a beaker of potassium nitrate solution. Join the Cu^{2+}/Cu and Zn^{2+}/Zn half-cells using the salt bridge. Attach two wires to the voltmeter and clip the other end of one wire to the copper electrode. Momentarily touch the loose end of the second wire to the zinc electrode. If the needle of the voltmeter is deflected onto the scale, clip this loose end of the wire to the zinc electrode and proceed with the next step. If, however, the needle of the voltmeter is deflected below zero, swap the wires at the terminals of the voltmeter before continuing.

3 Use Table 1 to record the voltage and identify the positive and negative electrodes. (The positive electrode is connected to the positive terminal of the voltmeter.)

4 Disconnect the leads. Remove and discard the salt bridge.

5 Repeat steps 2–4 for each of the other five combinations of half-cells.

Variables

i Identify the independent variable.

ii Identify the dependent variable variable.

iii Identify any controlled variable.

Analysing

Raw data

1 Record your results in Table 1.

TABLE 1 Voltage and electrode polarity

Cell	Voltage (V)	Positive electrode
Cu^{2+}/Cu and Zn^{2+}/Zn		
Fe^{3+}/Fe^{2+} and Zn^{2+}/Zn		
Fe^{3+}/Fe^{2+} and I_2/I^-		
Cu^{2+}/Cu and I_2/I^-		
Cu^{2+}/Cu and Fe^{3+}/Fe^{2+}		
I_2/I^- and Zn^{2+}/Zn		

Processed data

2 Draw a diagram of the cell constructed from Cu^{2+}/Cu and I_2/I^- half-cells and the cell constructed from Fe^{3+}/Fe^{2+} and Zn^{2+}/Zn half-cells. Label the contents of the half-cells, the positive and negative electrodes, the anode and cathode, the direction of electron flow through the external circuit and the direction the ions move in the salt bridge.

Cu^{2+}/Cu and I_2/I^- cell	Fe^{3+}/Fe^{2+} and Zn^{2+}/Zn cell

Reflect and check that your data analysis demonstrates these characteristics

- ☐ Effective investigation of phenomena is demonstrated by the collection of sufficient and relevant raw data.
- ☐ Accurate application of algorithms, visual and graphical representations of data is demonstrated by appropriate processing and presentation of data to aid the analysis and interpretation of data.

Analysis

3 In the following table, show half-equations for the reactions occurring in each half-cell and then the overall equation for the reaction in each cell.

Cell	Anode reaction	Cathode reaction	Overall reaction
Cu^{2+}/Cu and Zn^{2+}/Zn			
Fe^{3+}/Fe^{2+} and Zn^{2+}/Zn			
Fe^{3+}/Fe^{2+} and I_2/I^-			
Cu^{2+}/Cu and I_2/I^-			
Cu^{2+}/Cu and Fe^{3+}/Fe^{2+}			
I_2/I^- and Zn^{2+}/Zn			

4 Compare the order of your equations in question **3** with that of the equations listed in the table of standard electrode potentials in the data booklet. Consider whether or not they are the same. Evaluate why differences might arise.

5 Explain the function of the salt bridge in an electrochemical cell.

6 Explain why it was necessary to use a new salt bridge for each electrochemical cell.

7 Consider a Pb^{2+}/Pb half-cell. If lead is a stronger reducing agent than copper, but $Pb^{2+}(aq)$ is a stronger oxidising agent than $Zn^{2+}(aq)$, state where in your table of standard electrode potentials you would place the following equation.

$$Pb^{2+}(aq) + 2e^- \; Pb(s)$$

Reflect and check that your analysis demonstrates these characteristics
☐ Systematic and effective analysis of evidence is demonstrated by a thorough and appropriate error analysis.
☐ Systematic and effective analysis of evidence is demonstrated by a thorough identification of relevant trends, patterns and relationships.
☐ Insightful and valid interpretation of evidence is demonstrated by drawing a valid and defensible conclusion based on the analysis.

Interpreting and communicating

Conclusion

1 Examine the results you have obtained and construct the four half-cell reactions as reduction reactions, listing them in order of increasing reducing agent strength. (Your list should show the strongest oxidising agent in the lower left corner and the strongest reducing agent in the upper right corner.) This is a table of standard electrode potentials.

Evaluation

2 Briefly evaluate the reliability of the data, including a discussion of errors.

Improvements

3 Briefly discuss any problems you have encountered and possible modifications.

Reflect and check that your evaluation demonstrates these characteristics
☐ Critical evaluation of processes is demonstrated by a discussion of the reliability and validity of the experimental process supported by evidence such as the quality of the data (as quantified in the error analysis).
☐ Critical evaluation of the conclusion is demonstrated by a discussion of the veracity of the conclusions with respects to the error analysis and limitations or sufficiency of the data
☐ Insightful evaluation of processes and conclusions is demonstrated by a suggestion of improvements or extensions to the experiment that are logically derived from the analysis of the evidence.

Chapter review

06

KEY TERMS

accumulator
alkaline cell
battery
electrochemical cell
electrochemical series
electrode
electrolyte
electrolytic cell
electromotive force
external circuit
galvanic cell
galvanometer
half-cell
internal circuit
lead–acid battery
lithium–ion cell
nickel–metal hydride cell
non-rechargeable cell
potential difference
primary cell
rechargeable cell
salt bridge
secondary cell
spontaneous reaction
standard conditions
standard electrode potential
standard hydrogen half-cell
standard reduction potential
volt
voltaic cell
voltmeter

KEY QUESTIONS

Retrieval

1 Identify which one of the following statements best describes the role of the salt bridge in a galvanic cell.

A It provides a pathway for electrons to move between the half-cells.
B It allows movement of ions to balance charges formed at the electrodes.
C It allows reactants from one half-cell to mix with reactants from the other half-cell.
D It allows positive charges to accumulate in one half-cell and negative charges to accumulate in the other.

2 Identify which one of the following statements about a galvanic cell is correct.

A The electrode where oxidation occurs is the cathode.
B Electrons flow towards the electrode where oxidation occurs.
C The electrode where oxidation occurs has a negative polarity.
D Anions flow into the half-cell containing the electrode where reduction occurs.

3 **a** Name the half-cell that is used as the reference for the measurement of standard electrode potential (E°).

b Indicate the meaning of the term 'standard conditions'.

4 Select the correct definitions for the following terms.

Term	Definition
galvanic cell	a rechargeable galvanic cell
primary cell	a device that converts chemical energy into electrical energy
secondary cell	a non-rechargeable galvanic cell

Comprehension

5 Mains electricity costs about 5 cents per MJ of energy, or less, depending on the tariff. The cost of the same amount of electrical energy produced by a cell is far more—about $1300 for a dry cell and even more for a button cell. Discuss why people are prepared to use cells and pay such relatively high prices for electricity.

6 Identify which one of the following materials would be least suitable for use as an electrode in a $Cl_2(g)/Cl^-(aq)$ half-cell.

A iron
B gold
C graphite
D platinum

7 Identify which one of the following statements about the oxidising and reducing agents in a galvanic cell is correct.

A The stronger oxidising agent is in the half-cell that acts as the anode.
B The stronger reducing agent is in the half-cell that acts as the cathode.
C The stronger reducing agent is in the half-cell with the negative electrode.
D The stronger oxidising agent is in the half-cell with the negative electrode.

8 Identify which one of the following metals you would expect to be coated with nickel when immersed in a solution of nickel(II) nitrate.

A tin
B zinc
C silver
D copper

9 Identify which one of the following cells or batteries is least likely to be a secondary cell or battery.
- **A** phone battery
- **B** laptop battery
- **C** watch battery
- **D** car battery

10 Most modern mobile phones contain lithium-ion cells. Select the correct statement about the process that occurs when a phone battery is recharged.
- **A** A spontaneous reaction occurs and the lithium-ion cell acts as a galvanic cell.
- **B** A spontaneous reaction occurs and the lithium-ion cell acts as an electrolytic cell.
- **C** A non-spontaneous reaction occurs and the lithium-ion cell acts as a galvanic cell.
- **D** A non-spontaneous reaction occurs and the lithium-ion cell acts as an electrolytic cell.

11 Explain how the electrochemical series can be used to identify the relative strengths of oxidising agents and reducing agents.

12 Deduce the correct terms in bold by completing the following sentences.
A spontaneous redox reaction will occur if an oxidising agent (on the **left/right** of the electrochemical series) reacts with a reducing agent (on the **left/right** of the series) that has a half-reaction with **more/less** positive $E°$ value. **Electrical/heat** energy is released.

13 Fill in the blanks in the following passage about galvanic cells.
The redox reaction occurring in a galvanic cell takes place in two _____. The electrode at which oxidation occurs is called the _____, whereas the other electrode where reduction occurs is the _____. The polarity of the anode is _____ and the polarity of the cathode is _____. Galvanic cells can be classified as either primary cells, which _____ be recharged, or secondary cells, which _____ be recharged.

14 Describe the features that enable secondary cells such as lithium-ion cells to be recharged.

15 The overall reaction for a galvanic cell constructed from the $Cl_2(g)/Cl^-(aq)$ and $Pb^{2+}(aq)/Pb(s)$ half-cells is:

$$Cl_2(g) + Pb(s) \rightarrow 2Cl^-(aq) + Pb^{2+}(aq)$$

Draw a diagram of the galvanic cell and on your diagram show the:
- **a** direction of electron flow in the external circuit
- **b** half-equation for the reaction at each electrode
- **c** anode electron
- **d** positive electrode
- **e** direction of cation flow in the salt bridge.

16 Two half-cells are set up. One contains a solution of magnesium nitrate with a strip of magnesium as the electrode. The other contains lead nitrate with a strip of lead as the electrode. The solutions in the two half-cells are connected by a piece of filter paper soaked in potassium nitrate solution. When the electrodes are connected by wires to a galvanometer, the magnesium electrode is shown to be negatively charged.
- **a** Sketch the galvanic cell described. Label the positive and negative electrodes. Mark the direction of the electron flow.
- **b** Construct the half-equations for the reactions that occur in each half-cell and an equation for the overall reaction.
- **c** Label the anode and cathode.
- **d** Indicate the direction in which ions in the salt bridge migrate.

17 Show that under standard conditions, according to the electrochemical series (Table 2 in Appendix E), the Daniell cell (Figure 6.1.3 on page 154) should have a cell potential difference of 1.10 V.

18 Each of these pairs of half-cells combines to form a galvanic cell.
- **i** $Ag^+(aq)/Ag(s)$ and $Zn^{2+}(aq)/Zn(s)$
- **ii** $Fe^{2+}(aq)/Fe(s)$ and $Pb^{2+}(aq)/Pb(s)$
- **iii** $Ni^{2+}(aq)/Ni(s)$ and $Cu^{2+}(aq)/Cu(s)$

Draw a diagram of each galvanic cell and on your diagrams show the:
- **a** direction of electron flow in the external circuit
- **b** half-equation for the reaction at each electrode
- **c** equation for the overall reaction in the galvanic cell
- **d** anode electron
- **e** positive electrode
- **f** direction negative ions flow in the salt bridge.

19 Explain the difference between:
- **a** anode and cathode
- **b** cell and battery
- **c** discharge and recharge.

20 Use the electrochemical series (Table 2 in Appendix E) to determine whether:
- **a** elemental iodine is an oxidising agent or a reducing agent
- **b** calcium metal is a strong or weak reducing agent
- **c** nickel is a better reducing agent than silver
- **d** $Cu^{2+}(aq)$ is a better oxidising agent than $Ag^+(aq)$
- **e** $Fe^{2+}(aq)$ can act as an oxidising agent and a reducing agent.

Analysis

21 The E° for the half-equation:

$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(aq)$ is +0.17 V. Deduce which one of the following species would react with $H_2S(aq)$ but not with $H_2O(l)$ under standard conditions.

A $Cl_2(g)$
B Cu(s)
C Mg(s)
D $Ag^+(aq)$

22 Consider the following two half-equations and their standard potentials.

$$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s) \quad E^\circ = -0.14\ V$$
$$Be^{2+}(aq) + 2e^- \rightleftharpoons Be(s) \quad E^\circ = -1.85\ V$$

Determine which one of the following is the strongest oxidising agent.

A Sn(s)
B Be(s)
C $Sn^{2+}(aq)$
D $Be^{2+}(aq)$

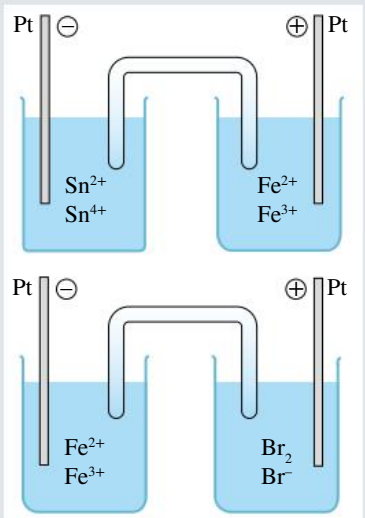
23 Explain the difference between:

a an oxidising agent and a reducing agent
b a conjugate redox pair and a conjugate acid–base pair
c an external circuit and an internal circuit.

24 A cell is constructed from $Pb^{2+}(aq)/Pb(s)$ and $Ni^{2+}(aq)/Ni(s)$ half-cells. If the $Ni^{2+}(aq)/Ni(s)$ half-cell is negative, deduce the:

a half-cell that acts as the anode
b overall equation for the cell reaction
c strongest oxidising agent in the cell.

25 The two galvanic cells shown below were constructed under standard conditions.

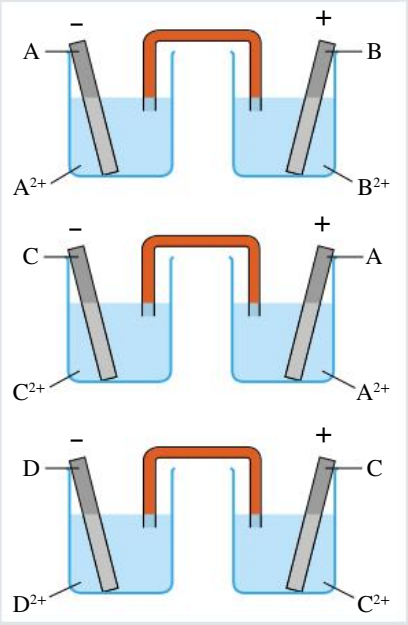


On the basis of the electrode polarities, determine the order of reducing agent strength from strongest to weakest.

26 Consider the four galvanic cells made from half-cells as listed below. Use the electrochemical series (Table 2 in Appendix E) to rank the galvanic cells in order of the maximum voltage they could generate under standard conditions.

- $Fe^{2+}(aq)/Fe(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$
- $Ni^{2+}(aq)/Ni(s)$ and $Fe^{2+}(aq)/Fe(s)$
- $Ni^{2+}(aq)/Ni(s)$ and $Br_2(l)/Br^-(aq)$
- $Ni^{2+}(aq)/Ni(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$

27 Four half-cells, $A^{2+}(aq)/A(s)$, $B^{2+}(aq)/B(s)$, $C^{2+}(aq)/C(s)$ and $D^{2+}(aq)/D(s)$, are used to make the cells shown below.



Rank the half-cells in increasing order of their reduction half-cell potentials, i.e. from lowest to highest.

28 The following equations appear in the order shown in the electrochemical series:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$
$$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$$
$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$$

i Predict whether a redox reaction would occur in the following mixtures. Assume concentrations of $1\ mol\ L^{-1}$ and gas pressures of 1 bar.

For mixtures where you predict a reaction will occur, construct:

ii separate half-equations for the oxidation and reduction reactions
iii an overall equation.

a $Cl_2(g)$ and Zn(s)
b $Ag^+(aq)$ and Ag(s)
c $Ag^+(aq)$ and Zn(s)
d $Zn^{2+}(aq)$ and $Cl^-(aq)$

29 Use the electrochemical series (Table 2 in Appendix E) to predict whether a reaction will occur in each of the following situations. Construct an equation for each reaction that you predict will occur.

- **a** Copper(II) sulfate solution is stored in an aluminium container.
- **b** Sodium chloride solution is stored in a copper container.
- **c** Silver nitrate solution is stored in a zinc container.
- **d** An iron nail is placed in 1 mol L^{-1} hydrochloric acid solution.
- **e** A plumber uses hydrochloric acid to clean copper pipes.

30 The following equations form part of the electrochemical series. They are ranked in the order shown.

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$$
$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$
$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$$
$$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$$
$$Ag^{+}(aq) + e^- \rightleftharpoons Ag(s)$$

- **a** Determine which species is the strongest oxidising agent and which species is the weakest oxidising agent.
- **b** Determine which species is the strongest reducing agent and which species is the weakest reducing agent.
- **c** Lead rods are placed in solutions of silver nitrate, iron(II) sulfate and magnesium chloride. Determine in which solutions you would expect to see a coating of another metal form on the lead rod. Explain.
- **d** Determine which of the metals silver, zinc or magnesium might be coated with lead when immersed in a solution of lead(II) nitrate.

31 **a** Use the electrochemical series to predict what might be expected to occur if hydrogen gas were bubbled through a solution containing Fe^{3+} ions.

- **b** Construct an equation for the predicted reaction.
- **c** When the reactants were mixed in an experiment, no reaction was observed. Suggest possible reasons for this.
- **d** Describe the limitations that need to be considered when using the electrochemical series to predict whether or not a certain reaction will occur.

Knowledge utilisation

32 A student was given the following three half-cells:

$$Mn^{2+}(aq)/Mn(s)$$
$$Fe^{2+}(aq)/Fe(s)$$
$$Al^{3+}(aq)/Al(s)$$

Explain how the student could experimentally determine the relative positions of the three redox pairs in the electrochemical series.

33 Explain the following observations.

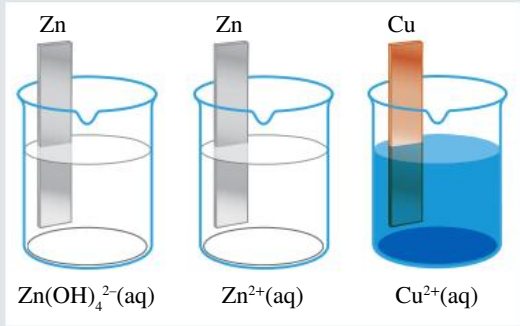
- **a** Bromine reacts with iodide ions in solution but does not react with chloride ions.
- **b** Hydrogen peroxide (H_2O_2) solution can spontaneously decompose to form water and oxygen.
- **c** Tin metal is added to solutions of tin(II) chloride to prevent oxidation of the tin(II) ions by oxygen in air.
- **d** Blocks of zinc are attached to the iron hulls of ships to reduce corrosion.

34 A student working in the laboratory spilled an iodine solution over the bench, causing a dark brown stain to form. Suggest how the student could remove the iodine stain.

35 Many of the 'alkaline cells' on the market contain zinc electrodes in contact with an electrolyte containing hydroxide ions. The half-cell reaction might be represented as:

$$Zn(s) + 4OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq) + 2e^-$$

To investigate if the standard electrode potential (E°) of these half-cells is the same as that of a half-cell reaction using a zinc electrode in contact with a zinc nitrate electrolyte (for which the electrode reaction would be $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$), a student was provided with the two half-cells shown below, as well as a $Cu^{2+}(aq)/Cu(s)$ half-cell.



- **a** Construct a net equation for the reaction in a galvanic cell in which the 'alkaline zinc half-cell' is connected to the Cu^{2+}/Cu half-cell.
- **b** Carefully explain how the student could use the half-cells that were provided to determine whether the two different half-cells containing zinc had the same E° value. Include fully-labelled diagrams with your answer and explain how the results could be interpreted.

CHAPTER

07 Production of chemicals by electrolysis

A large number of chemicals are produced through electrolysis. Some of these chemicals can be difficult to obtain by other means. This makes the process of electrolysis important.

Electrolysis is used in a number of important applications in the chemical industry, such as plating a thin film of metal on the surfaces of other metals to improve their appearance or prevent corrosion, extracting reactive metals from their ores, and the production of copper and zinc.

Throughout this chapter, you will explore the reactions that occur in electrolytic cells and compare them to the reactions that occur in galvanic cells.

Syllabus subject matter

Topic 2 • Oxidation and reduction

ELECTROCHEMICAL CELLS

- understand that electrochemical cells, including 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).

ELECTROLYTIC CELLS

- understand that electrolytic cells use an external electrical potential difference to provide the energy to allow a non-spontaneous redox reaction to occur, and appreciate that these can be used in small-scale and industrial situations, including metal plating and the purification of copper
- predict and explain the products of the electrolysis of a molten salt and aqueous solutions of sodium chloride and copper sulfate. Explanations should refer to E° values, the nature of the electrolyte and the concentration of the electrolyte
- describe, using a diagram, the essential components of an electrolytic cell; including source of electric current and conductors, positive and negative electrodes, and the electrolyte.

SCIENCE AS A HUMAN ENDEAVOUR

- **Electrochemistry for clean water:** Electrochemistry has a wide range of uses, ranging from industrial scale metal extraction to personal cosmetic treatments.

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7.1 Electrolytic cells



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand that an electrolytic cell uses an external energy source to force a non-spontaneous redox reaction to occur
- identify the key components of an electrolytic cell and explain how the cell operates
- construct half-equations for the processes that occur within the compartments of an electrolytic cell and use the half-equations to construct an overall equation for the cell reaction
- use standard electrode potentials to predict the reactions that will occur in different electrolytic cells
- describe some of the small-scale and industrial applications of electrolysis.



FIGURE 7.1.1 During electrolysis, electrical energy is used to make redox reactions occur. In this experiment, electricity passing through dilute sodium chloride solution creates bubbles of hydrogen gas at the left-hand electrode and bubbles of oxygen gas at the right-hand electrode. The gases are being collected in the test tubes.

In Chapter 6 you learnt that a spontaneous redox reaction can occur between an oxidising agent and a reducing agent that is higher in the electrochemical series. If the reaction occurs when the reactants are mixed directly, the chemical energy of the reactants is converted into heat energy. If, however, the same reaction occurs in a galvanic cell, the chemical energy generates electrical energy.

In this chapter you will learn that the reverse reaction can be made to occur in a process called electrolysis. Electrolysis involves the passage of electrical energy from a power supply, such as a battery, through a conducting liquid. The electrical energy causes redox reactions that are non-spontaneous to occur. An example of this is shown in Figure 7.1.1, where an electric current is being passed through a dilute sodium chloride solution, causing water to decompose into hydrogen gas and oxygen gas.

PRINCIPLES OF ELECTROLYSIS

Chemical reactions occur when an electric current from a direct current (DC) power supply passes through a conducting liquid. This process is called **electrolysis** and the apparatus used for electrolysis is called an electrolytic cell. A diagram of a typical electrolytic cell is shown in Figure 7.1.2. The two electrodes in the cell act as conductors of electricity and are connected to a power supply. The electrode connected to the positive terminal of the power supply is called the positive electrode and the electrode connected to the negative terminal is called the negative electrode.

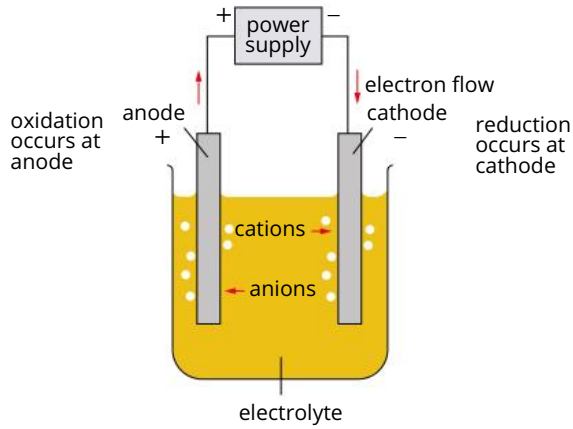


FIGURE 7.1.2 A representation of an electrolytic cell

During electrolysis, reactions occur at the surface of both electrodes. The electrical energy required for these reactions to occur is provided by the power supply. The power supply can be regarded as a type of 'electron pump', withdrawing electrons through the external circuit from the positive electrode and pushing them onto the negative electrode.

As a consequence, oxidation occurs at the positive electrode, which is known as the anode. Reduction occurs at the negative electrode, which is known as the cathode.

The overall reaction that occurs is non-spontaneous—a reaction that would not occur naturally—and involves the conversion of electrical energy into chemical energy.

The conducting liquid in an electrolytic cell is called the electrolyte, and can be either a molten ionic salt, such as NaCl(l), or a solution of an ionic solid, such as NaCl(aq). The ions in the electrolyte move towards the terminals in order to balance the charges formed during electrolysis; anions move towards the anode and cations move towards the cathode just as they do in galvanic cells.

The electrolytic process usually takes place in one container. Unlike galvanic cells, there is no need to locate the electrodes in separate containers because a **non-spontaneous reaction** is involved. However, the products do need to be kept apart as they are produced. Otherwise, they can spontaneously react with each other to re-form the original reactants.

Examples of electrolysis that involve molten ionic salts and solutions of ionic solids are described below.

In an electrolytic cell:
- oxidation occurs at the anode, which is the positive electrode
- reduction occurs at the cathode, which is the negative electrode.

In an electrolytic cell:
- anions move towards the anode
- cations move towards the cathode.

ELECTROLYSIS OF A MOLTEN SALT

A diagram showing the electrolysis of a molten salt, NaCl(l), in a simple electrolytic cell is shown in Figure 7.1.3.

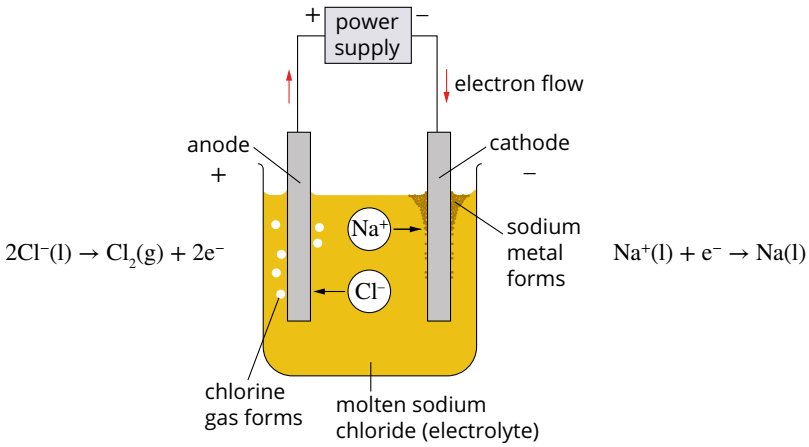


FIGURE 7.1.3 Electrolysis of molten sodium chloride, NaCl(l)

Platinum metal or graphite is used for the electrodes because they allow the passage of electrons to and from the power supply. Because platinum and graphite are **inert** (unreactive), the electrodes do not react with the contents of the cell.

The molten sodium chloride acts as an electrolyte because it is a conducting liquid. The electrolyte is composed of Na^+ ions and Cl^- ions. Sodium chloride melts at 801°C, so this process must occur at a high temperature. No water is present.

At the negative electrode

The power supply pushes electrons towards the negative electrode. Na^+ ions in the electrolyte are attracted to the negative electrode, where they accept electrons and become sodium atoms:

$$Na^+(l) + e^- \rightarrow Na(l)$$

Because this is a reduction reaction, this electrode is known as the cathode.

Sodium is solid at room temperatures, but it is liquid at the temperatures required to melt sodium chloride. It is less dense than molten sodium chloride and floats to the top of the cell.

At the positive electrode

Chloride ions in the electrolyte migrate towards the positive electrode to give up electrons and form chlorine atoms. These atoms quickly form molecules of Cl_2 and bubbles of chlorine gas appear at the electrode:

$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

The electrons from the chloride ions move through the electrode towards the power supply. Because this is an oxidation reaction, this electrode is known as the anode.

The overall reaction that takes place in the cell is:

$$2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$$

This is a **non-spontaneous reaction**. The electrical energy from the power supply is converted into chemical energy in the products.

Since Cl_2 is a strong oxidising agent and Na is a strong reducing agent, the products at the two electrodes must be kept apart. Otherwise, they will react to re-form sodium chloride. This reverse reaction, between sodium and chlorine, is a spontaneous reaction.

The Downs cell

The electrolysis of molten sodium chloride described above is performed on a commercial scale to produce sodium and chlorine. The electrolytic cell used for this purpose is called the Downs cell, as shown in Figure 7.1.4.

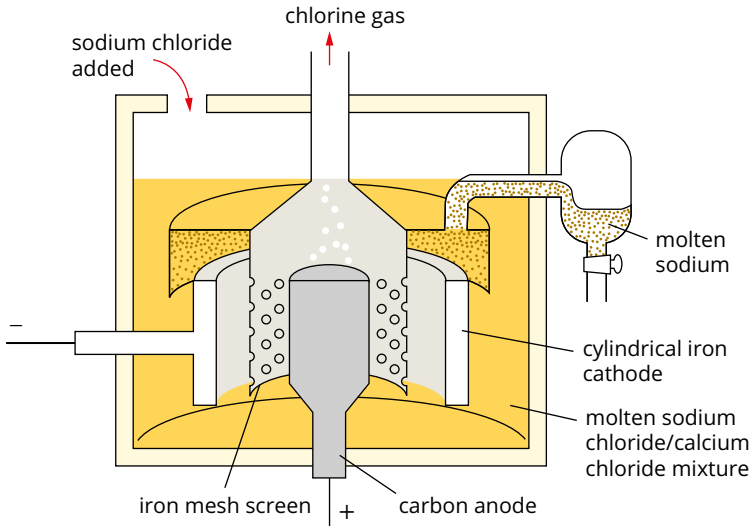


FIGURE 7.1.4 Diagram of a Downs cell, which produces chlorine gas and sodium

In the electrolysis of a molten electrolyte:

- anions are oxidised at the anode (positive)
- cations are reduced at the cathode (negative)
- water is not present to interfere with the desired reactions.

The anode of the Downs cell is made of an inert conducting material, such as graphite or platinum, and is not consumed in the reaction. The cathode is made of iron, which is effectively inert because electrons are pumped onto this electrode, preventing the iron from reacting.

An iron mesh screen is used in the cell to keep the products at the anode and cathode apart. If the Cl_2 and Na come in contact, they will react to re-form sodium chloride and the products from the electrolysis will be lost.

The advantage of using a molten electrolyte in the Downs cell is that there is no water present to interfere with the desired reactions. As you will learn later, if aqueous sodium chloride were used as the electrolyte instead of molten sodium chloride, water would react at the cathode and form hydrogen gas.

In general, the main disadvantage of using a molten electrolyte is that the process requires much more energy. Energy must be expended to maintain the electrolyte in a molten state and at the temperature needed for electrolysis to proceed efficiently.

ELECTROLYSIS OF AQUEOUS SOLUTIONS

In some electrolytic cells there may be several chemicals present at each electrode that might be able to react. If an aqueous electrolyte is used instead of a molten salt, then water is a potential reactant. Even the material used for the electrodes may participate in the reaction.

In these cases, you can use the electrochemical series (Table 2 in Appendix E) to predict which of the possible reactions would be most likely to occur.

During electrolysis the:

- strongest oxidising agent usually reacts at the cathode (i.e. the lowest reaction in the electrochemical series that can occur in the forward direction is likely to occur at the cathode)
- strongest reducing agent usually reacts at the anode (i.e. the highest reaction in the series that can occur in reverse is likely to occur at the anode).

To illustrate the use of the electrochemical series for the prediction of electrode reactions, we will examine the electrolysis of an aqueous solution of sodium chloride.

> **i** Just as in galvanic cells, in electrolytic cells the strongest reducing agent reacts at the anode and the strongest oxidising agent reacts at the cathode.

Electrolysis of sodium chloride solution

Consider the electrolysis of a $1.0\,mol\,L^{-1}$ solution of sodium chloride using **inert electrodes**, as shown in Figure 7.1.5. With water present in the cell as well as $Na^+(aq)$ and $Cl^-(aq)$, there are a number of species that might be able to react.

- $H_2O(l)$ could be oxidised or reduced.
- Na^+ ions could be reduced.
- Cl^- ions could be oxidised.

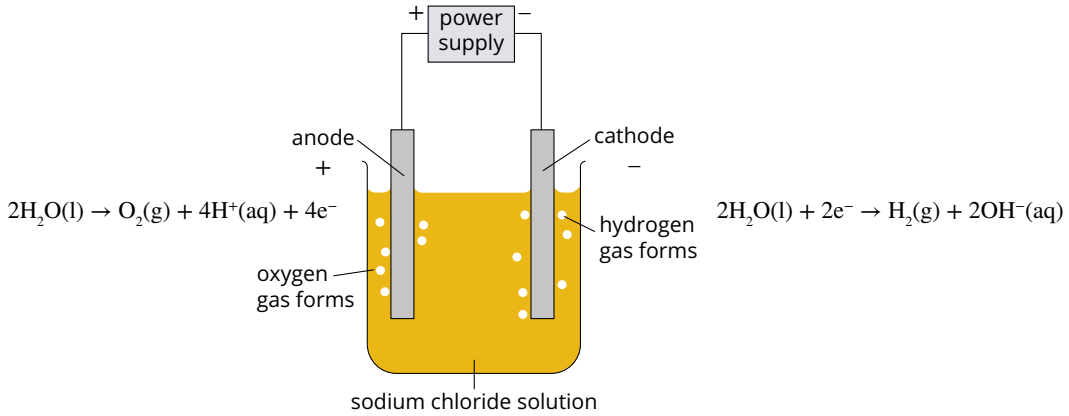


FIGURE 7.1.5 Electrolysis of aqueous sodium chloride solution

At the cathode

The power supply pushes electrons towards the negative electrode and Na^+ ions are attracted to the negative electrode. If you look on the left-hand side of the electrochemical series (Table 6.2.1 in Chapter 6 and Appendix E), you will see that there are two species in the cell that can act as oxidising agents and therefore could react at this electrode. These two species are H_2O and Na^+:

$$Na^+(aq) + e^- \rightarrow Na(s) \qquad E^\circ = -2.71V$$
$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ = -0.83V$$

Reactions lower in the electrochemical series involve stronger oxidising agents and are more likely to occur as reduction reactions. The reduction of water requires less energy than the reduction of sodium ions (the E° of the half-equation for H_2O is less negative the half-equation for Na^+). Water will therefore be reduced at the cathode and hydrogen gas will form:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

The sodium ions will not react and will remain in solution as spectator ions.

At the anode

Electrons are withdrawn from this electrode by the power supply. On the right-hand side of the electrochemical series are two species in the cell that can act as reducing agents and could react at this electrode, Cl^- and H_2O:

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \qquad E^\circ = +1.23V$$
$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(l) \qquad E^\circ = +1.36V$$

Reactions higher in the series involve stronger reducing agents and have a greater tendency to occur as oxidation reactions. While the two reactions are close together in the series, the oxidation of water requires less energy than the oxidation of H_2O (the E° of the half-equation for H_2O is less positive than the half-equation for Cl^-). The predicted anode reaction is:

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

The overall reaction is:

$$6H_2O(l) \rightarrow 2H_2(g) + O_2(g) + 4H^+(aq) + 4OH^-(aq)$$

If the $H^+(aq)$ ions formed at the anode are allowed to come in contact with the $OH^-(aq)$ formed at the cathode, they react to form water. The overall equation can then be written as:

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

Therefore, water is being broken up into its elements in this process.

Electrolysis of concentrated sodium chloride solution

In practice, it is possible for either of the anode reactions to occur when sodium chloride solution is electrolysed, depending on conditions such as the concentration of the solution. In some cases, O_2 and H^+ are formed and in others Cl_2 is produced.

Recall that the electrochemical series was determined for reactions under standard conditions (concentrations of $1\,mol\,L^{-1}$, gas pressures of 1 bar) and at a temperature of 25°C. When the conditions are not standard and the concentration of sodium chloride is much higher than $1\,mol\,L^{-1}$, chlorine gas is produced at the anode.

Comparing molten and aqueous electrolytes

Table 7.1.1 summarises the differences between the reactions that occur during the electrolysis of molten and aqueous sodium chloride. Note that the products formed at each electrode depend on the state and, in the case of an aqueous electrolyte, on the concentration of the electrolyte.

TABLE 7.1.1 A comparison of the electrolysis of molten NaCl with aqueous NaCl

	Molten NaCl	Aqueous dilute NaCl	Aqueous concentrated NaCl
Temperature	high	room temperature	room temperature
Anode reaction	$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
Cathode reaction	$Na^+(l) + e^- \rightarrow Na(l)$	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
Overall reaction	$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$	$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$	$2Cl^-(l) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2OH^-(aq)$

The products formed at the electrodes in an electrolytic cell depend on the state and, in the case of an aqueous electrolyte, the concentration of the electrolyte.

Where possible, aqueous electrolytes are used in industrial situations in preference to molten electrolytes. It takes energy to maintain an electrolyte in a molten state and so a cell that uses an aqueous electrolyte is usually more cost-effective.

ELECTROLYSIS INVOLVING REACTIVE ELECTRODES

In the examples of electrolysis that you have encountered so far, the electrodes do not take part in the reaction and are described as inert electrodes. However, in many electrolytic cells the electrodes are consumed in the cell reaction. Such electrodes are called **reactive electrodes**.

Consider the electrolysis of a $1.0\,mol\,L^{-1}$ solution of copper(II) sulfate using copper electrodes, as shown in Figure 7.1.6. With water present in the cell, as well as $Cu^{2+}(aq)$ and the copper electrodes, the following species might react. (SO_4^{2-} ions do not react under these conditions.)

- H_2O could be oxidised or reduced.
- Cu^{2+} ions could be reduced.
- Cu metal in the electrodes could be oxidised.

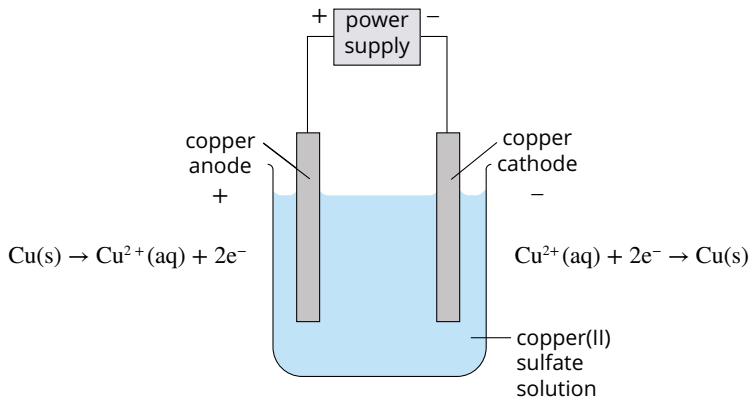


FIGURE 7.1.6 Electrolysis of copper(II) sulfate solution

At the cathode

The power supply pushes electrons towards the negative electrode and Cu^{2+} ions are attracted to the negative electrode where a reduction reaction occurs. If you look on the left-hand side of the electrochemical series (Table 6.2.1 on page 163 and Table 2 in Appendix E), you will see that the species in the cell that can act as oxidising agents are Cu^{2+} and H_2O:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ = -0.83V$$
$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E^\circ = +0.34V$$

Reactions lower in the electrochemical series (with more positive E° values) involve stronger oxidising agents and are more likely to occur as reduction reactions. Therefore, Cu^{2+} ions will be reduced at the cathode and a layer of copper metal will be deposited:

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

At the anode

On the right-hand side of the electrochemical series are two species in the cell that can act as reducing agents and could react at this electrode, the copper electrode and H_2O:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E^\circ = +0.34V$$
$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \qquad E^\circ = +1.23V$$

Reactions higher in the series (with a less positive E° value) involve stronger reducing agents and have a greater tendency to occur as oxidation reactions. The predicted anode reaction is therefore:

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

The metal anode will dissolve and form $Cu^{2+}(aq)$ ions.

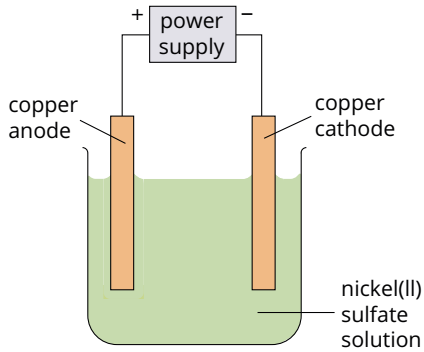
Note that, for this particular cell, when you add the anode and cathode half-reactions together, all species cancel and there is no overall reaction. The overall concentration of Cu^{2+} ions in the electrolyte remains constant. Nevertheless, copper metal at the anode will dissolve and copper metal will be formed at the cathode. The metal is being transferred from one electrode to the other by electrical energy.

This process is used as the basis of a technique for purifying copper metal, called **electrorefining**, which is described later in this module.

Worked example 7.1.1

PREDICTING THE PRODUCTS OF ELECTROLYSIS

Use the electrochemical series (Table 2 in Appendix E) to predict the products of the electrolysis of 1 mol L^{-1} nickel(II) sulfate solution with copper electrodes at 25°C. A diagram of this electrolytic process is shown below.



Thinking	Working
Identify which species are present in the solution.	$Ni^{2+}(aq)$, $SO_4^{2-}(aq)$ and $H_2O(l)$
Identify what the electrodes are made of.	copper
Refer to the electrochemical series (Table 2 in Appendix E) to identify the possible reactions. Write these half-equations in the order they appear in the series.	By referring to the electrochemical series, you can see that a number of reactions need to be considered because the cell contains two oxidising agents, Ni^{2+} and H_2O, and two reducing agents, Cu and H_2O. $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ –0.83 V $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ –0.24 V $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ +0.34 V $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ +1.23 V The SO_4^{2-} ions are not involved in the reaction.
Determine the reactions that could occur at the anode.	At the anode (+), oxidation reactions that could occur are: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Determine the most likely reaction at the anode.	The strongest reducing agent, Cu(s), will be oxidised: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Determine the reactions that could occur at the cathode.	At the cathode (–), reduction reactions that could occur are: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
Determine the most likely reaction at the cathode.	The strongest oxidising agent, $Ni^{2+}(aq)$, will be reduced: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
Combine the two half-reactions to obtain the overall reaction in the electrolysis cell.	The overall equation is: $Ni^{2+}(aq) + Cu(s) \rightarrow Ni(s) + Cu^{2+}(aq)$

➤ Try yourself 7.1.1

PREDICTING THE PRODUCTS OF ELECTROLYSIS

Use the electrochemical series (Table 2 in Appendix E) to predict the products of electrolysis of 1 mol L^{-1} zinc sulfate solution with copper electrodes at 25°C.

It is important to bear in mind that, while the electrochemical series can be used in this way to make predictions, the series is based on standard conditions. Most of the electrolysis reactions that occur in the laboratory and in industry are not at standard conditions. Experiments are the only sure way to find out what products form in a particular instance. In practice, reactions are affected by factors such as electrolyte concentration, gas pressures, current, voltage and the use of different electrodes.

APPLICATIONS OF ELECTROLYSIS

Chemical industries tend to avoid using electrolysis for the manufacture of chemicals because of the relatively high cost of electrical energy. Nevertheless, this process enables some chemicals to be produced that could not be readily produced any other way.

Earlier, you saw that sodium and chlorine are manufactured commercially by electrolysis using the Downs cell. Let us now look at two further industrial applications of electrolysis: electroplating and electrorefining.

Electroplating

If you browse through a jeweller's shop you will see many shiny 'silver' articles, such as bracelets, necklaces and trays. The main materials present in many of these articles will be inexpensive metals such as copper, zinc and nickel—not silver! Often the only silver present is a thin surface coating only a fraction of a millimetre thick that has been applied by electrolysis.

The deposition of a layer of metal on the surface of another metal is called electroplating. Electroplating plants can be found as small-scale industries, sometimes located in residential neighbourhoods, or be part of large-scale industries (Figure 7.1.7).



FIGURE 7.1.7 A worker prepares a rack of objects for immersion in an electroplating tank. The objects to be plated are connected to the negative electrode. The positive electrode is usually made of the metal that is being coated.

WS 3.2.5 PA 3.2.2



FIGURE 7.1.8 Tin cans are used as packaging for a wide range of products. The tin coating on the can prevents it from corroding.

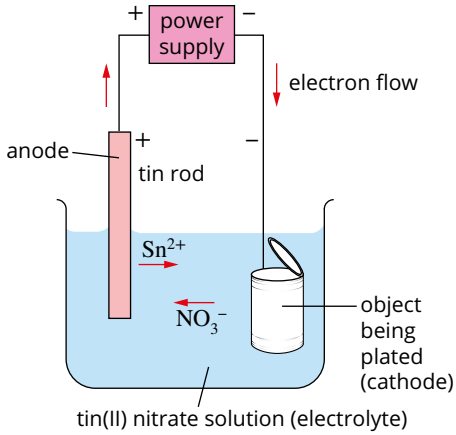


FIGURE 7.1.9 A cell used for electroplating tin

The set-up of an electroplating cell can be summarised as follows.

- **The object being plated is at the cathode (negative).**
- **An electrode of the metal is at the anode (positive).**

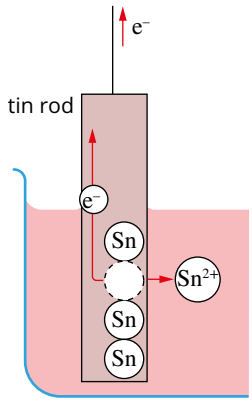


FIGURE 7.1.11 A representation of the reaction at the anode in the process of tin plating

While electroplating can be used to make an object more decorative, it can also be used to improve the resistance of metals to corrosion. For example, 'tin' cans are used extensively for packaging food items as varied as soups, fruit and fish, as shown in Figure 7.1.8. Although they are commonly called 'tin' cans, they are mainly composed of steel, which is an alloy of iron and carbon. There is just a thin layer of tin plated over the surface of the steel can. Tin corrodes very slowly and prevents contact between the iron, moisture and air. Effectively, the tin prevents the iron from rusting.

Electroplating is performed in electrolytic cells, such as the simplified one shown in Figure 7.1.9 for tin plating. The object to be plated is connected by a wire to the negative terminal of a power supply. This object becomes the negative electrode in the cell.

The object is immersed in an electrolyte solution, such as tin(II) nitrate solution, which contains ions of the metal to be plated. The Sn^{2+} ions in the solution move towards the negative electrode (the object to be plated) and are reduced. The NO_3^- ions move towards the positive electrode, allowing current to pass through the cell.

An electrode of tin metal is connected to the positive terminal of the power supply.

At the negative electrode (cathode)

As shown in Figure 7.1.10, tin ions are attracted to the negative electrode, where they accept electrons and are reduced to tin metal:

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

A coating of tin is formed on the object.

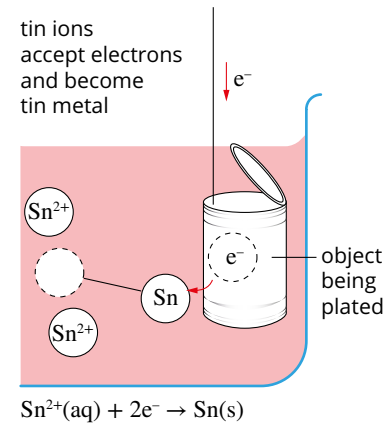


FIGURE 7.1.10 A representation of the reaction at the cathode in the process of tin plating

At the positive electrode (anode)

As shown in Figure 7.1.11, the positive terminal of the power supply withdraws electrons from the tin electrode, causing an oxidation reaction to occur. Tin metal slowly dissolves as Sn^{2+} ions are formed:

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

This reaction replaces Sn^{2+} ions in solution that were consumed by the reaction at the negative electrode. The concentration of tin ions in the electrolyte therefore remains constant.

Although the NO_3^- ions in the electrolyte are attracted to the anode, the NO_3^- ion cannot be oxidised as it contains nitrogen in its highest oxidation state (+5). The NO_3^- ions are not involved in the electrode reactions of the cell.

The overall result of the electroplating process is the metal anode dissolves and a coating of metal is formed on the object at the cathode.

Electrorefining of copper

Copper metal is extracted from its ores by **smelting**. The process involves several stages in which the copper ore is heated strongly in air to produce impure copper metal.

As hot gases escape, the copper surface becomes blistered and it is commonly known as 'blister copper'. It contains about 2% of impurities such as sulfur, iron, antimony, silver and gold.

Blister copper is purified by electrolysis. Sheets of blister copper are placed in a large tank of sulfuric acid and thin sheets of pure copper are positioned between them. An external power source is connected so that the blister copper acts as a positive electrode (anode) and the pure copper acts as a negative electrode (cathode), as shown in Figure 7.1.12.

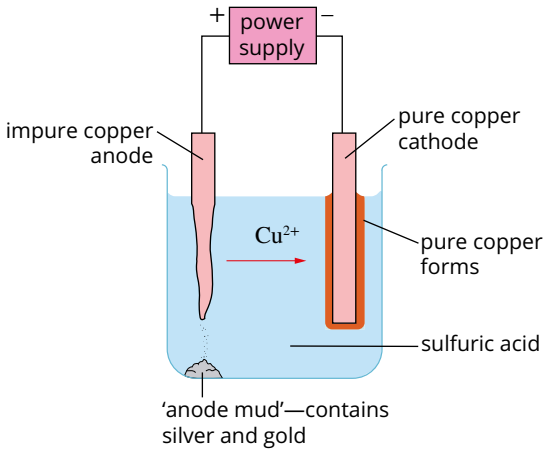


FIGURE 7.1.12 Electrorefining of copper metal by electrolysis

At the anode, electrons are drawn away from the blister copper anode to the positive terminal of the power source. Copper and impurities such as nickel and zinc that are more reactive (stronger reducing agents) than copper are oxidised and enter the solution as ions:

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

Impurities less reactive than copper, such as silver, gold and platinum, are not oxidised and simply fall from the anode, collecting at the bottom of the tank. This anode residue is sometimes called 'anode mud'. The precious metals are later recovered from the valuable mud.

At the pure copper cathode, copper metal is deposited as electrons from the power source are accepted by metal ions from solution. Since copper ions are the strongest oxidising agents present in solution, copper is the only metal formed:

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

Copper of 99.99% purity is obtained this way.

Electrorefining uses a good deal of electrical energy, so a refinery must be located close to a source of abundant, cheap power. Because of this, copper produced in the smelter at Mount Isa in Queensland is shipped to Townsville for refining. Australia ranks fifth in the world in terms of copper production.

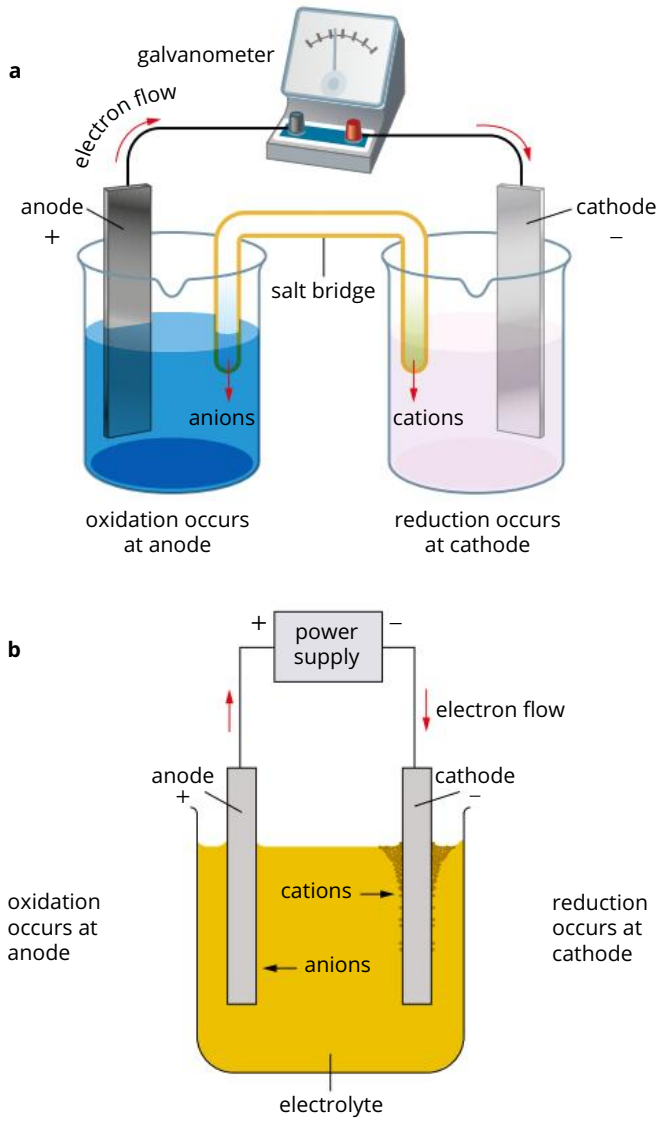
COMPARISON OF ELECTROLYTIC AND GALVANIC CELLS

Before concluding this module, let us compare the features of electrolytic cells with those of galvanic cells that you studied in Chapter 6. Galvanic cells and electrolytic cells are types of electrochemical cells. While both cells involve the conversion between electrical energy and chemical energy, there are important differences between them.

Table 7.1.2 and Figure 7.1.13 summarise the similarities and differences between galvanic and electrolytic cells.

TABLE 7.1.2 A summary of the similarities and differences between galvanic and electrolytic cells

Galvanic cells	Electrolytic cells
produce electricity	consume electricity
have spontaneous reactions	have non-spontaneous reactions
convert chemical energy to electrical energy	convert electrical energy to chemical energy
oxidation occurs at the anode and reduction occurs at the cathode	oxidation occurs at the anode and reduction occurs at the cathode
anode is negative and cathode is positive	anode is positive and cathode is negative



WS 3.2.6

FIGURE 7.1.13 General construction of (a) a galvanic cell and (b) an electrolytic cell.

Cleaning water by electrolysis

Electrolysis has a wide range of uses. The everyday process of charging a phone or laptop computer involves electrolysis. When a battery is being recharged, the chemical reaction that occurs in the battery of the phone or computer when it is generating electrical energy is reversed and the products of the reaction are converted back into the original reactants. The battery 'charger' is a source of electrical energy that has a potential difference a little greater than the potential difference of the cell.

Many home swimming pools use a salt water chlorination unit to maintain the water in the pool in healthy condition. The basis of the chlorination unit is an electrolytic cell that uses concentrated sodium chloride as the electrolyte (Table 7.1.1 on page 188). Dissolved salt in the pool water undergoes electrolysis to produce chlorine gas. The chlorine reacts with the water, producing hypochlorous acid (HClO) and hypochlorite ions (ClO^-) which act as sanitising agents and kill pathogens in the water.

On a larger scale, there are several techniques for the purification of waste water from factories and other industries that involve electrolysis. Electrochemical methods offer a cheap and efficient alternative for the removal of some of the most common pollutants. These methods are also more environmentally friendly than other forms of clean-up that are currently in use.

Electrocoagulation is one technique used to remove metal ions, colloidal solids and soluble inorganic pollutants from waste water. It is based on an electrolytic cell that uses an anode of a metal like iron or aluminium, as shown in Figure 7.1.14. The metal anode is oxidised and corrodes when the cell is in use. These anodes are referred to as sacrificial anodes and need to be regularly replaced. The material used for the cathode does not react because it is connected to the negative terminal of the power supply and receives a continual supply of electrons; instead, water undergoes reduction at the cathode to form hydrogen gas and OH^- ions.

As the metal anode is oxidised, there is a continual release of metal ions into the water. These ions can then remove contaminants either by precipitation or other chemical reactions. The ions also cause colloidal materials to flocculate and fall to the bottom of the cell as a sediment. Furthermore, other pollutants, such as oils, can undergo a range of complex reactions and processes that allow them to be removed.

The polluted water passing through the electrolytic cell separates into clear water, a floating layer and a sediment made up of the flocculated colloidal materials and precipitated ions. Settling tanks are used to remove the sediment and the floating layer is separated using an overflow weir. The clear water may then be recycled back to the industry for further use.

Review

1 Select the correct words to complete the following statements.

Waste water can be purified by a process called **electrorefining/electrocoagulation**. The process uses a(an) **electrolytic/galvanic** cell in which the anode is **positively/negatively** charged. When the cell is in operation **chemical/electrical** energy is converted into **chemical/electrical** energy and **oxidation/reduction** occurs at the anode.

2 Explain why the anode in an electrocoagulation cell is described as a 'sacrificial' electrode.

3 Construct half-equations for the reactions that occur at the anode and cathode of an electrocoagulation cell with an aluminium anode.

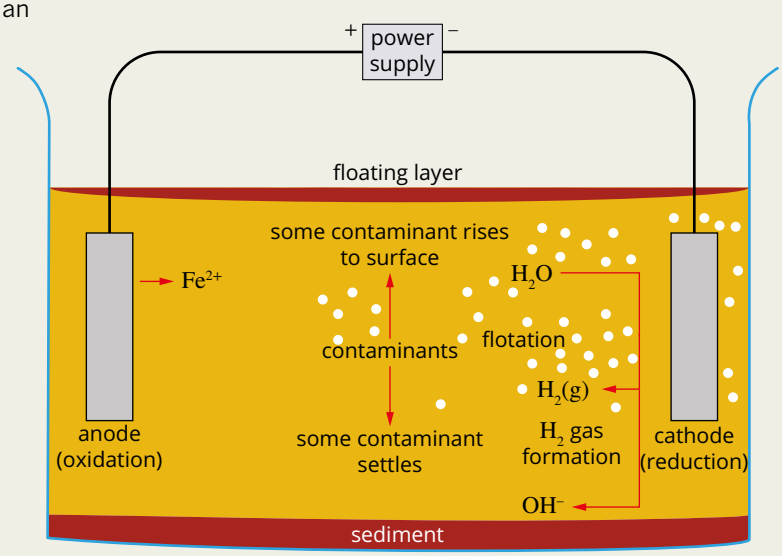


FIGURE 7.1.14 Electrocoagulation is a technique for purifying waste water. This cell uses an iron anode.

7.1 Review

SUMMARY

- Electrolytic cells convert electrical energy to chemical energy, whereas galvanic cells convert chemical energy to electrical energy.
- Non-spontaneous redox reactions occur in electrolytic cells.
- The anode is defined as the electrode at which oxidation occurs; the cathode is the electrode at which reduction occurs.
- In electrolytic cells, the anode is the positive electrode and the cathode is the negative electrode.
- When several reactions may be possible at the anode of a particular cell, generally the strongest reducing agent undergoes oxidation. Reactions higher in the electrochemical series (with more negative E° values) involve stronger reducing agents and are more likely to occur as oxidation reactions.
- When several reactions may be possible at the cathode of a particular cell, generally the strongest oxidising agent undergoes reduction. Reactions lower in the electrochemical series (with more positive E° values) involve stronger oxidising agents and are more likely to occur as reduction reactions.
- The electrochemical series can be used to predict the products of electrolysis.
- The electrodes used in electrolysis can be either inert or reactive.
- Both molten and aqueous electrolytes can be used in electrolysis.
- Electrolysis has a wide range of uses including electroplating, electrorefining and water purification. Commercial applications of electrolysis are found in small-scale and industrial situations.

KEY QUESTIONS

Retrieval

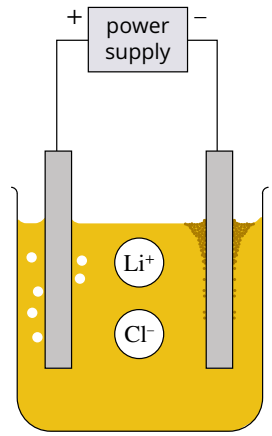
1 Recall the meaning of the following terms.
- **a** anode
- **b** electrolyte
- **c** inert electrode
- **d** electrolytic cell
- **e** electrochemical cell

2 Select the correct words to complete the following statements.
In electrolytic cells:
- **a** the reactions are **spontaneous/non-spontaneous**
- **b** **chemical/electrical** energy is converted into **chemical/electrical** energy
- **c** the anode is **negative/positive** and the cathode is **negative/positive**
- **d** **oxidation/reduction** occurs at the anode and **oxidation/reduction** occurs at the cathode
- **e** if several reactions are possible at the anode, the strongest **oxidising/reducing** agent usually undergoes oxidation.

3 Name three industrial uses for electrolysis.

Comprehension

4 The diagram below shows an electrolytic cell that uses molten lithium chloride (LiCl) as the electrolyte.
- **a** Show the anode, cathode, positive electrode and negative electrode.
- **b** Use arrows to show the direction of electron flow and movement of the Li^+ and Cl^- ions in the cell.
- **c** Construct half-equations for the reactions that occur at the:
  - **i** anode
  - **ii** cathode.



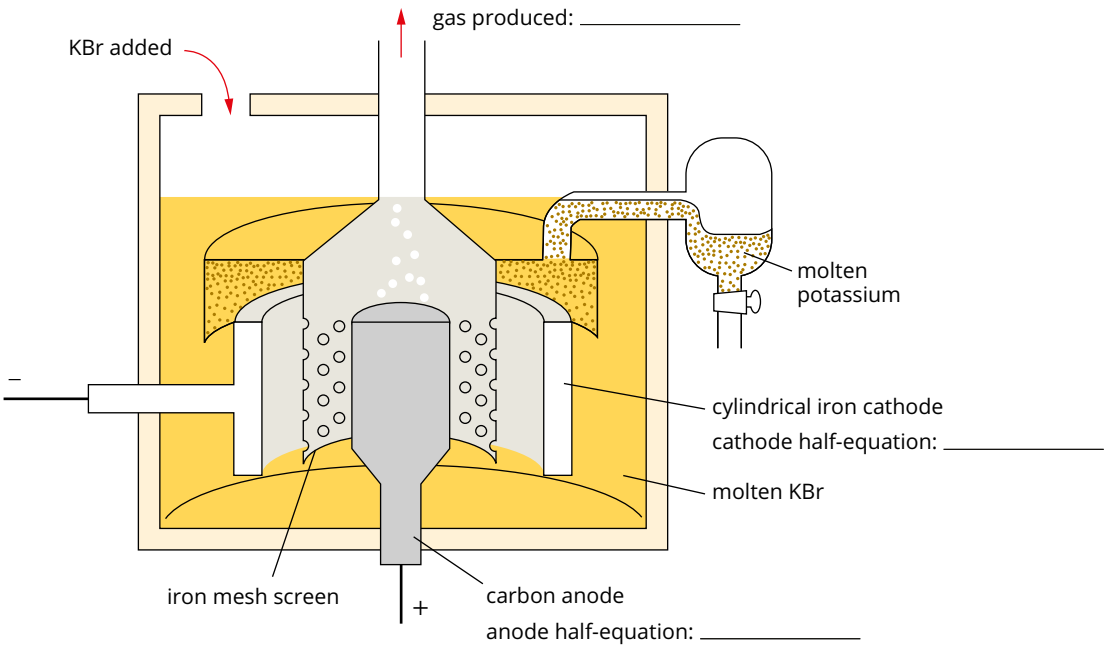
5 Draw a diagram of a cell suitable for copper plating a key that uses a rod of copper metal as the anode.

- **a** Label the positive and negative electrodes.
- **b** Identify a suitable electrolyte for the cell.
- **c** Explain what happens to the concentration of metal ions in the electrolyte as the cell is in use.

6 Determine whether the following statements about a copper electrorefining cell are true or false.

- **a** Impure copper is the anode of the cell.
- **b** The electrolyte in the cell is molten copper chloride.
- **c** Pure copper is collected at the positive electrode.
- **d** The concentration of Cu^{2+} ions in the electrolyte remains constant during the electrorefining process.

7 In the cell shown in the following diagram, potassium can be produced by using molten potassium bromide as the electrolyte. Deduce the correct terms by completing the missing labels for this cell.



Analysis

9 A student sets up an electrolysis experiment using a cell made of a lead anode, an iron cathode and a magnesium nitrate solution as the electrolyte.

- **a** Refer to the electrochemical series (Table 2 in Appendix E) and identify the possible reactions that could occur. Represent these half-equations in the order they appear in the series.
- **b** Identify the correct equations for the reactions that occur at the anode and cathode.
- **c** Construct an equation for the overall reaction.

8 In an electrolysis experiment, a student is provided with an aqueous solution of nickel(II) nitrate ($Ni(NO_3)_2$). The student sets up an electrolytic cell using an unreactive carbon rod as the positive electrode and a nickel rod as the negative electrode.

- **a** Determine on which electrode a nickel coating will appear during the operation of the cell.
- **b** Identify the half-equations for the reactions that occur at each electrode.
- **c** Construct an equation for the overall reaction.

10 An electrolysis cell was constructed using a copper electrode and an iron electrode in a zinc nitrate solution. The copper electrode was connected to the positive terminal of the power supply and the iron electrode was connected to the negative terminal.

- **a** Identify the half-equations for the reactions that occur initially at the anode and cathode.
- **b** Construct an equation for the overall reaction.

continued over page

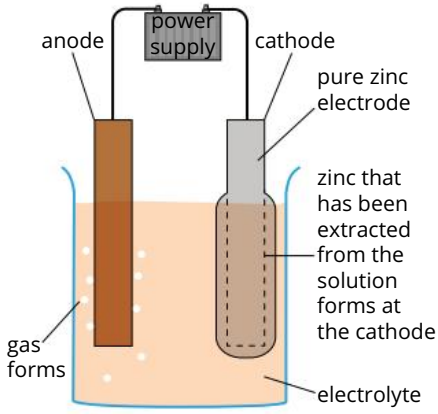
7.1 Review *continued*

11 Using the electrochemical series (Table 2 in Appendix E), predict the initial products at each electrode for the electrolysis of:

- **a** molten calcium iodide using platinum electrodes
- **b** molten sodium bromide using graphite electrodes
- **c** a $1.0\,mol\,L^{-1}$ aqueous solution of calcium iodide using platinum electrodes
- **d** a $1.0\,mol\,L^{-1}$ aqueous solution of sodium bromide using copper electrodes.

12 Zinc can be extracted from its compounds by electrolysis at room temperature with the cell shown in the diagram below.

- **a** Determine why an aqueous solution of zinc nitrate, instead of molten zinc nitrate, is used as the electrolyte in this cell.
- **b** Identify the gas formed at the anode.



13 Determine why:

- **a** most chlorine is produced by electrolysis of sodium chloride solution, rather than by electrolysis of the molten salt
- **b** fluorine was first isolated from fluorine compounds by electrolysis
- **c** although zinc is an impurity in blister copper, zinc metal is not formed at the cathode in an electrorefining cell (see Figure 7.1.12 on page 193).

14 Use the electrochemical series (Table 2 in Appendix E) to determine why aluminium cannot be produced by the electrolysis of aqueous solutions of aluminium compounds.

15 Compare an electrolytic cell with a galvanic cell. Describe two ways in which the cells are:

- **a** different
- **b** similar.

Chapter review

WS 3.2.7 WS 3.2.8

07

KEY TERMS

electrolysis
electrorefining
inert
inert electrode
non-spontaneous reaction
reactive electrode
smelting

KEY QUESTIONS

Retrieval

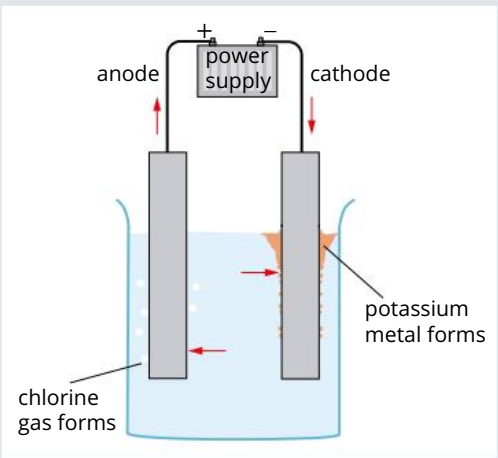
1 Identify which one of the following applies to both galvanic and electrolytic cells.

A Both cells have non-spontaneous reactions.
B The anode is negative and cathode is positive.
C Both cells convert chemical energy to electrical energy.
D Oxidation occurs at the anode and reduction occurs at the cathode.

2 For electrolytic and galvanic cells, recall the:

a polarity of the anode and cathode
b direction of electron flow
c energy transformation occurring in the cells
d tendency of the cell reaction to occur spontaneously.

3 The electrochemical cell shown below is set up to produce potassium metal. Identify the parts of the cell using the following labels (labels may be used more than once): Cl^-, molten potassium chloride, platinum, K^+.



Comprehension

4 Select the products of electrolysis of molten potassium iodide using inert electrodes.

A Iodine at the anode and hydrogen at the cathode.
B Potassium at the anode and iodine at the cathode.
C Potassium at the cathode and iodine at the anode.
D Iodine at the negative electrode and potassium at the positive electrode.

Analysis

5 State the electrode reactions and overall reaction when molten $ZnCl_2$ is used as the electrolyte in an electrolytic cell with inert electrodes.

6 Two electrolytic cells were set up for the electrolysis of aqueous copper(II) sulfate. One cell contained copper electrodes and the other contained platinum electrodes. Determine the reactions that would occur at the electrodes of both cells.

7 An aqueous zinc sulfate solution was electrolysed using copper electrodes.

a Refer to the electrochemical series and identify the possible reactions that could occur. Write these half-equations in the order they appear in the series.
b Identify the correct half-equations for the reactions that occur at the anode and cathode.
c Construct an equation for the overall reaction.

8 Using the electrochemical series (Table 2 in Appendix E), predict the initial products of each of the following electrolysis experiments by completing the following table.

Experiment	Electrolyte	Electrodes	Cathode reaction	Anode reaction
a	molten potassium iodide	platinum		
b	copper(II) sulfate solution	platinum		
c	potassium bromide solution	copper		
d	a mixture of copper(II) nitrate and nickel(II) nitrate solutions	carbon		
e	lithium fluoride solution	platinum		

9 Sodium and chlorine are manufactured by passing direct current through molten sodium chloride. Determine why it is necessary for the electrolyte to be molten and not aqueous.

10 When constructing a galvanic cell in the laboratory, determine why two half-cells are usually used, whereas the reactants of an electrolysis cell are often placed in a single container.

Knowledge utilisation

11 Design a cell that would allow magnesium metal to be electroplated onto an iron electrode. Draw and fully label a diagram of your cell.

12 Create a concept map that includes the following terms: electrolysis, electrolytic cell, chemical energy, electrical energy, anode, cathode, reducing agent, oxidising agent, reduction, oxidation, electrolyte, non-spontaneous reactions.

REVIEW QUESTIONS

Equilibrium, acids and redox reactions

TR 3.1 TR 3.2

Topic 1: Chemical equilibrium systems

Multiple choice

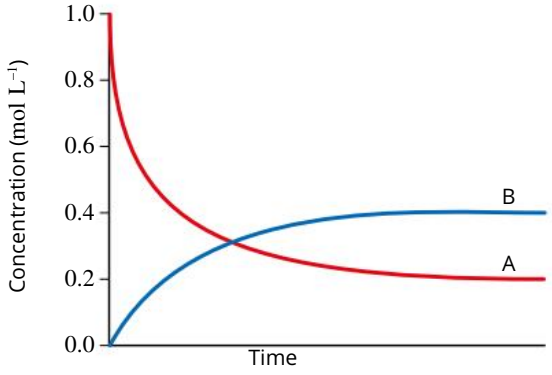
1 Identify the statement that correctly describes a closed system. In a closed system:

A only matter is exchanged with the surroundings.
B only energy is exchanged with the surroundings.
C both matter and energy are exchanged with the surroundings.
D neither matter nor energy is exchanged with the surroundings.

2 Select an example that involves a reversible chemical reaction.

A an electric car powered by a fuel cell
B the rechargeable battery in a mobile phone
C combustion of a fuel to produce heat for cooking
D the setting of a two-part epoxy glue after the parts are mixed

3 Examine the following concentration–time graph.



Identify the equation represented by this graph.

A $A \rightleftharpoons B$
B $B \rightleftharpoons A$
C $2A \rightleftharpoons B$
D $A \rightleftharpoons 2B$

4 In a sealed vessel, nitrogen monoxide, oxygen and nitrogen dioxide exist together in the following equilibrium.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g);\ \Delta H = -114\ kJ\,mol\,L^{-1}$$

Identify the set of conditions likely to give the highest yield of nitrogen dioxide gas.

A 200°C and 1 atm pressure
B 200°C and 2 atm pressure
C 300°C and 1 atm pressure
D 300°C and 2 atm pressure

5 A sample of chlorine (NOCl) is allowed to come to equilibrium according to the following equation.

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

The volume of the mixture is halved and it is allowed to come to a new equilibrium with the temperature remaining constant. Predict how the number of moles and concentration of chlorine has changed at the new equilibrium.

A number of moles has decreased in amount and decreased in concentration
B number of moles has increased in amount and decreased in concentration
C number of moles has decreased in amount and increased in concentration
D number of moles has increased in amount and increased in concentration

6 Carbon dioxide gas dissolves to a small extent in water, forming carbonic acid in an exothermic reaction. This is the reaction involved in forming fizzy drinks.

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq);\ \Delta H \text{ negative}$$

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

Predict which one of the following strategies would not be effective at increasing the amount of dissolved carbon dioxide.

A decreasing the pH of the solution
B decreasing the temperature of the solution
C increasing the pressure of the carbon dioxide gas
D increasing the concentration of carbon dioxide in the gas

7 Consider the following equation.

$$A + 3B \rightleftharpoons 2C + 4D$$

Select the correct expression for the equilibrium constant.

A $\frac{[A][3B]^3}{[2C]^2[4D]^4}$
B $\frac{[C]^2[D]^4}{[A][B]^3}$
C $\frac{[A][B]^3}{[C]^2[D]^4}$
D $\frac{[2C][4D]}{[A][3B]}$

8 The reaction between nitrogen monoxide and ozone is:

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$

$$K = 6 \times 10^{34} \text{ at } 25°C$$

Equal amounts of NO and O_3 are used. Identify which of the following statements cannot be inferred from the magnitude of the equilibrium constant.

A At equilibrium, $[NO_2][O_2] >> [NO][O_3]$.
B The reaction has a low activation energy.
C Very little ozone will remain at equilibrium.
D The equilibrium of the reaction lies well to the right.

9 Compare 0.1 mol L^{-1} solutions of HNO_3, HNO_2 and H_2SO_4. The K_a values for the acids are:
$K_a(HNO_3) = 25$
$K_a(HNO_2) = 7 \times 10^{-4}$
$K_a(H_2SO_4) = 10^9$
Identify the statement that correctly describes the properties of these acids.
A A solution of 0.1 mol L^{-1} HNO_3 has a higher pH than a solution of 0.1 mol L^{-1} H_2SO_4.
B A 20.0 mL solution of 0.1 mol L^{-1} HNO_2 has a higher pH than a 10.0 mL solution of 0.1 mol L^{-1} HNO_2.
C A 10.0 mL solution of 0.1 mol L^{-1} HNO_3 will require a greater volume of 0.2 mol L^{-1} NaOH solution for its neutralisation than a 10.0 mL solution of 0.1 mol L^{-1} HNO_2.
D A 0.1 mol L^{-1} solution of HNO_3 will produce a greater volume of hydrogen at STP on reaction with excess magnesium than the same volume of 0.1 mol L^{-1} HNO_2.

10 Identify the dilute solution of a strong acid.
A 6.0 mol L^{-1} HNO_3
B 0.10 mol L^{-1} HNO_3
C 8.0 mol L^{-1} CH_3COOH
D 0.01 mol L^{-1} CH_3COOH

11 The pH of a 0.01 mol L^{-1} aqueous sodium hydroxide is:
A equal to 2
B equal to 7
C equal to 12
D between 7 and 11.

12 Four beakers contain samples of acid as described below.
Beaker I 10 mL of 0.0001 mol L^{-1} HCl
Beaker II 10 mL of 5.0 mol L^{-1} HCl
Beaker III 2500 mL of 0.01 mol L^{-1} HCl
Beaker IV 2500 mL of 5.0 mol L^{-1} HCl
Identify the beaker(s) that contains the solution that has the highest pH.
A I only
B II only
C I and III only
D II and IV only

13 Identify the conjugate acid formed in the hydrolysis of the carbonate ion, CO_3^{2-}, in aqueous solution.
A H_3O^+
B CO_3^{2-}
C HCO_3^-
D $H_2CO_3^-$

14 Select the reaction in which water is acting as a Brønsted–Lowry acid.
A $H_2O(l) + NH_3(g) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
B $H_3O^+(aq) + HS^-(aq) \rightleftharpoons H_2S(aq) + H_2O(l)$
C $H_2O(l) + HCO_3^-(aq) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$
D $2Na(s) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g)$

15 Select the statement about the use of indicators in monoprotic acid–base titrations that is correct.
A Indicators are coloured compounds that are strong acids or bases.
B Phenolphthalein is a good indicator for all titrations because its colour change is so distinctive.
C Acid–base indicators must change colour at pH 7 when the acid and base have neutralised each other.
D An indicator should change colour at the point when the reactants are in the mole ratio indicated in the reaction equation.

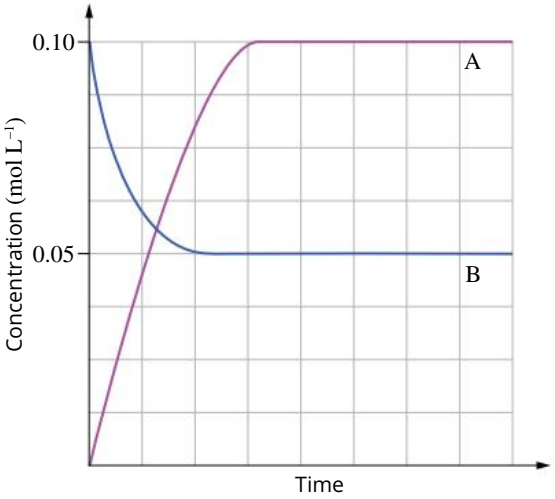
Short answer

1 The three phases of water, when placed in a sealed container at 0.1°C and 0.006 atm pressure, exist in a stable equilibrium. This is known as the triple point of water.
a Construct equations that demonstrate the equilibrium at the triple point between:
i ice and water
ii water and water vapour
iii ice and water vapour.
b State why these are considered to be physical reactions.
c At 2000°C water dissociates into its constituent elements.
i Construct a balanced equation for this reaction.
ii State why this is considered to be a chemical reaction.

2 The gases dinitrogen tetroxide (N_2O_4) and nitrogen dioxide (NO_2) coexist according to the following equilibrium reaction:

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

A concentration–time graph for the system coming to equilibrium is shown below.



a Identify A and B.

b Construct an expression for the equilibrium constant of the decomposition of N_2O_4.

c On the graph provided sketch the line showing the effect on A if a catalyst had been present in the mixture from the beginning.

d Calculate K_c for the reaction at equilibrium according to this concentration graph.

3 Carbon monoxide and iodine pentoxide react to form iodine and carbon dioxide in the following equilibrium reaction:

$$5CO(g) + I_2O_5(s) \rightleftharpoons I_2(g) + 5CO_2(g) \quad \Delta H = -1175\,kJ$$

Using your knowledge of Le Châtelier's principle, complete the following table by predicting the effect the change (column 1) will have on the quantity (column 2). Assume that the change listed is the only one taking place (e.g. if I_2 is added, the volume and the temperature are kept constant).

	Change	Quantity	Increase/ decrease/ no change
a	increase T	K_c	
b	decrease T	amount $I_2O_5(s)$	
c	add $I_2(g)$	K_c	
d	add $CO_2(g)$	amount $I_2(g)$	
e	double volume	amount of CO_2	
f	double volume	concentration CO_2	
g	remove CO	amount of CO_2	
h	add catalyst	amount $I_2(g)$	
i	add inert gas Ar	K_c	

4 A student is given the task of reducing the concentration of free metal ions in various aqueous samples using ammonia solution. Ammonia is capable of reacting with metal ions and forming complex ions. The student adds the same volume of ammonia solution (an excess) to each test tube initially containing 0.1 mol L^{-1} solutions of the metal ions. The information about each reaction is shown below.

Test tube	Metal ion	Equilibrium reaction	Equilibrium constant
1	Cd^{2+}	$Cd^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cd(NH_3)_4^{2+}(aq)$	1×10^7
2	Cu^{2+}	$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$	1×10^{13}
3	Zn^{2+}	$Zn^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Zn(NH_3)_4^{2+}(aq)$	1×10^9

Explain which of the three test tubes will contain the smallest concentration of 'free' metal ions.

5 The pH and electrical conductivity of four different mixtures were measured, as shown in the following table.

Mixtures	Conductivity (mA)	pH
A 0.1 mol L^{-1} HCl	260	1
B 0.1 mol L^{-1} CH_3COOH	5	3
C Mixture made by mixing equal volumes of 0.2 mol L^{-1} HCl and 0.2 mol L^{-1} NaCl	340	1
D Mixture made by mixing equal volumes of 0.2 mol L^{-1} HCl and 0.2 mol L^{-1} $NaCH_3COO$	80	3

a State why the conductivity of mixture A is higher than the conductivity of mixture B, yet the pH of A is lower than the pH of B. Include relevant equations in your answer.

b State why the pH of mixture C is the same as the pH of mixture A.

c State why the conductivity of mixture C is higher than the conductivity of mixture A.

d State why the pH of mixture D is the same as the pH of mixture B.

6 The pH of three different acids is given below.

Acid	Concentration (mol L^{-1})	pH
nitric acid (HNO_3)	0.010	2.0
propanoic acid (C_2H_5COOH)	0.010	3.4
sulfuric acid (H_2SO_4)	0.010	1.7

The three acids have the same concentration. Explain why:

a propanoic acid has the highest pH of the three acids

b sulfuric acid has the lowest pH of the three acids.

7 **a** Represent the self-ionisation of water as an equation.

b The temperature of water placed in the refrigerator decreases to about 4°C. At this temperature, the value of the equilibrium constant for the reaction shown in part **a**, K_w, is 1.2×10^{-15}. Calculate the pH of pure water at 4°C using this information.

c Predict if pure water at 4°C is neutral, acidic or basic. Explain your answer.

8 **a** A solution has a pH of 5.2. Calculate:

i the concentration, in mol L^{-1}, of hydroxide ions in the solution at 25°C

ii the pOH of the solution.

b 75 mL of a 0.0150 mol L^{-1} solution of hydrochloric acid is added to 125 mL of a 0.0100 mol L^{-1} solution of sodium hydroxide. Both solutions are at 25°C. Calculate the pH of the resultant solution.

9 The concentration of a solution of ammonium chloride was determined by titration against a standard solution of sodium hydroxide. The sodium hydroxide solution was placed in a burette and the ammonium chloride solution was pipetted into a conical flask.

Identify the solution or liquid you would use to rinse the following pieces of equipment just prior to use.

Equipment	Wash with:
burette	
pipette	
conical flask	

10 A chemistry class was asked to prepare a solution of a primary standard to titrate a solution of hydrochloric acid. In response to this task, a student carried out the following procedure.

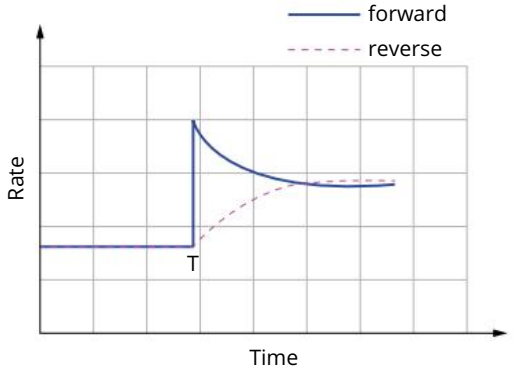
The student used sodium hydroxide solution as the primary standard, since he knew that sodium hydroxide and hydrochloric acid react. The student obtained a 500.00 mL volumetric flask which looked dirty so the student rinsed it out with detergent and hot tap water. The student weighed out 4.321 g of sodium hydroxide pellets on a watch glass and transferred the pellets into the volumetric flask by gently tapping the watch glass. Then, using a 50.00 mL pipette for greater accuracy, he put 500.00 mL of tap water into the flask. He used warm water to help the sodium hydroxide dissolve readily. He then shook the flask, preventing the solution from coming out by putting his thumb over the end, until all the solid had dissolved.

Identify five things the student did that would decrease the accuracy of the titration.

11 Consider the following readily reversible gas-phase reaction:

$$W(g) + 2X(g) \rightleftharpoons Y(g) + Z(g)$$

The graph below shows the changes to the rates of the forward and reverse reactions when some additional reactant, W, is added to an equilibrium mixture of these gases at time T.



a Explain how this graph shows that the mixture was at equilibrium before time T.

b Explain the changes in the rates of the forward and reverse reactions from time T using collision theory.

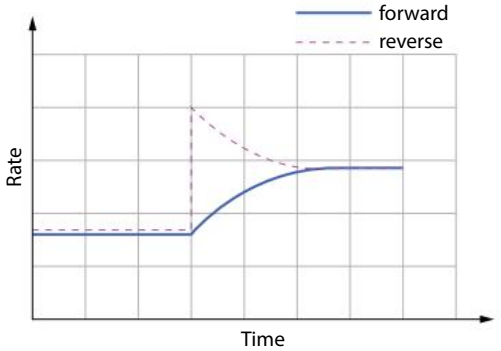
c The process was repeated several times, each time with a different change occurring at time T.

Changes tested included:

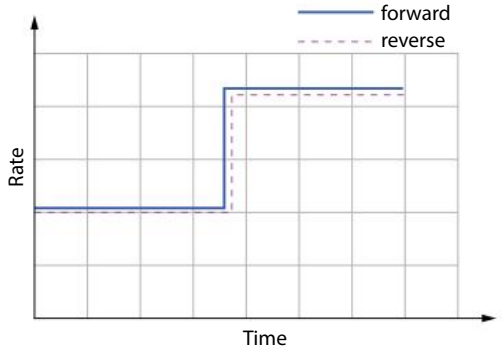
- removing W from the mixture
- removing Y
- adding Y
- adding an inert gas (argon)
- adding a catalyst
- increasing the volume of the container.

Select a change from this list that is consistent with the rate changes depicted in each of the graphs below. In each case briefly justify your choice.

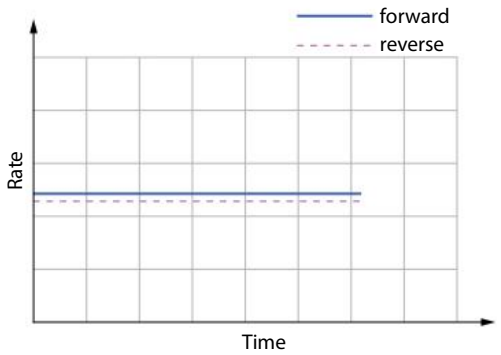
i



ii

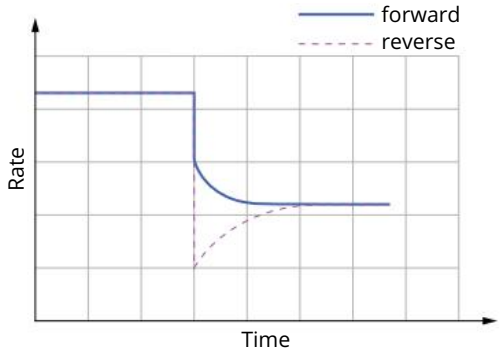


iii



Use the following information to answer question parts d, e and f.

The graph below shows the rate changes after lowering the temperature at time T.



d Explain why lowering the temperature causes an initial drop in both reaction rates.

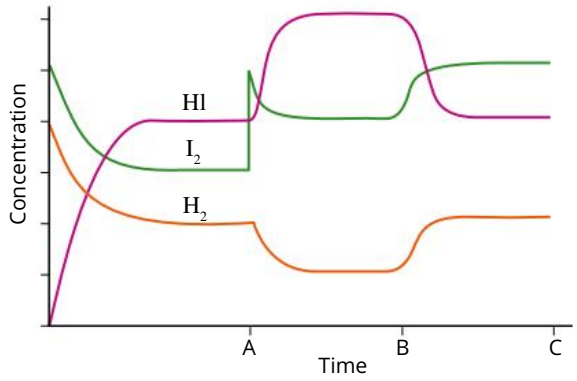
e Predict in which direction the equilibrium shifts during the period when the rates are unequal.

f Determine whether the reaction is exothermic or endothermic. Explain your reasoning.

12 The reaction between hydrogen and iodine in the gaseous phase to produce hydrogen iodide is described by the following equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \Delta H \text{ negative}$$

The following diagram shows the change in concentration of gaseous hydrogen, iodine and hydrogen iodide as the equilibrium is reached and disturbed.



a At point A, a sudden change occurs to the system. Identify what might cause this change.

b At point B, another change has occurred. Identify a possible cause of this change.

c Show on the time axis of the graph, a point when the system is at equilibrium.

d Modify the graph, extending it past point C, to show what would happen to the concentration of the gases if the volume of the reaction vessel was doubled. Assume the temperature remains constant. Draw the curve until equilibrium is re-established.

13 Methanol is used as a fuel for some racing cars. The synthesis of methanol from methane involves two reactions:

- the reaction of methane with steam to yield carbon monoxide and hydrogen
- an exothermic reaction between carbon monoxide and hydrogen to produce methanol.

a Represent the two reactions as equations.

b The reaction of carbon monoxide with hydrogen is performed at about 250°C and 100 atm pressure. Copper, zinc oxide and alumina are also present.

i Identify the likely function of the copper, zinc oxide and alumina in the reactor.

ii Predict how the yield would be affected if the reaction were performed at a higher temperature.

iii State two advantages of employing such a high pressure.

c Any process involving carbon monoxide presents hazards because of its toxicity, which arises because of its ability to bind strongly to haemoglobin in competition with oxygen.

$$Hb_4 + CO \rightleftharpoons Hb_4{\cdot}CO \; K_{c1}$$
$$Hb_4 + O_2 \rightleftharpoons Hb_4{\cdot}O_2 \; K_{c2}$$

K_{c1} is 20 000 times greater than K_{c2}.

i Referring to these competing equilibria, explain why exposure to carbon monoxide leads to decreased levels of oxyhaemoglobin ($Hb_4{\cdot}O_2$) in the blood.

ii Treatment for carbon monoxide poisoning often includes hyperbaric oxygen (pure oxygen at a pressure well above 1 atm). Explain how this helps remove $Hb_4{\cdot}CO$ from the blood.

14 An equilibrium is established when, in a closed system, gaseous phosphorous pentachloride (PCl_5) dissociates into gaseous phosphorous trichloride (PCl_3) and chlorine (Cl_2).

a Construct a balanced equation for this equilibrium reaction.

b Determine the equilibrium law expression for this reaction.

c The following equilibrium concentrations exist at a particular temperature. $[PCl_5] = 0.5\,mol\,L^{-1}$, $[PCl_3] = 2.0\,mol\,L^{-1}$, $[Cl_2] = 1.6\,mol\,L^{-1}$. Calculate the value of the equilibrium constant at this temperature.

15 The K_a for hypobromous acid (HOBr) is 2.1×10^{-9}.

a Construct an equation for the dissociation of hypobromous acid in water.

b Given a $0.30\,mol\,L^{-1}$ HOBr solution, calculate the:

i pK_a

ii pH

iii percentage dissociation.

c In calculating the pH and percentage dissociation, it can be assumed that the concentration of hypobromous acid at equilibrium is approximately the same as the initial concentration of hypobromous acid. Explain why this assumption is justified. Give reasons for your answer.

16 Many household cleaners contain ammonia (NH_3) as the active ingredient. An acid–base titration is performed in order to determine the concentration of ammonia in a commercially available cleaner.

a The hydrochloric acid was standardised by titration against a 20.00 mL aliquot of a primary standard. The standard was prepared by dissolving 1.22 g of anhydrous sodium carbonate (Na_2CO_3) in a 250.0 mL volumetric flask that was filled to the calibration line with distilled water. The titration was carried out a number of times and the following titres were recorded: 20.01 mL, 19.40 mL, 19.39 mL, 18.92 mL and 19.38 mL.

i List the properties of anhydrous sodium carbonate that make it suitable for use as a primary standard.

ii Identify the volumes that should be used to calculate the average titre of hydrochloric acid.

iii Construct a balanced equation for the reaction between hydrochloric acid and the solution of sodium carbonate.

iv Calculate the concentration of the standard sodium carbonate solution. The molar mass of $Na_2CO_3 = 105.99\,g\,mol^{-1}$

v Determine the concentration of the hydrochloric acid solution.

b Distilled water is used to dilute 10.00 mL of the cleaner to 100.0 mL in a volumetric flask. Next, 20.00 mL of this diluted cleaning solution is placed in a dry conical flask and titrated against the standardised hydrochloric acid solution from part **a** using methyl orange as an indicator. The average of three concordant titres is 17.40 mL.

i Construct an equation for the reaction between ammonia and hydrochloric acid.

ii Calculate the concentration, in moles per litre ($mol\,L^{-1}$), of ammonia in the cleaner.

iii Calculate the mass, in grams, of ammonia in a 750 mL bottle of cleaner.

iv Methyl orange is pink at a pH lower than 3.2 and yellow at a pH greater than 4.4.
Explain why methyl orange is a suitable indicator for this titration and state the colour change that would be observed.

v State whether each of the following changes to this titration procedure would lead to a result that is higher, lower or the same for the concentration of ammonia in the cleaner. Give an explanation for each answer.

	Result would be higher/lower/the same as the actual concentration of ammonia	Explanation
20.00 mL of water was added to the 20.00 mL of diluted cleaner solution in the conical flask prior to titration.		
Phenolphthalein indicator was used instead of methyl orange. Phenolphthalein is colourless at a pH less than 8.3 and pink at a pH higher than 9.5.		
The conical flask was washed, then rinsed with the diluted cleaner solution before using it.		

17 Phenol red is an acid–base indicator. The protonated form of the indicator, represented for simplicity by HPhr, is yellow, while the deprotonated form, Phr^-, is red. Phenol red has a pK_a value of 7.9.

a i Construct a chemical equation showing the relationship between the protonated and deprotonated forms of phenol red.

ii Deduce the equilibrium law expression for this reaction.

b i Identify the pH at the end point of a titration using phenol red as the indicator.

ii Propose a pH range over which phenol red would be expected to change colour.

iii Explain for which type of acid–base titration phenol red would be a suitable indicator.

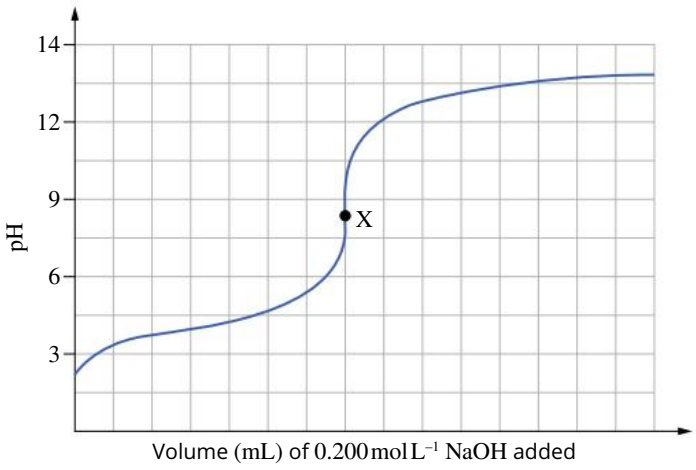
c Use your understanding of indicator chemistry to predict the colour of the indicator at the listed pH values. Justify your predictions.

pH	Phenol red colour	Justification
1.0		
7.0		
7.9		
8.4		
13.0		

18 Benzoic acid is a weak acid used as a preservative, for example in soft drinks. In aqueous solution it dissociates according to the equation:

$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^-(aq) + H_3O^+(aq)$

The graph shows the changes in pH that occur when 20.00 mL of 0.100 mol L^{-1} benzoic acid solution in a conical flask is titrated with 0.200 mol L^{-1} sodium hydroxide (NaOH) solution from a burette.



a Explain the significance of point X.

b Determine the volume of sodium hydroxide that has been added to the conical flask at point X.

c The pH range for the colour change is 3.0 (yellow) to 4.6 (blue) for the indicator bromophenol blue. Predict if bromophenol blue would be a suitable indicator for determining the equivalence point of a titration of benzoic acid with sodium hydroxide. Explain your answer.

d The reaction of benzoic acid with the base, sodium hydroxide, is often referred to as a neutralisation reaction. Explain why the pH of point X is not 7.

e Show the equivalence point, buffer region and the point where pK_a = pH on the graph.

f Determine the pK_a value of benzoic acid from the graph.

g Explain why the addition of a small volume of sodium hydroxide solution to the conical flask, in the buffer region, only causes a small change in pH.

h Describe the change in pH if a small amount of acid is added to a solution of a benzoic acid/benzoate buffer.

Topic 2: Oxidation and reduction

Multiple choice

1 Identify the option in which the nitrogen atoms are arranged in order of increasing oxidation state.

A NH_4^+, N_2, NO, NO_3^-

B NO_3^-, NO, NH_3^+, N_2

C NO_2, N_2, NO, HNO_3

D NO_3^-, NO, N_2, NH_3

2 Identify the option that is not an oxidation–reduction reaction.

A $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

B $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

C $Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$

D $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

3 Select the statement that is true for the reaction:

$H_2O_2(aq) + 2H^+(aq) + 2Cl^-(aq) \rightarrow 2H_2O(l) + Cl_2(g)$

A Hydrogen peroxide is reduced and the hydrogen ion is oxidised.

B The chloride ion is oxidised and the oxygen in hydrogen peroxide is reduced.

C Hydrogen peroxide is the reducing agent and the hydrogen ion is the oxidising agent.

D The oxidising agent is the chloride ion and the reducing agent is hydrogen peroxide.

4 Identify the equation involving antimony (Sb) that represents an oxidation–reduction reaction.

A $SbF_5 + KF \rightarrow KSbF_6$

B $2SbCl_3 + 3H_2O \rightarrow Sb_2O_3 + 6HCl$

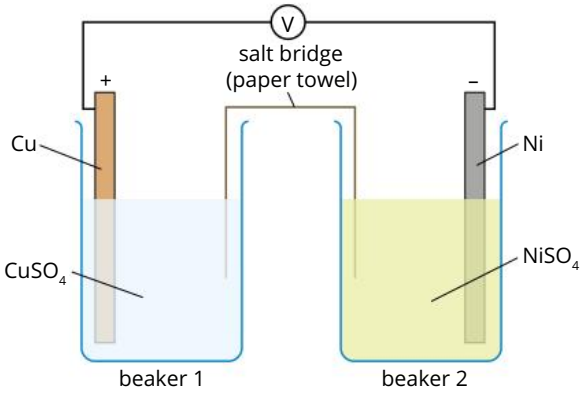
C $2Sb + 3Zn + 6HCl \rightarrow 2SbH_3 + 3ZnCl_2$

D $Sb_2(SO_4)_3 + 3H_2S \rightarrow Sb_2S_3 + 3H_2SO_4$

5 Select the alternative that best describes the features of an anode in a galvanic cell.

	Polarity	Electrode reaction
A	positive	oxidation
B	positive	reduction
C	negative	oxidation
D	negative	reduction

6 An electrochemical cell was made by dipping a copper rod into a solution of 1.0 mol L^{-1} $CuSO_4$ in one beaker and dipping a nickel rod into a solution of 1.0 mol L^{-1} $NiSO_4$ in another beaker. The metals were connected with wire and the two solutions were connected by a piece of paper towel that had been soaked in a potassium nitrate solution. The cell is shown in the following diagram.



The solution in beaker 1 was initially coloured blue, owing to the presence of Cu^{2+} ions. The solution in beaker 2 was initially coloured green because of the presence of Ni^{2+} ions. Predict which of the following changes might be possible to detect after the galvanic cell has been discharging for a period of time.

A The blue colour in beaker 1 has faded and the mass of the nickel electrode has increased.
B The blue colour in beaker 1 has faded and the mass of the nickel electrode has decreased.
C The green colour in beaker 2 has faded and the mass of the copper electrode has increased.
D The green colour in beaker 2 has faded and the mass of the copper electrode has decreased.

7 Using the electrochemical series (Table 2 in Appendix E), determine which one of the following reactions would not be expected to occur to an appreciable extent.

A $2I^-(aq) + Pb^{2+}(aq) \rightarrow I_2(s) + Pb(s)$
B $2Ag^+(aq) + Ni(s) \rightarrow 2Ag(s) + Ni^{2+}(aq)$
C $2H^+(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + H_2(g)$
D $Br_2(aq) + Fe^{2+}(aq) \rightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$

8 Hydrogen gas (H_2) is bubbled through a solution of $Sn^{4+}(aq)$. Predict which one of the following observations is most likely.

A no reaction will occur
B a precipitate of SnH_4 will form
C the pH of the solution will decrease
D oxygen gas will form from the dissociation of water

9 The following equations involve ions of the transition metal vanadium. The half-cell potential E^0 (V) is shown for each equation.

$V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$ $\quad E^\circ = -0.25\,V$
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$ $\quad E^\circ = +0.36\,V$
$VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$ $\quad E^\circ = +1.00\,V$

Identify the strongest oxidising and reducing agents of the ones listed below.

	Oxidising agent	Reducing agent
A	VO_2^+	V^{2+}
B	VO_2^+	VO^{2+}
C	V^{3+}	VO^{2+}
D	$V2^+$	VO_2^+

10 A ring is to be covered with a thin layer of gold by electroplating from a solution of Au^{3+}. Identify the terminal of the power supply to which the ring should be attached, and name this terminal.

A to the positive terminal of the power supply and acts as the anode
B to the negative terminal of the power supply and acts as the anode
C to the positive terminal of the power supply and acts as the cathode
D to the negative terminal of the power supply and acts as the cathode

11 Select the alternative that correctly indicates the polarity of the anode in a galvanic cell and in an electrolytic cell.

	Polarity of the anode in a galvanic cell	Polarity of the anode in an electrolytic cell
A	positive	negative
B	negative	positive
C	positive	positive
D	negative	negative

Short answer

1 For each of the reactions represented below:

- identify them as redox or non-redox reactions
- list the changes in oxidation state for each redox reaction
- identify the oxidising agent and the reducing agent for each redox reaction.

a $HIO_3(aq) + 3SO_2(g) \rightarrow 3SO_3(aq) + HI(aq)$

b $SO_3(g) + Ca(OH)_2(aq) \rightarrow CaSO_4(s) + H_2O(l)$

c $4Fe(OH)_2(s) + 2H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(aq)$

d $NaH(s) + H_2O(l) \rightarrow H_2(g) + NaOH(aq)$

e $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$

2 Balance each of the following unbalanced redox reactions. Identify the oxidising agent and the reducing agent.

a $Al(s) + Br_2(aq) \rightarrow Al^{3+}(aq) + Br^-(aq)$

b $ClO^-(aq) + S_2O_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + Cl^-(aq)$

c $H_2O_2(aq) + MnO_4^-(aq) \rightarrow O_2(aq) + MnO_2(s)$

d $U^{4+}(aq) + MnO_4^-(aq) + H_2O(l) \rightarrow Mn^{2+}(aq) + UO_2^+(aq) + H^+(aq)$

3 For the following reactions, use the standard electrode potentials provided to construct the:

- oxidation half-equation
- reduction half-equation
- overall ionic equation.

Conjugate redox pair (oxidising agent/reducing agent)	E°(volt)
$Cr_2O_7^{2-}(aq)/Cr^{3+}(aq)$	1.36
$Fe^{3+}(aq)/Fe^{2+}(aq)$	0.77
$I_2(s)/I^-(aq)$	0.54
$S(s)/H_2S(g)$	0.17

a A solution of sodium iodide is added to an acidified solution of potassium dichromate.

b Hydrogen sulfide gas is bubbled into a solution of iron(III) chloride.

c Predict, using the information provided in the table above, the identity of the two half-cells that, when used in a galvanic cell, will generate the greatest cell potential at standard conditions. Calculate the cell potential difference generated by this cell.

d Discuss the limitation of predictions based on standard electrode potentials.

4 Explain each of the following statements.

a A piece of iron metal that is partly exposed to a moist atmosphere and partly buried in the ground corrodes much more rapidly beneath the surface of the ground.

b It is unwise to use a copper nut on a steel bolt in an exposed environment.

5 A useful electrochemical cell for small articles, such as watches and phones, makes use of silver oxide and zinc as described by the equation:

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

The cell potential is 1.50 V.

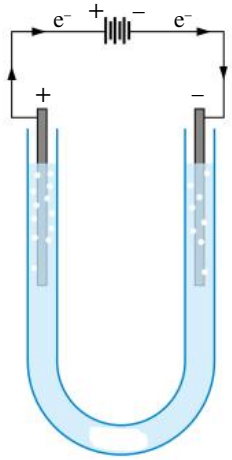
a Identify the anode and cathode and state the polarity of each electrode.

b Show half-equations for the reactions occurring at the anode and the cathode.

c Name the oxidising agent and the reducing agent in the cell.

d Determine the standard reduction potential for the half-cell containing $Ag_2O(s)$.

6 A series of electrolyses is carried out under standard conditions in a U-tube, as shown in the following diagram.



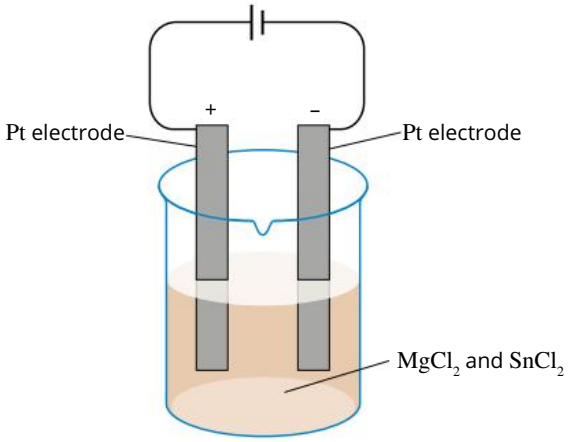
The electrolyte solution in each case and the electrode materials used are listed below.

Solution	Electrode materials	
	Positive electrode	Negative electrode
KI(aq)	carbon	carbon
$PbCl_2(aq)$	carbon	carbon
$AlCl_3(aq)$	copper	copper
Na_2SO_4	platinum	platinum

a Show half-equations for the reactions predicted to occur at the positive and negative electrodes.

b State one visible change you would observe to confirm the formation of your predicted products.

7 A 100 mL solution containing a mixture of magnesium chloride and tin(II) chloride is prepared by dissolving 0.025 mol of each in water. Platinum electrodes are placed in the solution and a small current is passed through it, as shown in the diagram below.



a Using the standard electrode potentials, show half-equations for the electrode reactions occurring just after electrolysis is started at the:
- **i** anode
- **ii** cathode.

b After electrolysis has been occurring for a considerable period of time, all of the metal that was first plated on the cathode will have been used up and a new electrode reaction will occur at the cathode. Show a half-equation for the next electrode reaction that occurs at the cathode.

c Identify the major difference that would occur in the cell if the solution that was used had been a saturated solution of tin(II) chloride.

8 Compare and explain the anode and cathode reactions that occur when a direct electric current is passed through:
- **a** molten sodium chloride
- **b** a 1.0 mol L^{-1} solution of sodium chloride
- **c** a concentrated solution of sodium chloride.

Assume that inert electrodes are used in each of the electrolyses.

9 Discuss briefly, using sodium and sulfur as examples, how the ability of elements to act as an oxidising or reducing agent can be predicted from their position in the periodic table.

10 This question requires you to compare galvanic cells with electrolytic cells.

a List two structural features (components) that both types of cell possess.

b Compare the energy transformations occurring in a galvanic cell with those occurring in an electrolytic cell.

c Explain why the negative electrode of a galvanic cell is the site of oxidation, whereas the negative electrode of an electrolytic cell is the site of reduction.

d Explain why a galvanic cell is always constructed to keep its reacting oxidising agent and reducing agent apart, while in an electrolytic cell they are usually combined in the same electrolyte mixture and instead steps are taken to keep the cell products apart.

11 In a commercially available dry cell, a voltage of about 1.48 V is produced by an electron transfer reaction between MnO_2 and Zn. In this reaction MnO_2(s) is converted to Mn_2O_3(s).

a State the names of MnO_2 and Mn_2O_3.

b Show the half-equations for the oxidation and reduction reactions in the dry cell.

c Calculate the reduction potential for the reduction reaction of MnO_2, assuming standard conditions.

d Suggest why the paste in the dry cell becomes less acidic as the cell operates.

e Explain why the dry cell described above is called a primary cell.

12 A half-cell is made by placing a copper electrode in a solution containing Cu^{2+} ions, and another is made by placing a graphite electrode in an aqueous solution of iodide ions and iodine (a brown colour in aqueous solution). The two half-cells are connected correctly.

a State what would need to be done to 'correctly connect' the two half-cells.

b Show two balanced half-equations for the reactions that occur at the electrodes. Write the net ionic equation for the cell.

c **i** State the direction of electron flow.
- **ii** State the direction of flow of the anions in the salt bridge.
- **iii** Identify the electrode that is the cathode. Identify the anode.
- **iv** Calculate the cell potential for the cell (assume standard conditions).
- **v** Explain the purpose of the graphite electrode. Determine whether any other solid material, such as Pb or Fe, could be used instead in this half-cell. Explain.
- **vi** Predict what you would observe to happen in each half-cell over a period of time.

13 **a** Briefly describe how an acidified solution of potassium permanganate can be used to distinguish between:
- **i** water and hydrogen peroxide
- **ii** iron(II) nitrate solution and iron(III) nitrate solution
- **iii** sodium oxalate and sodium sulfate solution.

b Predict any observations you would expect to make when potassium permanganate is added to the solutions list in part **a**. Justify your predictions in terms of the principles of redox chemistry you have studied in this course. Refer to the information provided in the table below. Use chemical equations where appropriate.

Conjugate redox pair (oxidising agent/reducing agent)	$E^{\ominus}$ (volt)
$O_2(g)/H_2O(l)$	1.23
$H_2O_2(aq)/H_2O(l)$	1.78
$O_2(g)/H_2O_2(aq)$	0.70
$Fe^{3+}(aq)/Fe^{2+}(aq)$	0.77
$Na^+(aq)/Na(s)$	2.71
$SO_4^{2+}(aq)/SO_2(g)$	0.16
$CO_2(g)/ C_2O_4^{2-}$	0.49
$MnO_4^-(aq)/Mn^{2+}(aq)$ (purple colourless)	1.49

14 A student designed an experiment to determine the order of the following four reduction reactions in the electrochemical series.

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

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

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

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$

The student prepared half-cells for each reaction. The concentration of reactants in each half-cell was kept constant. Different sets of half-cells were combined in pairs to make a series of galvanic cells. A fresh salt bridge containing a solution of potassium nitrate was used in each galvanic cell. A voltmeter was used to measure the potential difference (voltage) produced by each galvanic cell. The direction of the deflection of the needle of the voltmeter was used to determine the polarity of the half-cell.

The student's results are summarised in the following table.

Half-cell pair	Positive half-cell	Potential difference (volts)
$Pb^{2+}(aq)/Pb(s)$ and $Mg^{2+}(aq)/Mg(s)$	$Pb^{2+}(aq)/Pb(s)$	2.25
$Pb^{2+}(aq)/Pb(s)$ and $Cu^{2+}(aq)/Cu(s)$	$Cu^{2+}(aq)/Cu(s)$	0.46
$Pb^{2+}(aq)/Pb(s)$ and $Ag^+(aq)/Ag(s)$	$Ag^+(aq)/Ag(s)$	0.96
$Mg^{2+}(aq)/Mg(s)$ and $Cu^{2+}(aq)/Cu(s)$	$Cu^{2+}(aq)/Cu(s)$	2.71
$Mg^{2+}(aq)/Mg(s)$ and $Ag^+(aq)/Ag(s)$	$Ag^+(aq)/Ag(s)$	3.21
$Cu^{2+}(aq)/Cu(s)$and $Ag^+(aq)/Ag(s)$	$Ag^+(aq)/Ag(s)$	0.50

a Sort the reduction reactions in order from strongest oxidising agent to weakest oxidising agent using the results provided. Explain how you used the experimental evidence to determine the ordering of the relative strength of the oxidising agents.

b i Determine the potential difference provided by each half-cell if the potential provided by the $Cu^{2+}(aq)/Cu(s)$ half-cell is 0.36 V.

ii Sort the reduction equations into an electrochemical series.

iii Explain why these half-cell potentials do not match those provided in a table of standard electrode potentials.

c Draw a fully labelled diagram showing the galvanic cell produced by the combination of the $Mg^{2+}(aq)/Mg(s)$ and $Ag^+(aq)/Ag(s)$ half-cells.

d Explain the function of the salt bridge in a galvanic cell and why a fresh salt bridge is used in each galvanic cell.

e i Another way of determining the relative reactivity of metals and ions is to add a metal to a solution of metal ions. Complete the following table by indicating if a metal/metal ion displacement reaction is expected to occur when the combinations of metal and metal ions are mixed.

	Metal ions			
Metal	$Pb^{2+}(aq)$	$Mg^{2+}(aq)$	$Cu^{2+}(aq)$	$Ag^+(aq)$
Pb				
Mg				
Cu				
Ag				

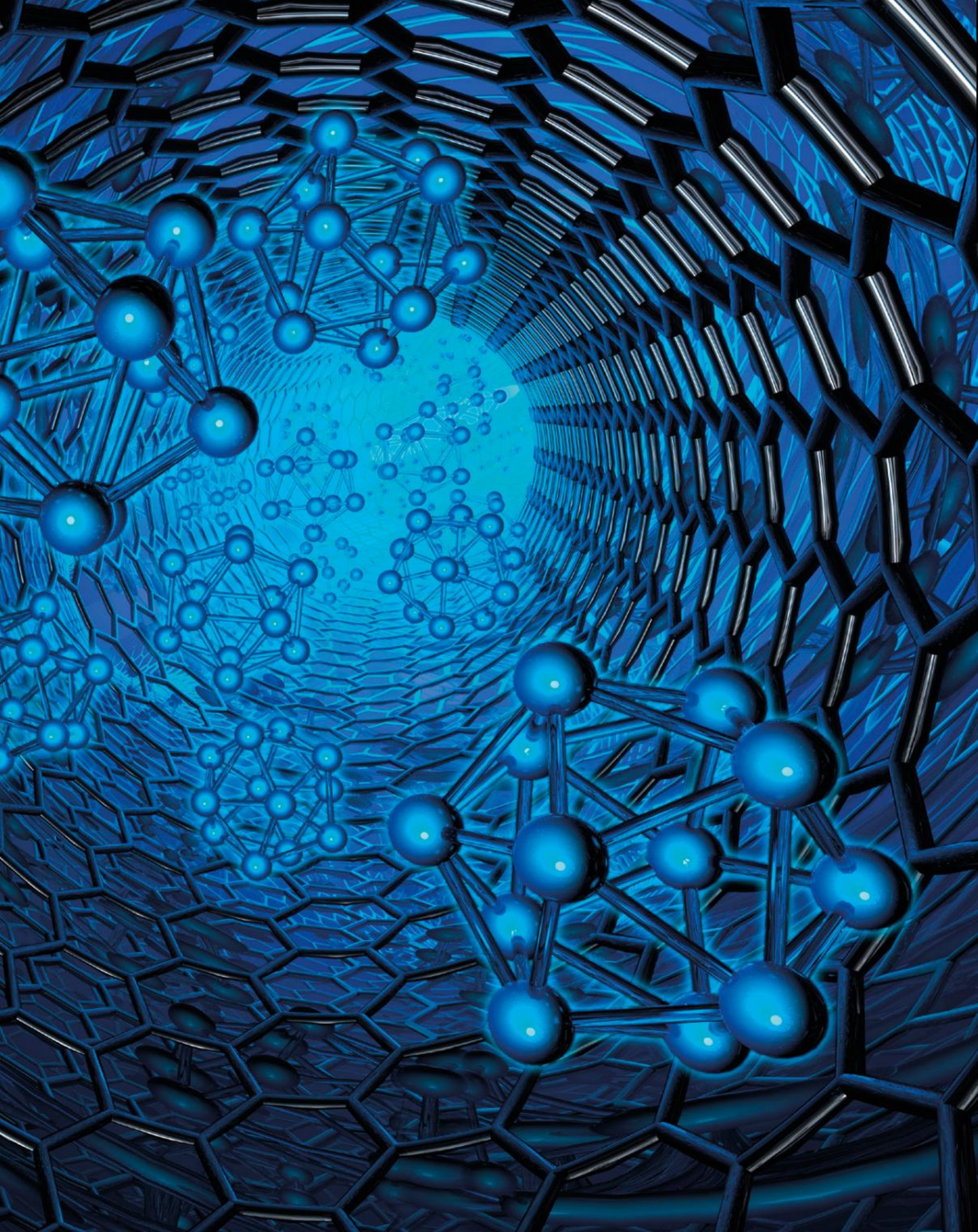
ii Show balanced equations for each reaction that occurs.

f Compare the energy changes that occur in a galvanic cell with the energy changes that occur when oxidising and reducing agents are in direct contact.

15 Electrolytic cells are used in industry to extract metals such as aluminium from their ore as well as to refine metals such as copper. Electrolysis is used to purify copper. A particular sample of copper contains 1% impurities. These impurities consist of silver, gold, zinc and lead.

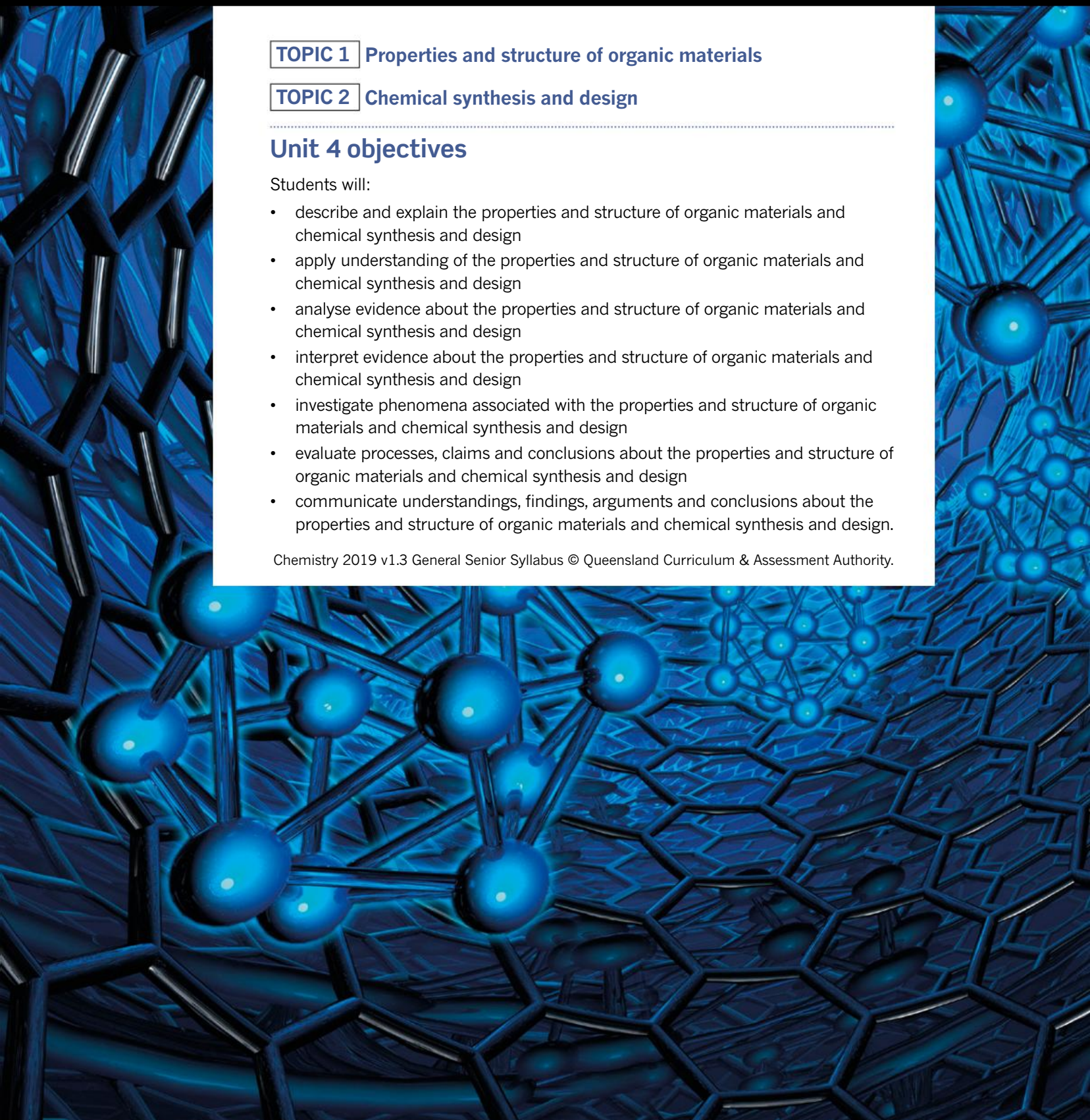
Explain how impure copper can be purified by electrolysis. Include in your answer:

- half-equations for any reaction that occurs
- a labelled diagram showing the essential features of the electrolytic cell
- a description of what happens to the metal impurities as the electrolysis proceeds.



UNIT 4

Structure, synthesis and design



TOPIC 1 Properties and structure of organic materials

TOPIC 2 Chemical synthesis and design

Unit 4 objectives

Students will:

- describe and explain the properties and structure of organic materials and chemical synthesis and design
- apply understanding of the properties and structure of organic materials and chemical synthesis and design
- analyse evidence about the properties and structure of organic materials and chemical synthesis and design
- interpret evidence about the properties and structure of organic materials and chemical synthesis and design
- investigate phenomena associated with the properties and structure of organic materials and chemical synthesis and design
- evaluate processes, claims and conclusions about the properties and structure of organic materials and chemical synthesis and design
- communicate understandings, findings, arguments and conclusions about the properties and structure of organic materials and chemical synthesis and design.

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CHAPTER

08 Structure and physical properties of organic compounds

Organic chemistry is the study of carbon-based compounds. With the exception of hydrogen, carbon forms more compounds than all of the other elements put together. In fact, scientists currently know of more than 10 million organic compounds and more are being discovered or synthesised all the time.

Organic compounds exhibit an enormous range of properties, which allows chemists to develop materials for applications as diverse as fuels, fibres, plastics, detergents, dyes, paints, medicines, perfumes and insecticides. Organic compounds also form the basis of every cell in all living organisms.

The study of organic chemistry is made easier by grouping organic compounds into classes. In this chapter, you will explore some of the different classes and learn how to identify them from their structures. You will examine the different ways in which atoms in organic molecules can be connected, and learn how to represent them using a variety of formulas. You will also learn how to name a range of organic compounds using a set of systematic rules. Finally, you will study the physical properties of various organic compounds and examine how the structures of these compounds determine their properties.

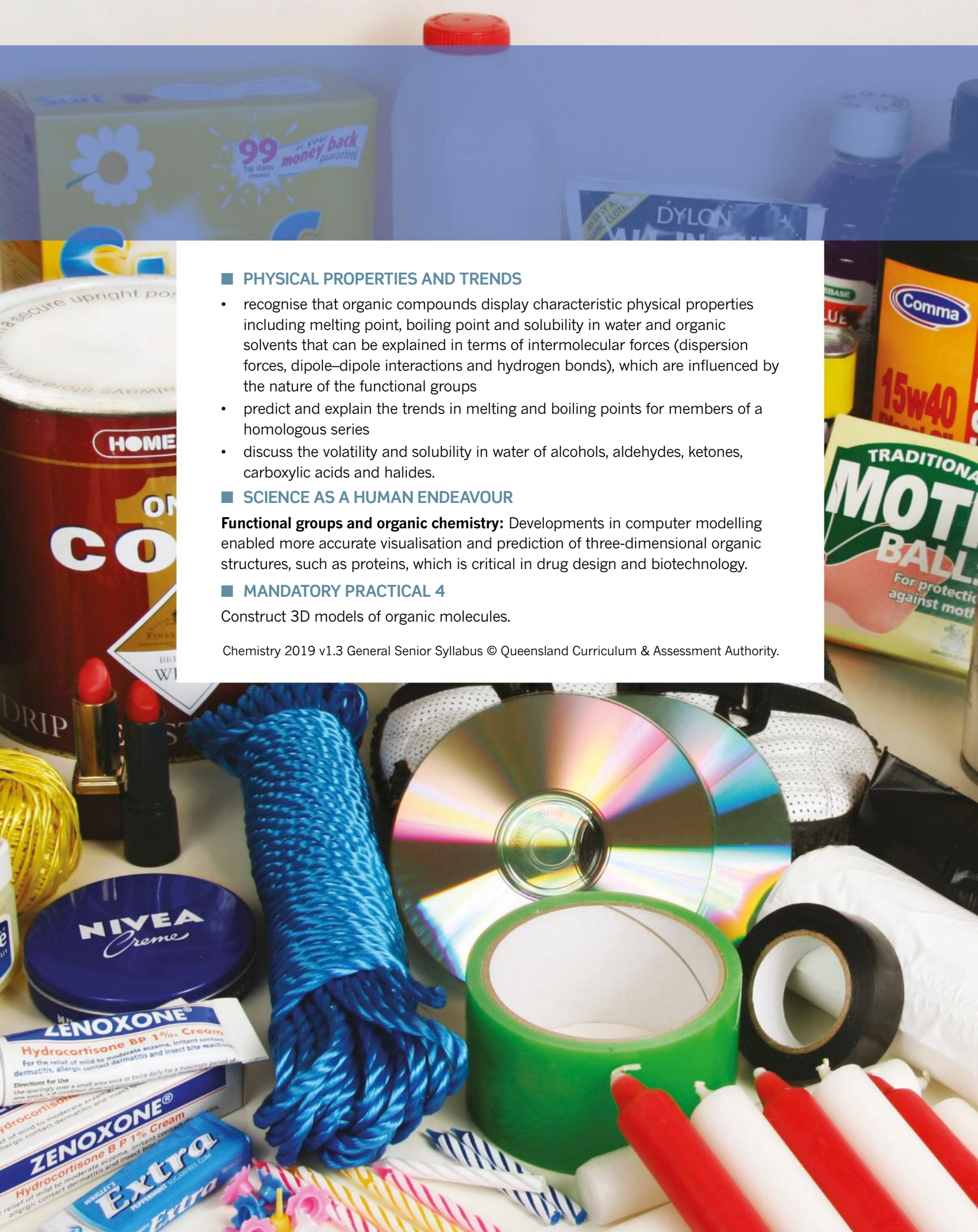
WS 4.1.1

Syllabus subject matter

Topic 1 • Properties and structure of organic materials

STRUCTURE OF ORGANIC COMPOUNDS

- recognise that organic molecules have a hydrocarbon skeleton and can contain functional groups, including alkenes, alcohols, aldehydes, ketones, carboxylic acids, haloalkanes, esters, nitriles, amines and amides, and that structural formulas (condensed and extended) can be used to show the arrangement of atoms and bonding in organic molecules
- deduce the structural formulas and apply IUPAC rules in the nomenclature of organic compounds (parent chain up to 10 carbon atoms) with simple branching for alkanes, alkenes, alkynes, alcohols, aldehydes, ketones, carboxylic acids, haloalkanes, esters, nitriles, amines and amides
- identify structural isomers as compounds with the same molecular formula but different arrangement of atoms; deduce the structural formulas and apply IUPAC rules in the nomenclature for isomers of the non-cyclic alkanes up to C_6
- identify stereoisomers as compounds with the same structural formula but with different arrangement of atoms in space; describe and explain geometrical (*cis* and *trans*) isomerism in non-cyclic alkenes.



PHYSICAL PROPERTIES AND TRENDS

- recognise that organic compounds display characteristic physical properties including melting point, boiling point and solubility in water and organic solvents that can be explained in terms of intermolecular forces (dispersion forces, dipole–dipole interactions and hydrogen bonds), which are influenced by the nature of the functional groups
- predict and explain the trends in melting and boiling points for members of a homologous series
- discuss the volatility and solubility in water of alcohols, aldehydes, ketones, carboxylic acids and halides.

SCIENCE AS A HUMAN ENDEAVOUR

Functional groups and organic chemistry: 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.

MANDATORY PRACTICAL 4

Construct 3D models of organic molecules.

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8.1 Diversity of organic compounds

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand why carbon is able to form such a diverse range of organic compounds
- recognise that almost all organic compounds have a hydrocarbon skeleton
- define what a functional group is and know that the major classes of organic compounds are characterised by their functional groups.



Organic chemistry is the study of carbon-based compounds. These compounds make up more than 90% of all chemical compounds and form the basis of all living systems (Figure 8.1.1). Historically, the association with living systems led to the study of carbon compounds being called 'organic chemistry' and the molecules of carbon compounds being referred to as 'organic molecules'. In fact, for a long time, scientists believed that carbon compounds only occurred in living systems, but Friedrich Wöhler disproved this idea in 1828 when he produced urea ($CO(NH_2)_2$) in the laboratory. The definition of organic chemistry now encompasses carbon-based compounds that originate from living and non-living matter, although there are a few compounds such as carbon monoxide (CO), carbon dioxide (CO_2), carbonic acid (H_2CO_3) and metal carbonates (e.g. Na_2CO_3) that, for historical reasons, are still not considered to be organic compounds.

In this module, you will be introduced to several different types of organic compounds and learn why carbon is able to form such a diverse range of these compounds. You will also learn how to represent the arrangement of atoms in organic molecules using structural formulas.



FIGURE 8.1.1 Different types of organic molecules form the basis of all living systems, including the child, tomatoes, timber and plants in this photograph.

BONDING IN CARBON COMPOUNDS

Why do so many organic compounds exist? To answer this question, we need to understand the bonding properties of carbon.

Carbon atoms contain six electrons—two electrons in the first shell and four in the second. The **electronic configuration** of a carbon atom can be written as 2,4 or $1s^2 2s^2 2p^2$. This means the following:

- Each carbon atom has four **valence electrons**, which gives it a **valence number** of four. The valence number of an element is equal to the number of valence electrons in an atom of that element. All four of carbon's valence electrons are available for bonding with other atoms.
- A carbon atom can form four covalent bonds with up to four other carbon atoms, each of which can also bond with up to four other carbon atoms, thus potentially forming long, branched chains, or even rings.
- Single, double or triple bonds can be formed between two carbon atoms. A molecule that contains only single carbon–carbon bonds is described as a **saturated molecule**. A molecule that contains one or more double or triple bonds is described as an **unsaturated molecule**.
- Single, double or triple bonds can also be formed between carbon atoms and atoms of other elements. For example, carbon can form a single bond with hydrogen, a double bond with oxygen and a triple bond with nitrogen.

STABILITY OF CARBON BONDS

The covalent bonds between carbon and other atoms each have a **bond energy**. As discussed in Unit 2, bond energy is a measure of **bond strength** and is the amount of energy required to break the covalent bond. The higher the bond energy, the stronger the bond.

The bond energies of a number of covalent bonds are listed in Table 8.1.1. You can see that a carbon–carbon triple bond has a higher bond energy, and so is a stronger bond than a carbon–carbon single bond. You can also see that there is a wide variation in the bond energies of single covalent bonds between carbon and other elements.

TABLE 8.1.1 Bond energies in common organic molecules

Covalent bond	Bond energy ($kJ\,mol^{-1}$)
C≡C	839
C=C	614
C–C	346
C–F	492
C–H	414
C–O	358
C–Cl	324
C–N	286
C–S	289

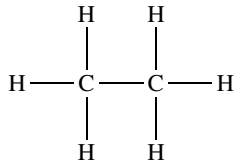


FIGURE 8.1.2 Ethane is a hydrocarbon because it is made up of only carbon and hydrogen.

FUNCTIONAL GROUPS

In its many millions of compounds, carbon is almost always associated with hydrogen. Some organic molecules are made up of only carbon and hydrogen, such as ethane, which is shown in Figure 8.1.2. Molecules made up of only carbon and hydrogen are defined as **hydrocarbons** and you will learn more about them in Module 8.2.

Most organic molecules contain elements in addition to carbon and hydrogen, such as oxygen, nitrogen, sulfur or chlorine. These molecules have a **hydrocarbon skeleton** but one or more of their hydrogen atoms has been replaced with other atoms or groups of atoms called **functional groups**.

A functional group is defined as an atom or a group of atoms that gives a characteristic set of chemical properties to a molecule containing those atoms. The major classes of organic compounds are characterised by their functional groups and several examples are shown in Figures 8.1.3 to 8.1.5.

Table 8.1.2 gives a summary of the major classes of organic compounds and shows the functional groups that characterise each class. Note that the symbols R and R' usually represent the hydrocarbon chain that makes up the rest of the organic molecule, but they can also be used to represent any group of atoms.

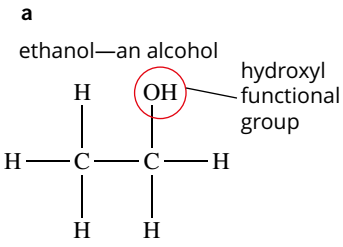


FIGURE 8.1.3 (a) Ethanol belongs to the class of compounds called alcohols. Alcohols contain the hydroxyl (OH) functional group. (b) Ethanol is used in alcoholic drinks and as a fuel.

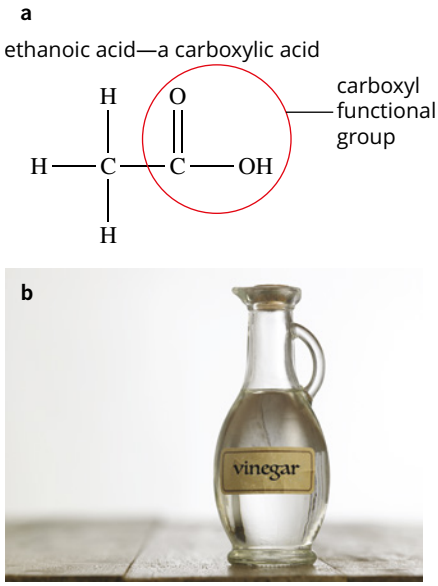


FIGURE 8.1.4 (a) Ethanoic acid belongs to the class of compounds called carboxylic acids. Carboxylic acids contain the carboxyl (COOH) functional group. (b) Ethanoic acid is found in many kinds of foods such as vinegar and tomato sauce. It is also widely used in industry.

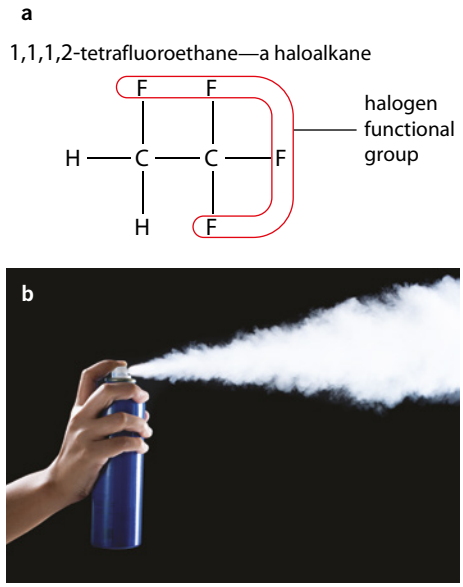
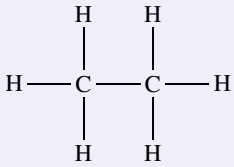
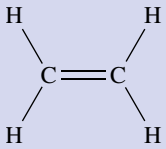
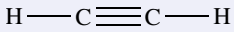
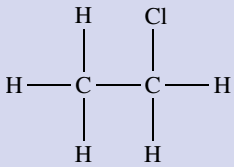
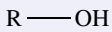
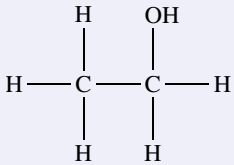
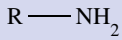
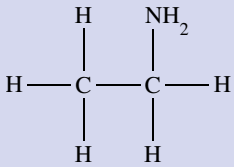
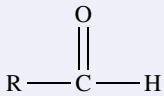
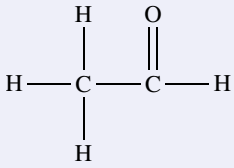
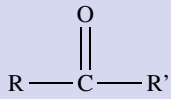
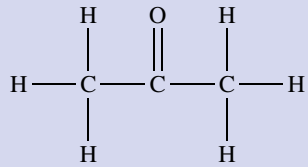
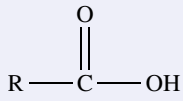
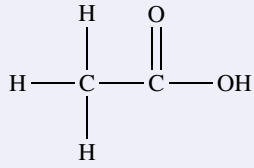
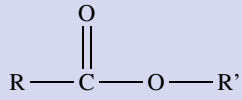
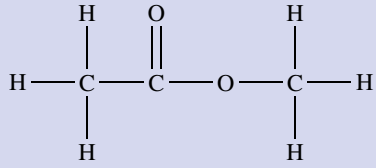
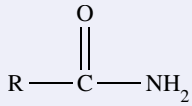
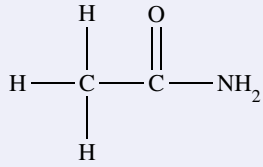
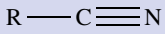
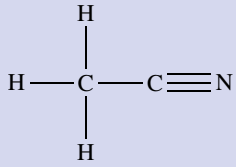


FIGURE 8.1.5 (a) 1,1,1,2-tetrafluoroethane belongs to the class of compounds called haloalkanes. Haloalkanes contain a halogen atom as their functional group. (b) 1,1,1,2-tetrafluoroethane is widely used as a refrigerant and in aerosols.

It is important to realise that even though **alkenes** and **alkynes** are hydrocarbons, their double and triple bonds are still considered to be functional groups because the multiple bonds are responsible for each class's chemistry. You will learn more about all of these different classes of organic compounds in Modules 8.2 and 8.4.

TABLE 8.1.2 Summary of the major classes of organic compounds

Class of organic compound	Functional group present	Example
alkane	none	ethane 
alkene	double bond	ethene 
alkyne	triple bond	ethyne 
haloalkane	halogen  (where X = F, Cl, Br, I)	chloroethane 
alcohol	hydroxyl 	ethanol 
amine	amino 	ethanamine 
aldehyde	carbonyl (attached to a hydrogen atom) 	ethanal 

ketone	carbonyl (attached to carbon atoms on either side) 	propanone 
carboxylic acid	carboxyl 	ethanoic acid 
ester	carboxylate 	methyl ethanoate 
amide	carboxamide 	ethanamide 
nitrile	nitrile 	ethanenitrile 

A functional group is defined as an atom or a group of atoms that gives a characteristic set of chemical properties to a molecule containing those atoms. The major classes of organic compounds are characterised by their functional groups.

8.1 Review

SUMMARY

- Organic chemistry is the study of carbon-based compounds.
- Carbon atoms can form covalent bonds with each other to create long chains or rings.
- Carbon atoms can form single, double or triple bonds with other carbon atoms as well as other non-metallic atoms such as hydrogen, oxygen or nitrogen.
- In its many millions of compounds, carbon is almost always associated with hydrogen, giving organic molecules a hydrocarbon skeleton.
- A saturated molecule is one that contains only single carbon–carbon bonds.
- An unsaturated molecule contains one or more double or triple bonds.
- A functional group is an atom or a group of atoms that gives a characteristic set of chemical properties to a molecule containing those atoms.
- Organic compounds can be grouped into classes.
- The many classes of organic compounds are characterised by their functional groups.

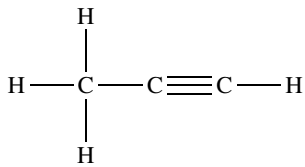
KEY QUESTIONS

Retrieval

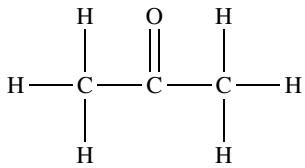
1 Define the following terms.
- **a** saturated molecule
- **b** functional group

2 Identify the functional groups in each of the following compounds.

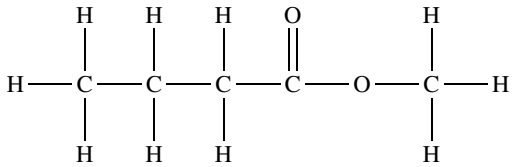
a



b



c



Comprehension

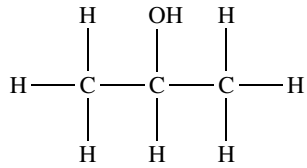
3 **a** Show the electron configuration of carbon.
- **b** Identify how many valence electrons carbon has.
- **c** Identify how many covalent bonds carbon forms.

4 Methane is the smallest hydrocarbon molecule.
- **a** Describe why methane is termed a hydrocarbon.
- **b** Explain why the carbon atom in a methane molecule bonds to four hydrogen atoms, rather than two, three, five or any other number of hydrogen atoms.

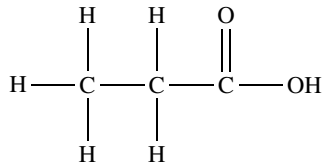
Analysis

5 Analyse the following molecules. Identify the functional group in each and categorise each molecule based on its functional group.

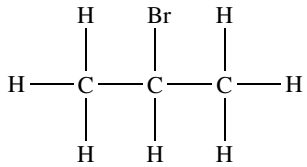
a



b



c



6 Explore why carbon can form so many different organic compounds.

8.2 Hydrocarbons



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- define hydrocarbons and know the main classes are alkanes, alkenes and alkynes
- define homologous series and understand that members of the same homologous series have a similar structure, the same pattern to their physical properties, the same chemical properties and the same general formula
- describe alkanes, alkenes and alkynes and be able to explain their differences in terms of their structure and general formulas
- use systematic naming rules to name alkanes, alkenes and alkynes
- write molecular and condensed structural formulas and also draw extended structural formulas for alkanes, alkenes and alkynes when given their systematic names.

i Hydrocarbons are organic compounds that are composed only of carbon and hydrogen.



FIGURE 8.2.1 Crude oil burning in a Petri dish

The simplest organic molecules are the hydrocarbons. Hydrocarbons are organic compounds that are composed only of carbon and hydrogen. Although hydrocarbons contain just these two elements, the different ways their atoms can be arranged to form molecules result in an enormous diversity of compounds.

Most hydrocarbons are produced from **crude oil**, which is also called **petroleum**. Crude oil is a liquid found in Earth's crust that has been formed over millions of years by the effects of heat and pressure on dead animals, plants and microorganisms trapped beneath sediment. Crude oil, which is shown in Figure 8.2.1, contains a complex mixture of hydrocarbons and is the source of many hydrocarbons used in industry.

Organic compounds can be grouped into several classes called **homologous series**. A homologous series is a class of molecules in which each member differs by $-CH_2-$ from the previous member. Homologous series contain members that have increasingly longer chains. Compounds that are members of the same homologous series have:

- a similar structure
- a pattern to their physical properties
- similar chemical properties
- the same general formula.

In this module, you will study three homologous series that are all hydrocarbons, the **alkanes**, alkenes and alkynes. You will examine the structure of the molecules in each series and look at the ways in which the molecules can be represented using molecular, extended structural and condensed structural formulas. You will also learn how to name the molecules in each series using a set of systematic rules.

Before exploring organic molecules further, you should revise the different ways that the formulas of molecules can be represented. The formulas used in this chapter were introduced in Units 1 and 2 and they are:

- **molecular formulas**
- **extended structural formulas**
- **condensed structural formulas**.

SATURATED HYDROCARBONS

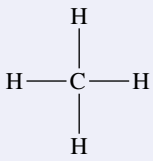
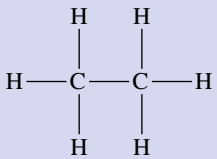
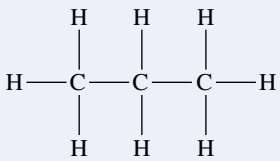
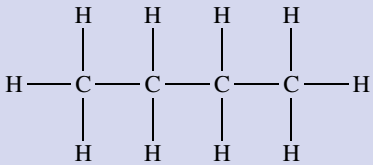
Alkanes

Alkanes are saturated hydrocarbons; they contain only single carbon–hydrogen bonds.

Methane is the simplest hydrocarbon; you were introduced to methane in Module 8.1. As shown in Table 8.2.1, methane contains one carbon atom covalently bonded with four hydrogen atoms to form a molecule with the formula CH_4. Methane is the first of the homologous series of compounds known as the alkanes. Alkanes are hydrocarbons that contain only single covalent bonds and are therefore described as being saturated. With the exception of **cycloalkanes** (which will be discussed later in the module), alkanes have the general formula C_nH_{2n+2}.

The formulas and uses of the first four members of the alkanes are shown in Table 8.2.1. You can see that successive members differ by a $-CH_2-$ unit and that each alkane follows the general formula C_nH_{2n+2}, where n represents the number of carbon atoms. Because the carbon atoms in alkanes are surrounded by four single bonds, the shape around each carbon atom is **tetrahedral**. However, to make the structures easier to interpret, the structural formulas are drawn so that the bonds are shown at right angles.

TABLE 8.2.1 Formulas and uses of the first four members of the alkanes

Name	Structural formula	Condensed structural formula	Molecular formula	Uses
methane		CH_4	CH_4	cooking, Bunsen burners, gas heating
ethane		CH_3CH_3	C_2H_6	conversion to ethene for the production of plastics
propane		$CH_3CH_2CH_3$	C_3H_8	liquid petroleum gas (LPG)
butane		$CH_3CH_2CH_2CH_3$	C_4H_{10}	fuel for cigarette lighters, aerosol propellant

Naming alkanes

The systematic naming of organic compounds is controlled by the **International Union of Pure and Applied Chemists (IUPAC)**. Under the IUPAC system, the name of the compound provides details of its structure. Learning to name the alkanes is important because the rules for naming all other organic compounds are based on the alkane names.

Naming simple alkanes

In the systematic name of simple 'straight-chain' alkanes, the **stem name** refers to the number of carbon atoms in the alkane molecule. Consider propane, which is the alkane in Table 8.2.1 with three carbon atoms. The stem name in propane (prop-) indicates there are three carbon atoms in the molecule. This same stem name is

used in other series for the compound that contains three carbon atoms in the main chain. The stem names used for molecules with between one and 10 carbon atoms are listed in Table 8.2.2.

TABLE 8.2.2 Stem names used for molecules with between one and 10 carbon atoms

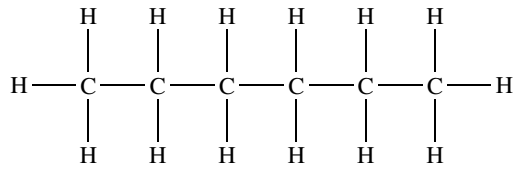
Stem name	Number of carbon atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

The names of all alkanes have the suffix (ending) '-ane' to indicate that the carbon–carbon bonds are all single bonds. Consider again the alkanes listed in Table 8.2.1. Combining the stem name and suffix, you can see that methane is an alkane that contains one carbon atom, ethane is an alkane that contains two carbon atoms, propane is an alkane that contains three carbon atoms and butane is an alkane that contains four carbon atoms.

Worked example 8.2.1

NAMING ALKANES

Represent the following alkane by its systematic name and molecular formula.

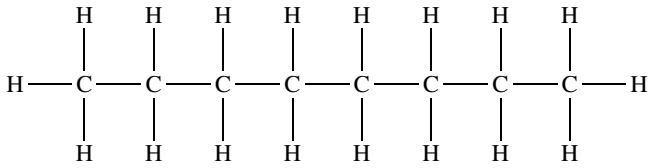


Thinking	Working
Count the number of carbon atoms in the chain to identify the stem name.	There are six carbon atoms, so the stem name will be 'hex'.
Identify the suffix name.	As the compound is an alkane, the suffix will be '-ane'.
Combine the stem name and suffix (the stem comes first).	The name of the alkane is hexane.
The general formula of an alkane is C_nH_{2n+2}, where n = number of carbon atoms. As this alkane has six carbon atoms, substitute 6 for n in the general formula.	As the alkane molecule has six carbon atoms, the number of hydrogens will be: $2n + 2 = 2 \times 6 + 2 = 14$ The molecular formula is C_6H_{14}.

➤ Try yourself 8.2.1

NAMING ALKANES

Represent the following alkane by its systematic name and molecular formula.



Naming branched alkanes

With the first three alkanes—methane, ethane and propane—there is only one way in which the carbon atoms can be arranged and that is in a straight-chain arrangement. This is shown in Figure 8.2.2.

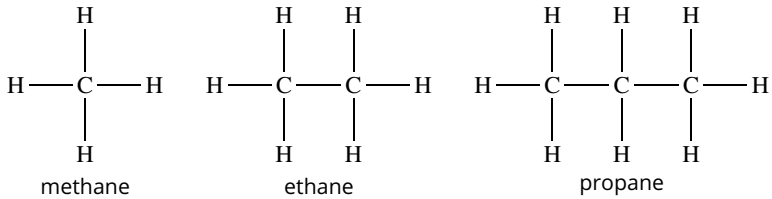


FIGURE 8.2.2 The carbon atoms in methane, ethane and propane can only be arranged in one way—a straight-chain arrangement.

However, when the number of carbon atoms in the alkane reaches four or above, then the carbon atoms can be arranged differently. Figure 8.2.3 shows two different molecules that have the molecular formula C_4H_{10}. Molecules that have the same molecular formula but different structures are known as **structural isomers**. You will learn more about structural isomers in Module 8.3.

Alkanes with four or more carbon atoms can have different arrangements. Figure 8.2.3a shows the straight-chain alkane butane, so named because the four carbon atoms are bonded in a continuous chain. Figure 8.2.3b is a branched alkane with a $–CH_3$ group attached. A $–CH_3$ group is called a methyl group, as its structure is similar to that of methane with one less hydrogen. The alkane shown in Figure 8.2.3b is named 2-methylpropane, as it can be regarded as a propane molecule with a methyl group attached to the second carbon atom in the propane chain. Note that single carbon–carbon bonds are all the same length, but sometimes longer carbon–carbon bonds are drawn for convenience, such as in the structure of 2-methylpropane shown here.

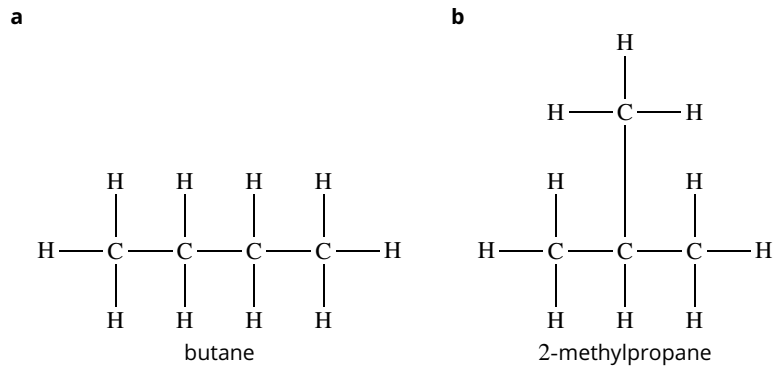


FIGURE 8.2.3 (a) Straight-chain alkane butane; (b) a branched alkane with a $–CH_3$ group attached

A methyl group is an example of an **alkyl side chain**. Alkyl side chains have one less hydrogen atom than the corresponding alkane of the same name. To name an alkyl side chain, take the name of the alkane from which the side chain is derived, drop the suffix '-ane' and add '-yl'. The names of the alkyl side chains with between one and five carbon atoms are listed in Table 8.2.3 on page 226.

TABLE 8.2.3 Names of the alkyl side chains with between one and five carbon atoms

Alkyl side chain	Corresponding alkane	Name of alkyl side chain
$-CH_3$	methane	methyl
$-CH_2CH_3$	ethane	ethyl
$-CH_2CH_2CH_3$	propane	propyl
$-CH_2(CH_2)_2CH_3$	butane	butyl
$CH_2(CH_2)_3CH_3$	pentane	pentyl

Rules for naming alkanes

It would be useful to have a short set of rules to assist us when naming any of the alkanes, no matter whether we are dealing with straight-chain or branched alkanes. Fortunately, all but the most complicated alkanes can be named using the following steps.

1 Identify the longest continuous carbon chain. This is the **parent alkane**. Carefully check which is the longest chain because sometimes it is not drawn in a straight line.
2 Number the carbon atoms in the chain from the end nearest the first branch point (so that the first alkyl side chain will have the smallest number).
3 Name the alkyl side chains after the alkane from which they are derived.
4 Place the number and position of each of the alkyl side chains before the parent alkane's name.
5 If two identical side chains are present, use 'di-' as a prefix; for three use 'tri-'. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas.
6 If there are alkyl side chains of different lengths on the molecule, list them in alphabetical order at the start of the name. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas.
7 Write the name as a single word with hyphens to separate numbers from letters and commas to separate numbers.

The following steps show the process of naming the branched alkane shown in Figure 8.2.4.

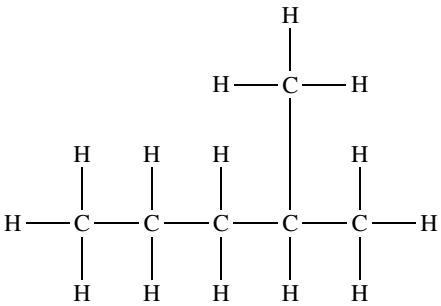
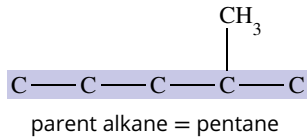
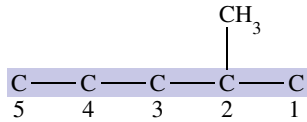


FIGURE 8.2.4 The IUPAC system will be used to name this branched alkane.

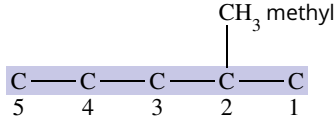
1 Identify the longest continuous carbon chain. This is the parent alkane.



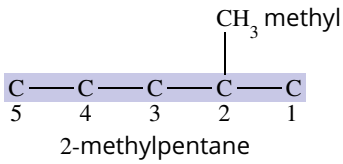
2 Number the carbon atoms from the end of the chain nearest the first branch point.



3 Name the alkyl side chains after the alkane from which they are derived.



4 Place the number and position of each of the alkyl side chains before the parent alkane's name.



2-methylpentane

Rules 5 and 6 are not required for this example.

7 Write the name as a single word with hyphens to separate numbers from letters and commas to separate numbers. The name of the compund is 2-methylpentane.

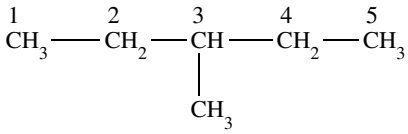
Figure 8.2.5 shows further examples of the application of these rules. There are a few important points to note about these examples.

1 Figures 8.2.5a and b show identical molecules even though their structures may appear different at first glance. This is because the longest chain in Figure 8.2.5b has not been drawn in a straight chain as it has in Figure 8.2.5a.

2 In Figure 8.2.5c, note the use of the prefix 'di-' to indicate the presence of two methyl side chains and the numbering to indicate the position of each of these side chains along the longest continuous carbon chain (the 2,2- indicates that both side chains come off the second carbon atom).

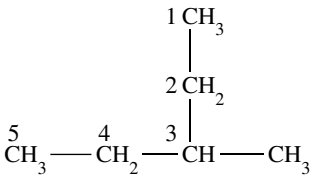
3 In Figure 8.2.5d, there are two different alkyl side chains, the methyl side chain on carbon number 2 and the ethyl side chain on carbon number 3. When two or more different side chains are present, they should be listed in alphabetical order in the name of the compound.

a



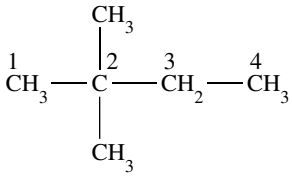
3-methylpentane

b



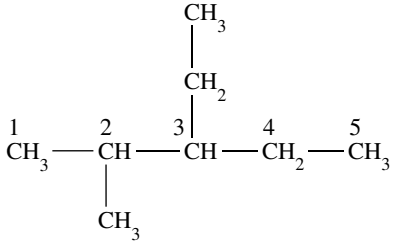
3-methylpentane

c



2, 2-dimethylbutane

d



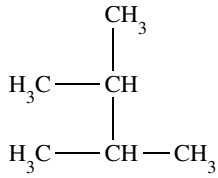
3-ethyl-2-methylpentane

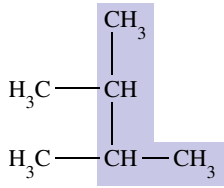
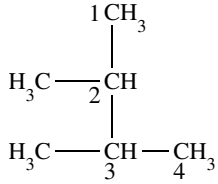
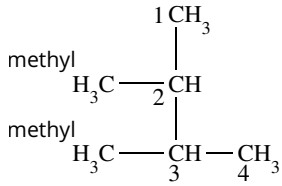
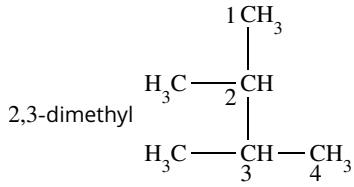
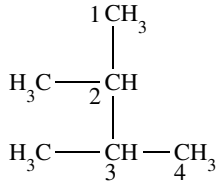
FIGURE 8.2.5 IUPAC systematic names for four alkanes. Note that there are no spaces in the names of these compounds.

Worked example 8.2.2

NAMING BRANCHED ALKANES

Analyse the following alkane and determine its systematic name.

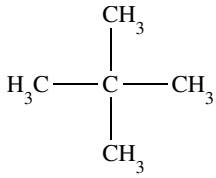


Thinking	Working
Identify the longest continuous carbon chain; this is the parent alkane. In this case, the longest continuous carbon chain is not the chain that is drawn in a straight line.	 4 carbons = butane parent alkane = butane
Number the carbon atoms from the end of the chain nearest the first branch point. Note that in this case it does not matter which end we start from; the two alkyl side chains appear on carbon numbers 2 and 3 irrespectively.	
Name the alkyl side chains after the alkane from which they are derived.	
Place the number and position of each of the alkyl side chains before the parent alkane's name. In this case, because two identical side chains are present, use 'di-' as a prefix.	
Represent the name as a single word with hyphens to separate numbers from letters and commas to separate numbers.	The name of the compound is 2,3-dimethylbutane. 

➤ Try yourself 8.2.2

NAMING BRANCHED ALKANES

Analyse the following alkane and determine its systematic name.



Cyclohexane

Cyclohexane is a hydrocarbon that is used as a solvent in paint stripper and to make other chemicals such as nylon. Figure 8.2.6 shows that the carbon atoms in the cyclohexane molecule form a ring. Molecules that form rings are known as **cyclic molecules**.

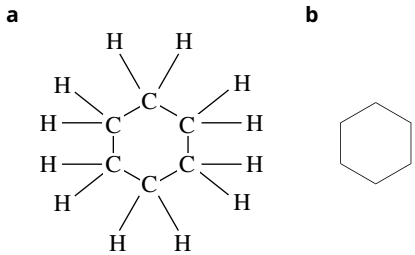


FIGURE 8.2.6 (a) The extended structural formula of cyclohexane (C_6H_{12}). (b) Cyclohexane is often represented as a line structure; in a line structure, the carbon–hydrogen bonds are not shown (they are implied).

Just like straight-chain hexane, cyclohexane is a saturated molecule that contains six carbon atoms. Because of the extra carbon–carbon bond that closes the ring structure, there are two less hydrogen atoms, making the formula of cyclohexane C_6H_{12}, whereas hexane is C_6H_{14}. Cyclohexane is a member of the cycloalkane homologous series.

UNSATURATED HYDROCARBONS

Carbon forms many compounds with hydrogen in which there are double or even triple bonds between the carbon atoms. These compounds are called unsaturated hydrocarbons. A double bond is formed when two pairs of electrons are shared and a triple bond is formed when three pairs of electrons are shared. Some of the most useful carbon compounds are unsaturated. This module focuses on the structures and naming of hydrocarbon compounds with carbon–carbon double bonds and triple bonds.

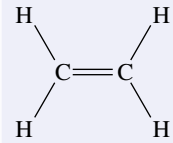
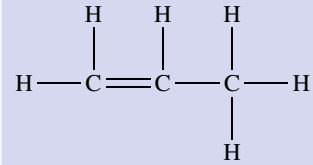
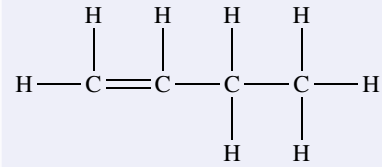
Alkenes

Alkenes are a homologous series of hydrocarbons with at least one carbon–carbon double bond. The carbon–carbon double bond is a functional group that gives alkenes their chemical properties and makes them much more reactive than alkanes. Alkenes with one carbon–carbon double bond have the general formula C_nH_{2n}.

The formulas and uses of the first three members of the homologous series of alkenes are shown in Table 8.2.4 on page 230. You can see that successive members differ by a $-CH_2-$ unit and that each alkene follows the general formula C_nH_{2n}, where n represents the number of carbon atoms. The shape around each carbon atom in the double bond is trigonal planar; however, to make the structures easier to interpret, the structural formulas are often drawn so that the bonds are shown at right angles.

i Alkenes are unsaturated hydrocarbons that contain at least one carbon–carbon double bond.

TABLE 8.2.4 Formulas of the first three members of the alkene homologous series

Name	Molecular formula	Extended structural formula	Condensed structural formula	Uses
ethene	C_2H_4		$CH_2{=}CH_2$	in the manufacture of a wide range of chemicals
propene	C_3H_6		$CH_2{=}CHCH_3$	in the manufacture of propene oxide and polymers
but-1-ene	C_4H_8		$CH_2{=}CHCH_2CH_3$	in the manufacture of butanol and polymers

Naming alkenes

The rules for naming alkenes follow the same general rules used for naming alkanes. However, there are a few differences, which are outlined below.

- Use '-ene' as the suffix for the parent name.
- Number the carbon atoms from the end of the chain closest to the double bond.
- Specify the position of the double bond by the number of the lowest-numbered carbon atom in the double bond.
- Insert the number into the name immediately before '-ene'.

The following steps show the process of naming the alkene in Figure 8.2.7.

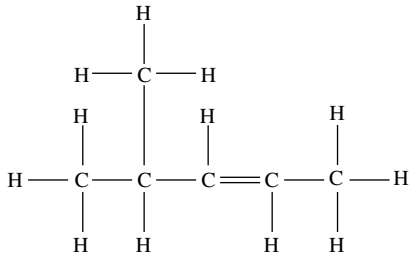
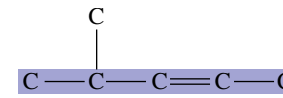


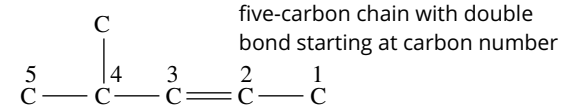
FIGURE 8.2.7 The IUPAC system will be used to name this alkene.

1 Identify the longest continuous carbon chain that contains the double bond. The name of the molecule is based on this chain.



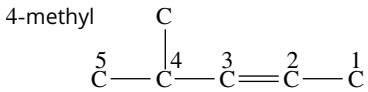
- It is a five-carbon chain so the name of the molecule is based on pentene.

2 Number the carbons, starting from the end closest to the double bond. Note the position of the double bond.



- It is a five-carbon chain with the double bond starting at carbon number 2. The parent name is therefore pent-2-ene.

3 Name each alkyl side chain and identify the number of the carbon atom in the main chain that each is attached to.



- There is a methyl group on carbon number 4. It will be named as 4-methyl.

4 If two identical side chains are present, use 'di-' as a prefix; for three use 'tri-'. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas (not required for this example).

5 If there are alkyl side chains of different lengths on the molecule, list them in alphabetical order at the start of the name. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas (not required for this example).

6 Combine all components to write the full name. Write the name as a single word with hyphens to separate numbers from letters and commas to separate numbers.

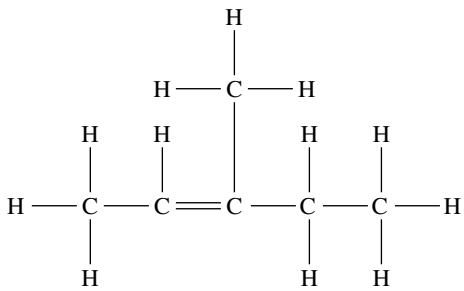
- The name of the molecule is 4-methylpent-2-ene.

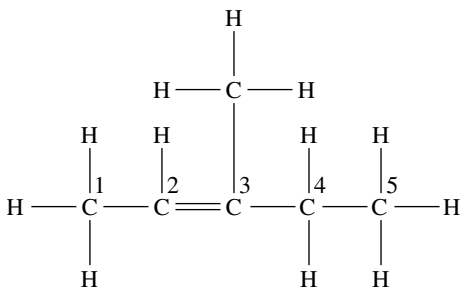
Worked example 8.2.3



IUPAC NAMING SYSTEM FOR ALKENES

Analyse the following molecule and determine its systematic name.

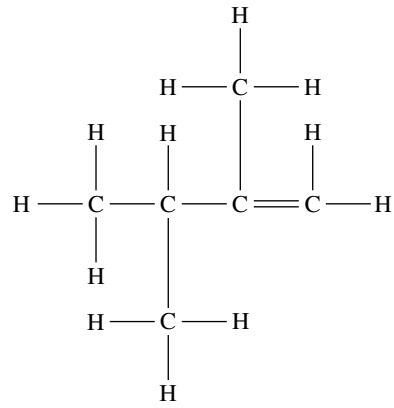


Thinking	Working
Identify the longest continuous carbon chain in the molecule that contains the double bond. The name of the molecule is based on this longest chain.	There are five carbon atoms in the longest chain. The name is based on pentene.
Number the carbon atoms starting from the end closest to the double bond. Note the position of the double bond.	 There is a double bond on carbon number 2, so the longest chain is pent-2-ene (this is the parent name).
Determine the name of each alkyl side chain and identify the carbon atom in the main chain that each is attached to. In this case, there is only one alkyl side chain.	The side chain is a methyl group and it is on carbon number 3. It will therefore be named as 3-methyl.
Combine all components to write the full name. Write the name as a single word with hyphens to separate numbers from letters and commas to separate numbers.	The systematic name of the molecule is 3-methylpent-2-ene.

➤ Try yourself 8.2.3

IUPAC NAMING SYSTEM FOR ALKENES

Analyse the following molecule and determine its systematic name.

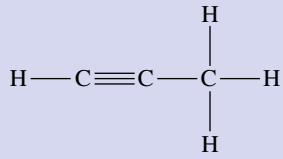
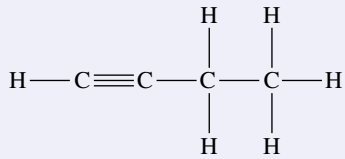


Alkynes

Alkynes are a homologous series of hydrocarbons with at least one carbon–carbon triple bond. The triple bond is a functional group that gives alkynes their chemical properties; just like the alkenes, alkynes are more reactive than alkanes because of their functional group. The general formula for alkynes with one triple bond is C_nH_{2n-2} and the presence of the triple bond means the alkynes are described as being unsaturated. The shape around each of the carbon atoms in the triple bond is linear.

The formulas and uses of the first three members of the homologous series of alkynes are shown in Table 8.2.5. You can see that successive members differ by a $-CH_2-$ unit and that each alkyne follows the general formula C_nH_{2n-2}, where n represents the number of carbon atoms.

TABLE 8.2.5 Formulas and uses of the first three members of the alkyne homologous series

Name	Molecular formula	Structural formula	Condensed structural formula	Uses
ethyne	C_2H_2		$CH{\equiv}CH$	welding: an oxy-acetylene (ethyne is also known as acetylene) flame has a temperature of about 3000°C
propyne	C_3H_4		$CH{\equiv}CCH_3$	possible rocket fuel
but-1-yne	C_4H_6		$CH{\equiv}CCH_2CH_3$	as a reactant in the synthesis of other organic compounds

Naming alkynes

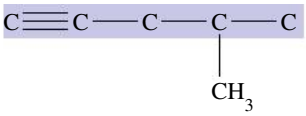
Like the alkenes, the rules for naming alkynes follow the same general rules used for alkanes. However, there are a few differences which are outlined below.

- Use the ending '-yne' as the suffix for the parent name.
- Number the carbon atoms from the end of the chain closest to the triple bond.
- Specify the position of the triple bond by the number of the lowest-numbered carbon atom in the triple bond.
- Insert the number into the name immediately before '-yne'.

i Alkynes are unsaturated hydrocarbons that contain at least one carbon–carbon triple bond.

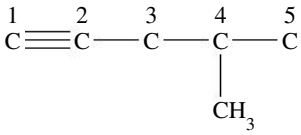
The following steps show the process of naming the alkyne shown in Figure 8.2.8.

1 Identify the longest continuous carbon chain that contains the triple bond. The name of the molecule is based on this chain.



- It is a five-carbon chain so the name of the molecule is based on pentyne.

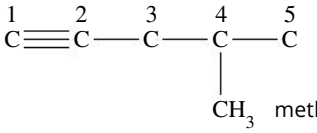
2 Number the carbons, starting from the end closest to the triple bond. Note the position of the triple bond.



five-carbon chain with triple bond on carbon number 1

- It is a five-carbon chain with the triple bond starting at carbon number 1. The parent name is therefore pent-1-yne.

3 Name each alkyl side chain and identify the number of the carbon atom in the main chain that each is attached to.



methyl group on carbon number 4
4-methyl

- There is a methyl group on carbon number 4. It will be named 4-methyl.

4 If two identical side chains are present, use 'di-' as a prefix; for three use 'tri-'. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas (not required for this example).

5 If there are alkyl side chains of different lengths on the molecule, list them in alphabetical order at the start of the name. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas (not required for this example).

6 Combine all components to write the full name. Write the name as a single word with hyphens to separate numbers from letters and commas to separate numbers.

- The name of the molecule is 4-methylpent-1-yne.

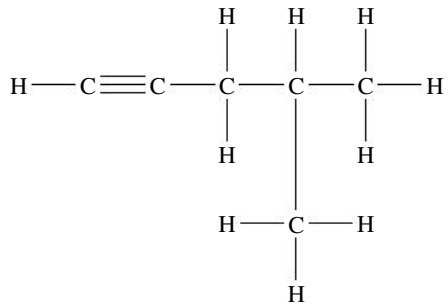


FIGURE 8.2.8 The IUPAC system will be used to name this alkyne.

Benzene

In 1825, Michael Faraday isolated a new hydrocarbon named **benzene** (C_6H_6). The structure of benzene puzzled scientists for 40 years. August Kekulé made a major contribution towards solving the puzzle in 1865. He proposed a ring structure in which six carbons were joined by alternating double and single bonds, as shown in Figure 8.2.9a.

It is now known that benzene does not have alternating double and single bonds. Single and double bonds have different bond lengths, but all the carbon–carbon bond lengths in benzene are identical and are between that of a single and double bond. The electrons that make up the double bonds are not in fixed positions; as shown in Figure 8.2.9b, they are **delocalised** and can move around the ring. Benzene is more stable (and therefore less reactive) than would be expected of an unsaturated molecule because its delocalised electrons are not as available to take part in reactions.

Due to the shared nature of the **delocalised electrons**, it is more correct to describe each carbon as having one and a half bonds to each neighbour. For this reason, the bonds are often represented as a ring of normal single bonds with a circle inside the ring, as shown in Figure 8.2.9c.

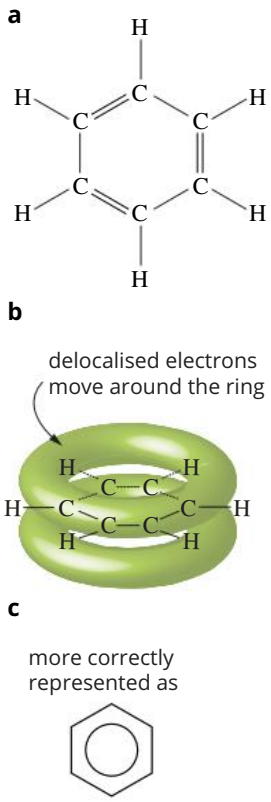


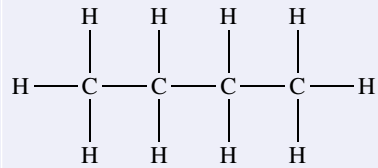
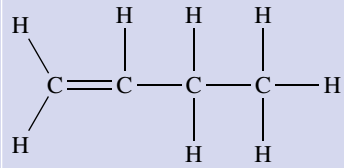
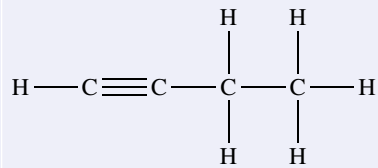
FIGURE 8.2.9 Representations of benzene's (C_6H_6) molecular structure showing (a) a representation with alternating double and single bonds, (b) the delocalised electrons in green, (c) the delocalised electrons represented as a circle inside the hexagon of carbon atoms. Note that this is a line structure of benzene; in a line structure, carbon–hydrogen bonds are not shown.

8.2 Review

SUMMARY

- Hydrocarbons are compounds containing carbon and hydrogen only.
- In a homologous series, each member has one more $–CH_2–$ unit than the previous member. Members of a homologous series have similar structures and chemical properties and have the same general formula.
- Alkanes are the simplest hydrocarbons. They are saturated hydrocarbon molecules because they only contain single covalent bonds.
- Alkanes have the general formula C_nH_{2n+2}.
- Alkanes have a tetrahedral shape around each carbon atom.
- Cyclohexane is a saturated cyclic hydrocarbon with the molecular formula C_6H_{12}.
- Unsaturated hydrocarbons are hydrocarbons that contain at least one carbon–carbon double or triple bond.
- Alkenes are a homologous series of hydrocarbons that contain at least one carbon–carbon double bond.
- Alkenes have the general formula C_nH_{2n}.
- Alkenes have a trigonal planar shape around each carbon atom in the double bond.
- Alkynes are a homologous series of hydrocarbons that contain at least one carbon–carbon triple bond.
- Alkynes have the general formula C_nH_{2n-2}.
- Alkynes have a linear shape around each carbon atom in the triple bond.
- Benzene is an unsaturated cyclic hydrocarbon that has the formula C_6H_6.
- The electrons that make up the double bond in benzene are delocalised and are shared across the six carbon atoms.
- Table 8.2.6 provides a summary of the main classes of hydrocarbons and the functional groups that each class contains.

TABLE 8.2.6 A summary of the main classes of hydrocarbons

Class	General formula	Functional group	Example
alkanes	C_nH_{2n+2}	none	 butane
alkenes	C_nH_{2n}	double bond	 but-1-ene
alkynes	C_nH_{2n-2}	triple bond	 but-1-yne

- The IUPAC naming system is used to provide systematic names for hydrocarbon molecules. The following conventions are used for naming hydrocarbons.
  - There are no spaces in a name.
  - The longest carbon chain is used to derive the parent name. The longest chain must include the double or triple bond for alkenes and alkynes.
  - Suffixes are used in the parent name to indicate whether the hydrocarbon is an alkane, alkene or alkyne; '-ane' is used for alkanes, '-ene' for alkenes and '-yne' for alkynes.
  - Numbers are used in the parent name to identify carbon atoms that contain double or triple bonds. The names and locations of alkyl side chains are added to this parent name.
  - If there is more than one type of alkyl side chain to be listed at the beginning of a name, they are listed in alphabetical order.
  - If there is more than one of the same type of alkyl side chain, the prefixes 'di-' or 'tri-' are used.
  - Numbers and letters are separated by dashes.
  - Numbers are separated from other numbers by commas.

KEY QUESTIONS

Retrieval

1 State the general formula for:
- **a** an alkane
- **b** a cycloalkane
- **c** an alkene
- **d** an alkyne.

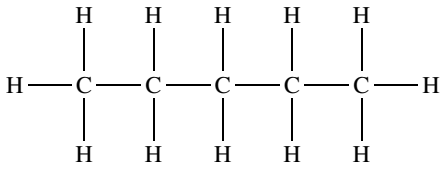
2 Define the following terms.
- **a** alkane
- **b** alkene
- **c** alkyne

3 The molecular formulas for three hydrocarbons are given below. Identify whether each is an alkane, an alkene or an alkyne.
- **a** C_4H_8
- **b** C_6H_{14}
- **c** C_2H_2

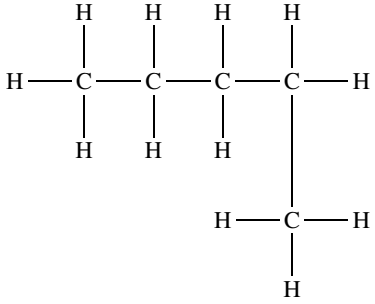
Comprehension

4 Use the systematic naming rules to determine the names of the following alkanes.

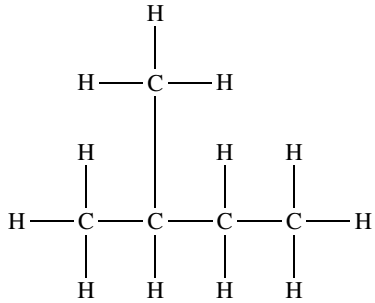
a



b



c



5 The following relates to the hydrocarbon with the molecular formula C_3H_8.
- **a** Draw the extended structural formula of this hydrocarbon.
- **b** Determine the name of this hydrocarbon.
- **c** Represent the hydrocarbon with its condensed structural formula.

Analysis

6 Categorise the following alkenes in order from lowest to highest number of carbon atoms:

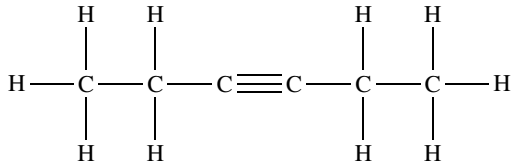
pent-1-ene, ethene, non-1-ene, oct-1-ene, prop-1-ene

continued over page

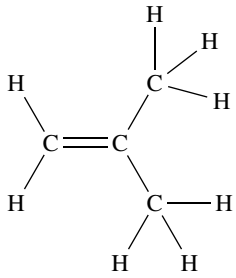
8.2 Review *continued*

7 Determine the systematic names of the unsaturated hydrocarbons shown below.

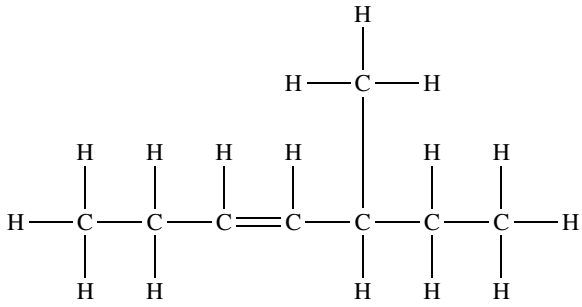
a



b



c



8 Analyse the names of the following alkanes. Show the extended structural formula and determine the condensed structural formula for each one.

a 2,4-dimethylpentane

b 2,2-dimethylhexane

c 4-ethyl-2-methylhexane

9 Analyse the following alkane names. Determine why they are incorrect and provide the correct name.

a 3-methylbutane

b 2-ethylpropane

c 1-methylpentane

10 Analyse the names of the following unsaturated hydrocarbons. Show the extended structural formula and determine the condensed structural formula for each one.

a 2,3-dimethylpent-2-ene

b 2,2-dimethyloct-3-yne

c 3-ethyl-2-methylhex-1-ene

8.3 Isomerism

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- define isomers and know that the two main types are structural isomers and stereoisomers
- know that isomers can have different properties
- define structural isomers and know that the two main types are chain isomers and positional isomers
- identify structural isomers from structural formulas (either extended or condensed)
- represent structural isomers when given either the molecular formula or the structural formula of another isomer
- define stereoisomers and know that geometric isomers are a type of stereoisomer
- define geometric isomers and know that they are also called *cis-trans* isomers
- understand that geometric isomers can occur when there is restricted rotation of bonds in a molecule
- identify molecules in which *cis-trans* isomers are possible
- represent structural formula for *cis-trans* isomers
- apply systematic naming rules to name structural and geometric isomers.



Isomers are molecules that have the same molecular formula (so contain the same number and type of atoms) but a different arrangement of atoms. The existence of isomers is a major reason why there are so many different organic compounds.

There are two main types of isomers:

- structural isomers
- stereoisomers.

STRUCTURAL ISOMERS

Structural isomers are molecules that have the same molecular formula but a different order of attachment of atoms. In other words, the atoms bond together in different arrangements giving the molecules different structures. Structural isomers can have very different chemical and physical properties. Two types of structural isomers are **chain isomers** and **positional isomers**.

Chain isomers

Chain isomers are a consequence of the branching that is possible in carbon chains. You saw an example of chain isomerism in Module 8.2 with the alkanes butane and 2-methylpropane. These molecules are shown again in Figure 8.3.1 on page 238. You can see that butane and 2-methylpropane both have the molecular formula C_4H_{10} but butane is a straight chain, whereas 2-methylpropane is branched.

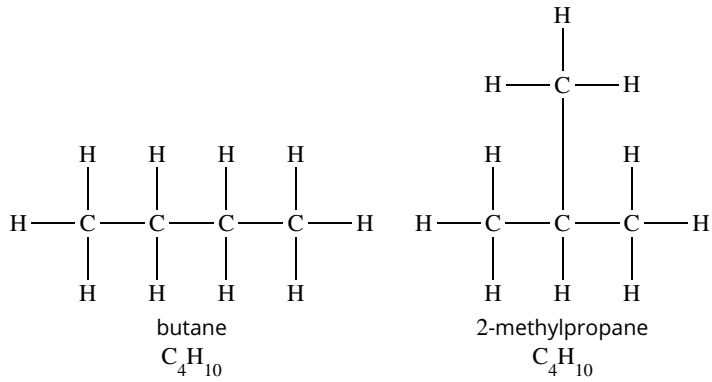


FIGURE 8.3.1 The two chain isomers for an alkane with the molecular formula C_4H_{10}

The more atoms there are in the molecule, the more structural isomers are possible. For example, there are five isomers possible for the alkane with the molecular formula C_6H_{14}. These isomers are shown in Figure 8.3.2. You can see that each isomer has a different name: hexane is the straight-chain alkane, whereas 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane and 2,3-dimethylbutane are branched.

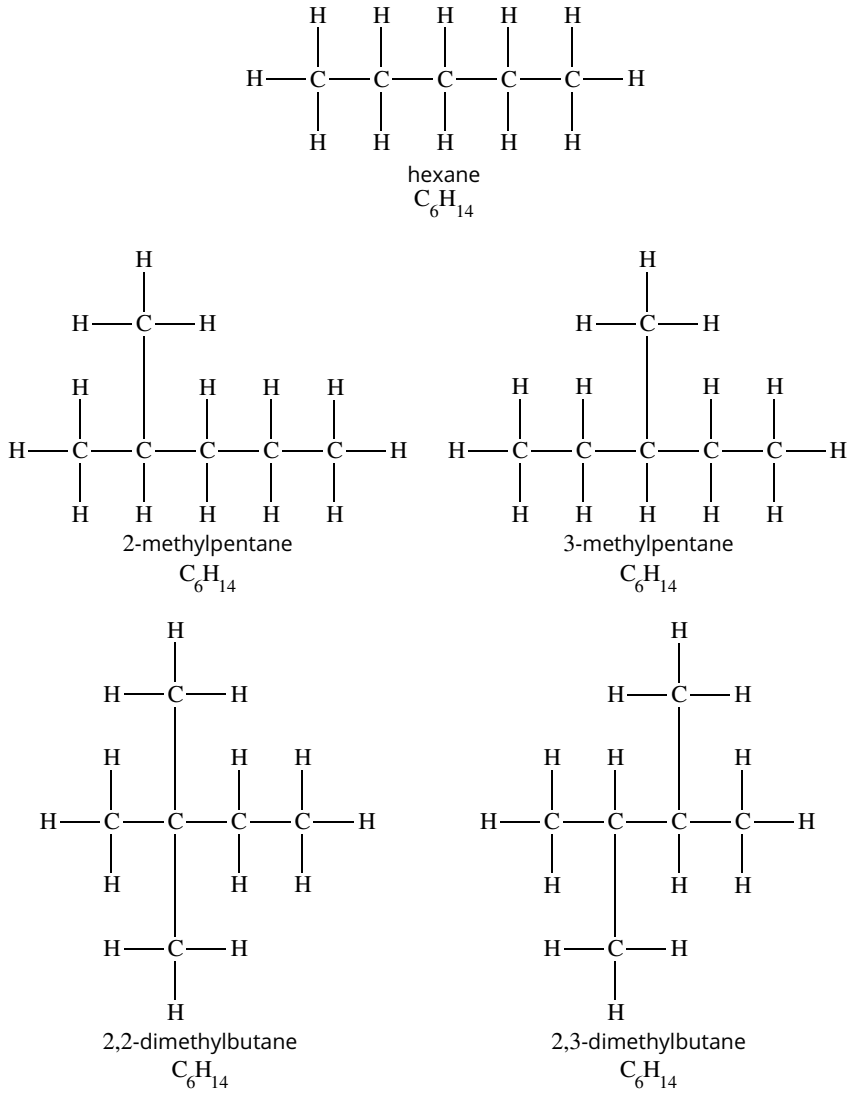


FIGURE 8.3.2 The five-chain isomers for an alkane with the molecular formula C_6H_{14}

As the carbon chain length increases, the number of structural isomers increases rapidly. Table 8.3.1 shows the number of chain isomers possible for a series of alkanes with an increasing number of carbon atoms.

TABLE 8.3.1 The number of chain isomers possible for a series of alkanes

Carbon atoms	Molecular formula	Number of chain isomers
1	CH_4	0
2	C_2H_6	0
3	C_3H_8	0
4	C_4H_{10}	2
5	C_5H_{12}	3
6	C_6H_{14}	5
7	C_7H_{16}	9
8	C_8H_{18}	18
9	C_9H_{20}	35
10	$C_{10}H_{22}$	75
15	$C_{15}H_{32}$	4347
20	$C_{20}H_{42}$	366 319
25	$C_{25}H_{52}$	>30 million!
30	$C_{30}H_{62}$	>4 billion!

Positional isomers

Positional isomers can occur for organic molecules that contain functional groups. Positional isomers are molecules with the same carbon chain and functional group but with the functional group attached at different locations in the molecule.

In Module 8.2 you learnt that alkenes are hydrocarbons that contain a carbon–carbon double bond and that the double bond is a functional group. Alkenes can have positional isomers where the double bond is attached to different carbon atoms in the molecule. For example, as shown in Figure 8.3.3, three positional isomers can be drawn for an alkene with the molecular formula C_6H_{12}. Like chain isomers, each positional isomer has a different name.

Figure 8.3.4 shows the two positional isomers of an alcohol with the molecular formula $C_4H_{10}O$. You will remember from Module 8.1 that alcohols are organic molecules that contain a hydroxyl (–OH) functional group. You will learn more about alcohols in Module 8.4.

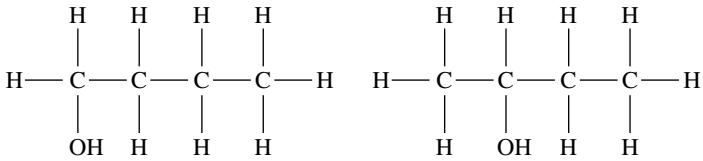


FIGURE 8.3.4 The two positional isomers for an alcohol with the molecular formula $C_4H_{10}O$

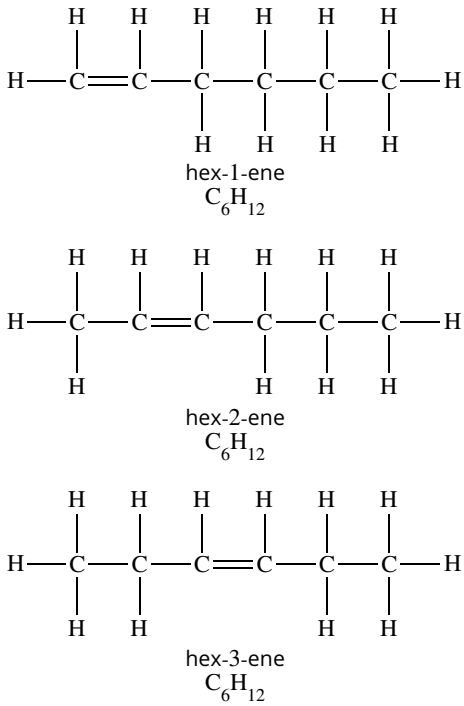


FIGURE 8.3.3 The three positional isomers possible for an alkene with the molecular formula C_6H_{12}

Positional isomers only exist for molecules that contain a functional group and have a long enough carbon chain so that different positions for the functional group are possible. When drawing positional isomers, be careful that you do not just draw the same molecule from a different perspective. You can see that the two structural formulas for an alkene with the molecular formula C_3H_6 in Figure 8.3.5 on page 240 do not represent positional isomers; if the first structure is flipped over, it is identical to the second. A good check to confirm whether two molecules are identical or whether they are isomers of each other is to name them. Using the naming conventions from Module 8.2, both of these alkenes are named 'prop-1-ene', which confirms that they

are identical. Interestingly, because prop-1-ene is the only positional isomer with the formula C_3H_6, it is often named just 'propene' because the double bond can only be between the first and second carbon atoms.

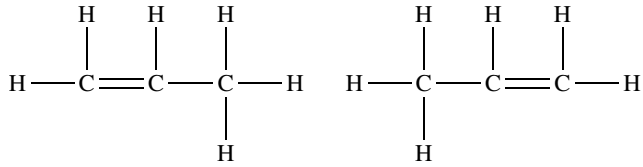


FIGURE 8.3.5 Two representations of the structure of prop-1-ene. These are not positional isomers; they are identical molecules.

It is possible for structural isomers to form both positional and chain isomers. Figure 8.3.6 shows two isomers of an alcohol with the molecular formula $C_4H_{10}O$. They are chain isomers of the molecules shown previously in Figure 8.3.4, and positional isomers of each other.

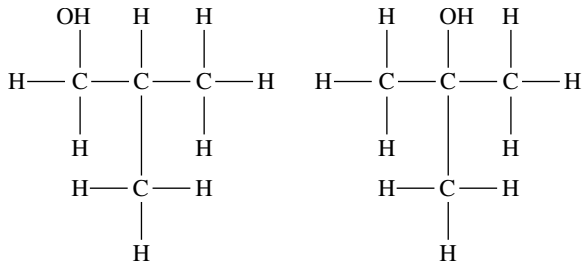


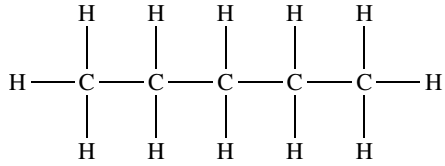
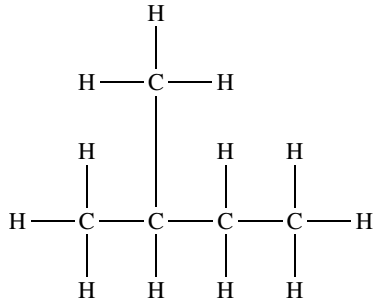
FIGURE 8.3.6 Two molecules that are alcohols with the molecular formula $C_4H_{10}O$

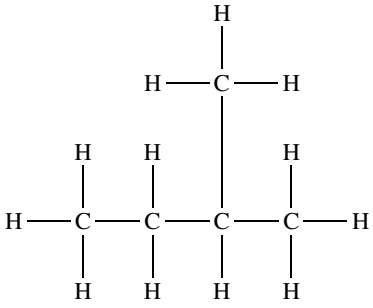
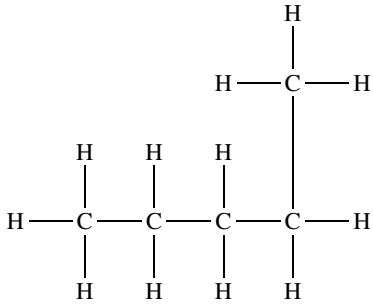
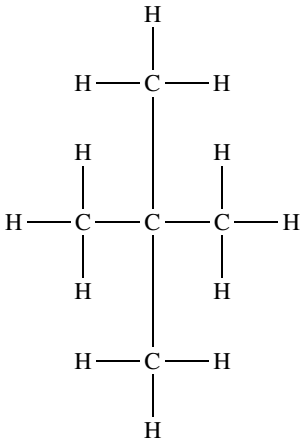
Structural isomers are molecules that have the same molecular formula but a different order of attachment of atoms. Structural isomers can have very different chemical and physical properties. Chain isomers and positional isomers are types of structural isomers.

Worked example 8.3.1

DRAWING STRUCTURAL ISOMERS

Determine the structural formulas for the three alkanes with the molecular formula C_5H_{12}.

Thinking	Working
Alkanes do not contain a functional group so the structural isomers will all be chain isomers. Identify the straight-chain molecule; draw and name it. This is the first alkane.	There are five carbon atoms in the chain. The name of this alkane is 'pentane'.  pentane
Determine the structural formula of the second alkane by drawing the main chain again, but this time with one less carbon atom. The parent alkane will now have four carbon atoms and will be based on a butane molecule. Next add a methyl group to as many positions in the main chain as possible so that you obtain different structures. Name the structures.	The methyl group can be added to carbon number 2 to make 2-methylbutane. This is the only structural isomer possible based on a butane molecule.  2-methylbutane

It is important to name each of the structures you draw to ensure that you do not draw the same molecule twice.	These structures below might seem different because you have added the methyl group to carbon numbers 3 and 4 in the chain respectively. However, when you name them, you can see that they are actually the molecules pentane and 2-methylbutane, which you have already drawn. Therefore, these are NOT new isomers.  2-methylbutane  pentane
Represent the structural formula of the third alkane by drawing the main chain with one less carbon again. The parent alkane will now have three carbon atoms and will be based on a propane molecule. Next, add two methyl groups to as many positions in the main chain as possible so that you obtain different structures. Name the structures.	The two methyl groups can be added to carbon number 2 to make 2,2-dimethylpropane. There are no more structural isomers possible based on the propane molecule.  2,2-dimethylpropane

➤ Try yourself 8.3.1

DRAWING STRUCTURAL ISOMERS

Determine the structural formulas for the three structural isomers of the alkene with the molecular formula C_4H_8.

STEREOISOMERS

Stereoisomers are isomers in which the atoms in two molecules are connected in the same order (so they have the same structure) but have different arrangements in space. It is because stereoisomers differ in their three-dimensional space that the name of this type of isomer begins with the stem 'stereo-'. Molecules that are stereoisomers can have very different chemical and physical properties.

There are two types of stereoisomers, **optical isomers** and **geometric isomers**. This module will only focus on geometric isomers.

Geometric isomers

Geometric isomers are also called ***cis-trans* isomers** and can occur when there is restricted rotation somewhere in a molecule. Restricted rotation can occur about a carbon–carbon double bond or a ring.

Cis-trans isomers of alkenes occur because the atoms associated with the carbon–carbon double bond are fixed in position.

Two atoms joined by a single bond can rotate freely around the single bond. You might think that the two models shown in Figure 8.3.7 show different molecules, but they are representations of the same molecule because there is free rotation around the single bond. The first structure can rotate around the central single bond to look exactly the same as the second.

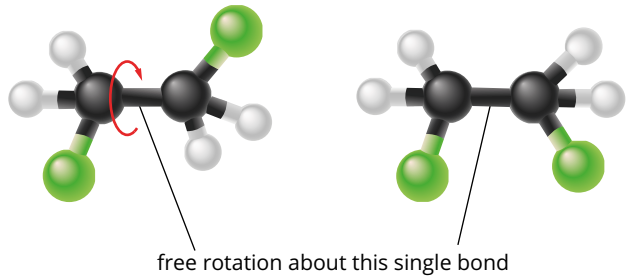


FIGURE 8.3.7 These two models represent the same molecule because the groups on either end can rotate around the single bond.

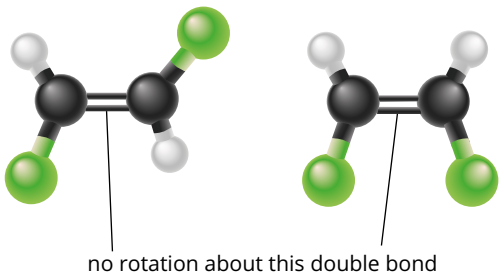


FIGURE 8.3.8 These two models represent different molecules because the groups on either end cannot rotate around the double bond.

However, because of the way that the electrons are arranged in a double bond, groups attached to the carbons on either side of the double bond are unable to rotate freely. The models in Figure 8.3.8 represent two molecules that cannot be rotated to form the same structure because a double bond is present.

Cis-trans isomers only occur when each carbon atom in the double bond is attached to two different groups, as shown in Figure 8.3.9 (if even just one of the carbon atoms in the double bond is attached to two groups that are identical then *cis-trans* isomerism cannot occur).

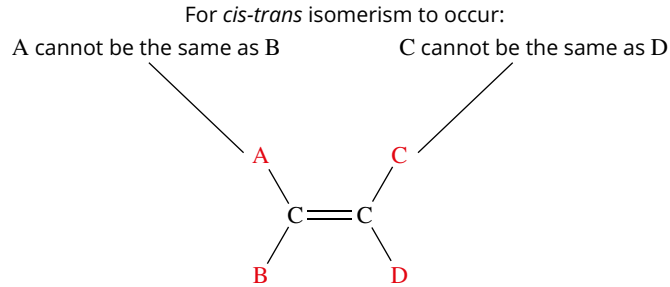


FIGURE 8.3.9 For *cis-trans* isomerism to occur, each carbon atom in the double bond must be attached to two different groups.

The different groups can be hydrogen atoms, functional groups or hydrocarbon chains of different lengths. There are two possible arrangements: the functional groups or hydrocarbon chains can be on the same side or opposite sides of the double bond. If they are on the same side, the isomer is called the ***cis*-isomer**. If they are on opposite sides, the isomer is called the ***trans*-isomer**.

Figure 8.3.10 shows the three possible structures of dibromoethene ($C_2H_2Br_2$). If both bromine atoms are attached to the first carbon atom, then it is called 1,1-dibromoethene. This molecule does not have geometric isomers because the two groups attached to each carbon atom in the double bond are identical. If the bromine atoms are attached to different carbon atoms, then it is called 1,2-dibromoethene, and has the condensed structural formula BrCH=CHBr. There are two geometric isomers possible: *cis*-1,2-dibromoethene and *trans*-1,2-dibromoethene.

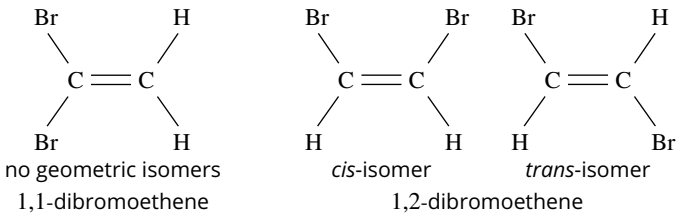


FIGURE 8.3.10 The possible structures of dibromoethene ($C_2H_2Br_2$). Note the position of the bromine atoms in the *cis*- and *trans*-isomers.

When considering longer alkenes, it is the longest alkyl groups attached to the carbon atoms in the double bond that are used to decide if the molecule is a *cis*- or *trans*-isomer.

- In *cis*-isomers, the longest alkyl groups on each carbon are located on the same side of the double bond.
- In *trans*-isomers, the longest alkyl groups on each carbon are located on opposite sides of the double bond.

Figure 8.3.11 shows the *cis*- and *trans*-isomers of but-2-ene. The two methyl groups are on the same side of the double bond in the *cis*-isomer. The methyl groups are opposite each other in the *trans*-isomer.

> **Stereoisomers** are isomers in which the atoms in two molecules are connected in the same order but have different arrangements in space. Stereoisomers can have very different chemical and physical properties. Geometric isomers are a type of stereoisomer; they are also called *cis-trans* isomers and occur when atoms are prevented from rotating around a bond, such as a carbon–carbon double bond in an alkene.

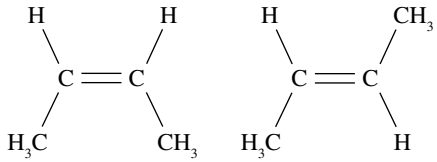
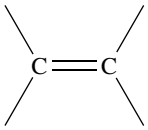
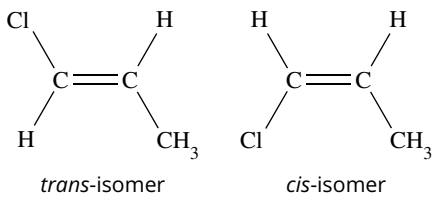


FIGURE 8.3.11 The two geometric isomers of but-2-ene

Worked example 8.3.2

DRAWING GEOMETRIC ISOMERS

Determine the *cis*- and *trans*-isomers of 1-chloroprop-1-ene.	
Thinking	**Working**
State the condensed structural formula of the molecule.	$ClHC{=}CHCH_3$
Draw the structural formula of the carbon skeleton around the double bond showing the trigonal planar shape.	
Analyse the condensed structural formula to identify the groups that are attached to each side of the double bond.	There is a hydrogen atom and a chlorine atom attached to the left-hand carbon in the double bond. There is a hydrogen atom and a methyl (CH_3) group attached to the right-hand carbon in the double bond.
In the *trans*-isomer, the chlorine and methyl groups will be located on opposite sides of the double bond. In the *cis*-isomer, the chlorine and methyl groups will be located on the same side of the double bond.	 *trans*-isomer *cis*-isomer

➤ Try yourself 8.3.2

DRAWING GEOMETRIC ISOMERS

Determine the *cis*- and *trans*-isomers of pent-2-ene.

8.3 Review

SUMMARY

- Isomers are molecules that have the same molecular formula but their atoms are arranged in different ways.
- Structural isomers are molecules that have the same molecular formula but a different connectivity of atoms (i.e. they have a different structure).
- Chain isomers are structural isomers that differ in their branching on the main carbon chain.
- Positional isomers are structural isomers that contain functional groups in different positions on the carbon chain.
- Stereoisomers are molecules that have the same molecular formula, the same connectivity of atoms, but a different arrangement of those atoms in space.
- Geometric isomers are stereoisomers that can occur where there is restricted rotation somewhere in a molecule. Restricted rotation can occur about a carbon–carbon double bond or a ring.
- Geometric isomers are also called *cis-* and *trans-* isomers. *Cis-trans* isomerism can occur in alkenes when there are two different groups attached to each carbon atom involved in the double bond.
- Figure 8.3.12 gives a summary of the different types of isomers.

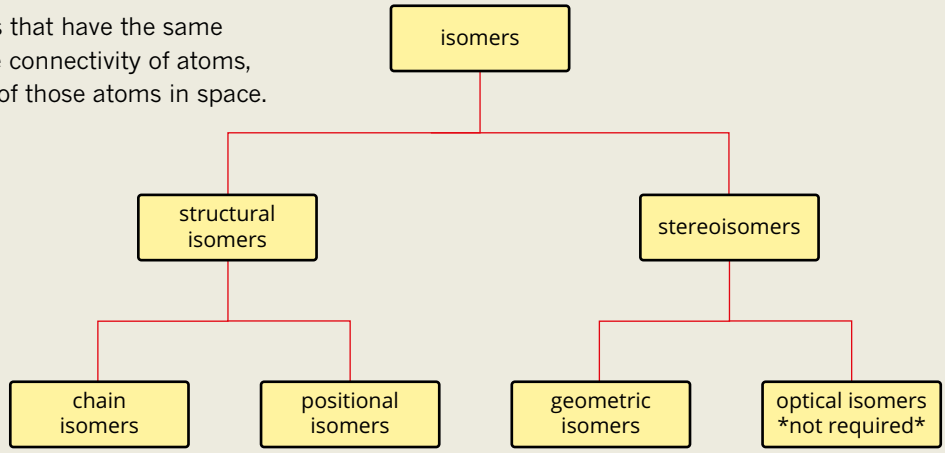


FIGURE 8.3.12 Isomers can be classified into two main groups: structural isomers and stereoisomers.

KEY QUESTIONS

Retrieval

1 Define isomers.

2 **a** State the two different types of structural isomers.
b State the two different types of stereoisomers.

Comprehension

3 Explain the difference between chain isomers and positional isomers.

4 Explain why geometric isomers occur in alkenes but not in alkanes.

Analysis

5 There are four structural isomers with the molecular formula $C_3H_6Br_2$. Determine the structural formulas for these isomers. (Hint: the isomers will all be positional isomers.)

6 Determine and name the five structural isomers of the alkanes with the molecular formula C_6H_{14}. (Hint: the isomers will all be chain isomers.)

7 Analyse the following condensed structural formulas of two different organic compounds.

$H_2C{=}CHCH_3$ prop-1-ene $H_3CHC{=}CHBr$ 1-bromoprop-1-ene

a Determine which molecule shows *cis-trans* isomerism.
b Draw the *cis-* and *trans-*isomers for this molecule.
c Explain why the other molecule cannot show *cis-trans* isomerism.

8 Determine why the name *cis*-hex-1-ene is incorrect.

9 **a** Determine the smallest chain length that any organic molecule could have and still show *cis-trans* isomerism.
b Determine the smallest chain length that a hydrocarbon molecule could have and still show *cis-trans* isomerism.

8.4 Hydrocarbon derivatives

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- recall that organic compounds are organised into classes or homologous series based on their functional groups
- identify the functional groups present in alcohols, aldehydes, ketones, carboxylic acids, esters, amines and amides
- deduce the structural formulas and apply IUPAC rules in the nomenclature of organic compounds with simple branching for alcohols, aldehydes, ketones, carboxylic acids, esters, amines and amides.



In Module 8.2 you studied the three classes of hydrocarbons, namely the alkanes, alkenes and alkynes, and learnt that the double bond in alkenes and the triple bond in alkynes are considered to be functional groups because they are responsible for the properties of the compounds in each class.

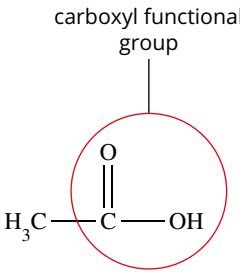
However, as discussed in Module 8.1, there are organic compounds that are not hydrocarbons as they contain other elements in addition to carbon and hydrogen. These compounds are known as hydrocarbon derivatives. Hydrocarbon derivatives have a hydrocarbon skeleton but contain functional groups in which one or more of the hydrogen atoms in the hydrocarbon skeleton have been replaced with other atoms or groups of atoms.

In this module, you will examine the functional groups that make up each class of the hydrocarbon derivatives and use systematic naming rules to name some of the compounds in these classes.

FUNCTIONAL GROUPS AND CLASSES OF HYDROCARBON DERIVATIVES

The presence of a particular functional group in a molecule gives a substance certain physical and chemical properties. For example, vinegar and wine both contain organic molecules based on ethane. The difference between their tastes and other properties is due to the different functional groups in each molecule. Vinegar contains ethanoic acid which has a carboxyl functional group and wine contains ethanol which has a hydroxyl functional group. This can be seen in Figure 8.4.1.







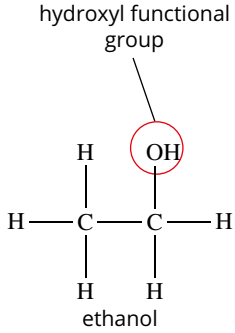
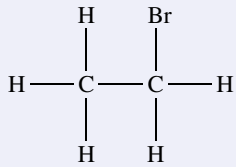
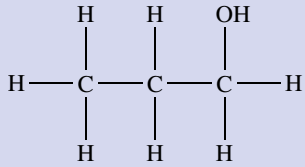
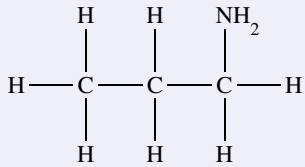
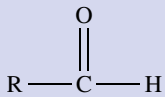
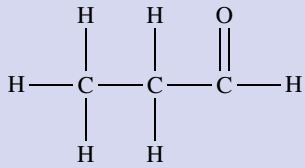
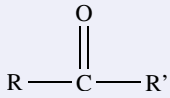
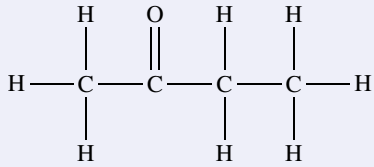
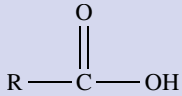
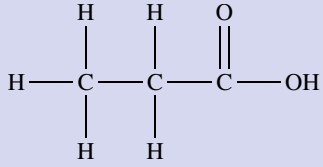


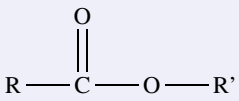
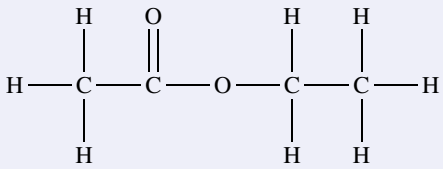
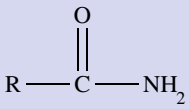
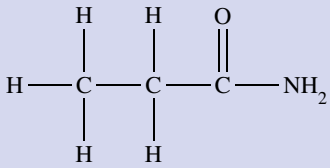
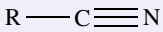
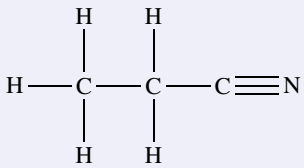
FIGURE 8.4.1 (a) Vinegar and (b) wine contain molecules with two carbon atoms. Vinegar contains ethanoic acid with a carboxyl functional group and wine contains ethanol with a hydroxyl group.

We can organise the millions of known organic compounds into classes or homologous series based on their functional groups; this makes it easier for us to understand the chemistry of many different compounds.

The different classes of hydrocarbon derivatives and the functional groups that make up each class are summarised in Table 8.4.1. Remember that the symbols R and R' usually represent the hydrocarbon chain that makes up the rest of the organic molecule, but they can also be used to represent any group of atoms.

TABLE 8.4.1 The different classes of hydrocarbon derivatives and the functional groups that make up each class

Class of hydrocarbon derivative	Functional group present	Example
haloalkane	halogen R-X (where X = F, Cl, Br, I)	bromoethane 
alcohol	hydroxyl R-OH	propan-1-ol 
amine	amino R-NH_2	propan-1-amine 
aldehyde	carbonyl (attached to a hydrogen atom) 	propanal 
ketone	carbonyl (attached to carbon atoms on either side) 	butanone 
carboxylic acid	carboxyl 	propanoic acid 

Class of hydrocarbon derivative	Functional group present	Example
ester	carboxylate 	ethyl ethanoate 
amide	carboxamide 	propanamide 
nitrile	nitrile 	propanenitrile 

The **carbonyl functional group**, which is shown in Figure 8.4.2, is a common group of atoms found in five of the nine classes of hydrocarbon derivatives. The carbonyl group is made up of a carbon atom doubly bonded to an oxygen atom and is present in **aldehydes**, **ketones**, **carboxylic acids**, **esters** and **amides**.

We will examine the different classes of hydrocarbon derivatives in two sections. The first part will focus on those hydrocarbon derivatives that do not contain the carbonyl group, and the second part will focus on those hydrocarbon derivatives that do contain the carbonyl group.

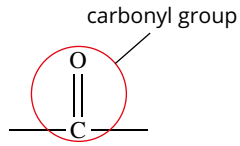


FIGURE 8.4.2 The carbonyl group contains a carbon atom doubly bonded to an oxygen atom. It is found in five of the nine classes of hydrocarbon derivatives.

HYDROCARBON DERIVATIVES WITHOUT THE CARBONYL GROUP

There are four classes of compounds that you should be familiar with that do not contain a carbonyl group. As shown in Figure 8.4.3, these are the **haloalkanes**, **alcohols**, **amines** and **nitriles**.

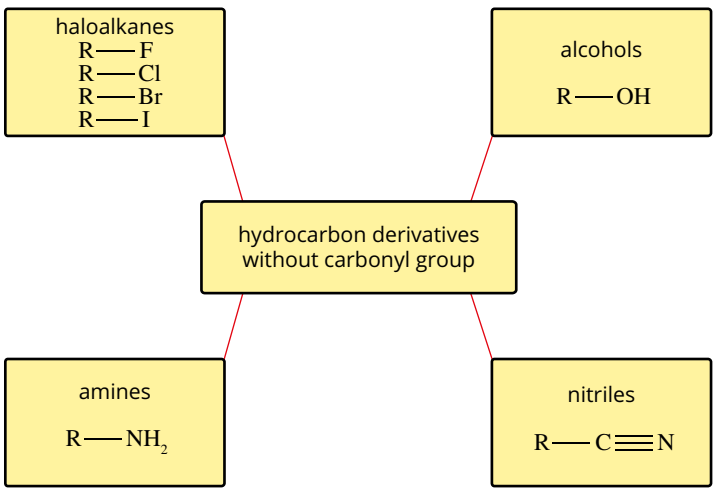


FIGURE 8.4.3 The four classes of hydrocarbon derivatives that do not contain a carbonyl group

WS 4.1.3

Haloalkanes



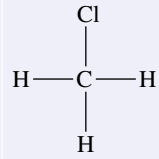
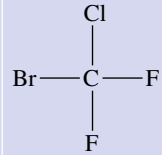
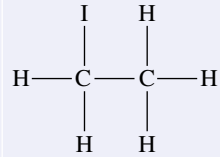
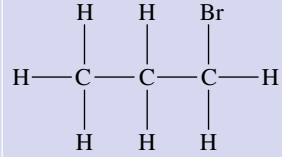
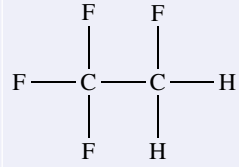
FIGURE 8.4.4 Bromomethane (CH_3Br) is a colourless, odourless, non-flammable gas that was used as a pesticide in the past. This photo shows a field covered in plastic sheeting to minimise loss of the pesticide from the soil.

Haloalkanes are a homologous series derived from alkanes in which at least one of the hydrogen atoms is replaced with a **halogen** atom.

Haloalkanes are used widely in industry as flame retardants, refrigerants, propellants, pesticides (Figure 8.4.4), solvents and pharmaceuticals. Some haloalkanes are ozone-depleting chemicals and their use has been phased out in many applications.

The halogen elements are in group 17 of the periodic table. All halogen atoms have seven valence electrons, which means they can form a single covalent bond with carbon atoms. The halogen elements that commonly form **halo functional groups** in organic compounds are fluorine, chlorine, bromine and iodine. Table 8.4.2 includes the names, structures and uses of some haloalkanes.

TABLE 8.4.2 Names, structures and uses of some haloalkanes

Name	Extended structural formula	Condensed structural formula	Use
chloromethane		CH_3Cl	refrigerant
bromochlorodifluoromethane		$CBrClF_2$	fire extinguishers
iodoethane		CH_3CH_2I	production of chemicals
1-bromopropane		$CH_3CH_2CH_2Br$	industrial solvent
1,1,1,2-tetrafluoroethane		CH_2FCF_3	refrigerant

Classifying haloalkanes

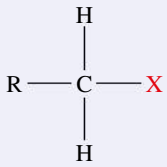
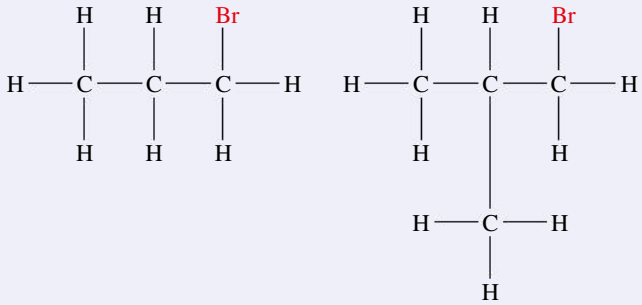
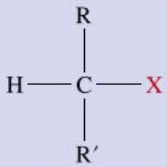
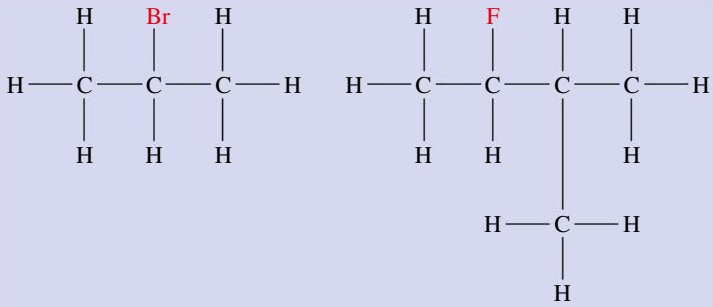
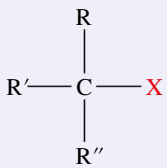
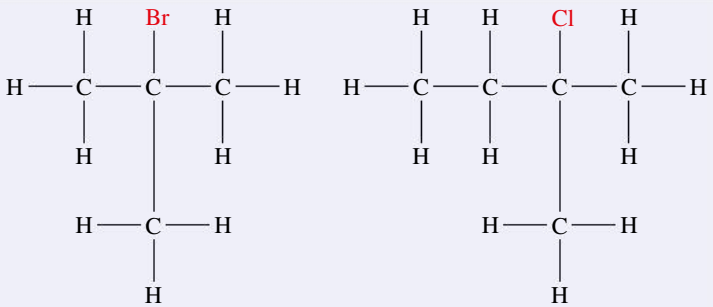
Haloalkanes are classified according to the number of alkyl groups attached to the carbon bonded to the halogen atom. The three different types of haloalkanes are:

- **primary haloalkanes**
- **secondary haloalkanes**
- **tertiary haloalkanes**.

Haloalkanes are a homologous series derived from alkanes in which at least one of the hydrogen atoms is replaced with a halogen atom.

The definition of each type and examples are shown in Table 8.4.3. Alkyl groups are represented by the general symbol R.

TABLE 8.4.3 The three different types of haloalkanes. The halogen group is shown in red.

Type of alcohol	Definition	General formula	Examples
primary	The carbon bonded to the halogen is only bonded to one alkyl group.	 where X = F, Cl, Br or I	
secondary	The carbon bonded to the halogen is also bonded to two alkyl groups.	 where X = F, Cl, Br or I	
tertiary	The carbon atom bonded to the halogen is also bonded to three alkyl groups.	 where X = F, Cl, Br or I	

Naming haloalkanes

The names of haloalkane functional groups are derived from the name of the halogen, as shown in Table 8.4.4.

The rules for naming haloalkanes follow the rules for naming alkanes. In addition, the following conventions are applied.

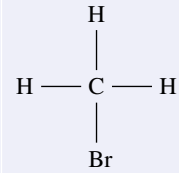
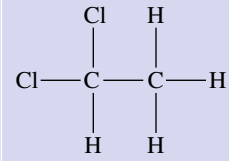
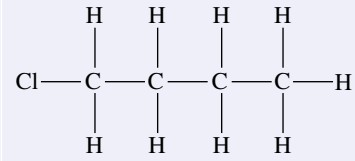
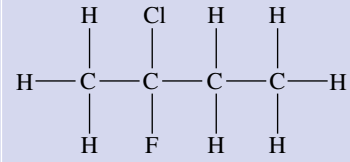
- Place the name of the specific halo functional group at the start of the parent alkane's name.
- If positional isomers are possible, number the carbon atoms in the parent chain beginning at the end nearer the first halo group or alkyl side chain (whichever comes first). Use the numbers to indicate the carbon to which the halo functional group is attached. A hyphen should be inserted into the name between a number and a letter.
- In compounds with more than one halo functional group of the same type, number each to show their position in the chain and separate the numbers by a comma. The prefixes 'di-', 'tri-' and 'tetra-' should also be used.
- If more than one type of halo functional group is present, or a halo functional group and an alkyl side chain are present together, list them in alphabetical order.

We can apply these rules to name the haloalkanes listed in Table 8.4.5 on page 250.

TABLE 8.4.4 Names of the haloalkane functional groups

Halogen	Functional group name
fluorine	fluoro-
chlorine	chloro-
bromine	bromo-
iodine	iodo-

TABLE 8.4.5 Examples of haloalkanes and their names

Name	Condensed structural formula	Extended structural formula
bromomethane	CH_3Br	
1,1-dichloroethane	CH_3CHCl_2	
1-chlorobutane	$CH_3CH_2CH_2CH_2Cl$	
2-chloro-2-fluorobutane	$CH_3CClFCH_2CH_3$	

Alcohols

Ethanol (shown in Figure 8.4.5) is a member of the homologous series of alcohols. Alcohols are found widely in nature and have many uses and applications. For example, ethanol is used as a fuel, a solvent in pharmaceuticals and toiletries, and it is also the alcohol found in alcoholic drinks.

Alcohols contain a hydroxyl (–OH) functional group attached to a saturated carbon atom. A representation of the hydroxyl group is shown in Figure 8.4.6.

Figure 8.4.7 shows the structural formulas of three more alcohols. You can think of the hydroxyl group as taking the place of a hydrogen atom in an alkane.

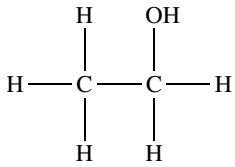


FIGURE 8.4.5 Ethanol is a member of the homologous series of alcohols.

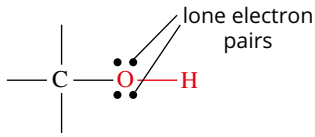
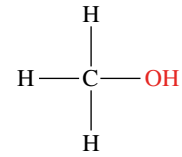


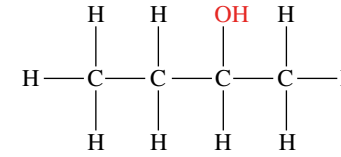
FIGURE 8.4.6 Alcohols contain the hydroxyl functional group –OH (in red above). There are two pairs of non-bonding electrons on the oxygen atom.

Alcohols contain a hydroxyl functional group attached to a saturated carbon atom.



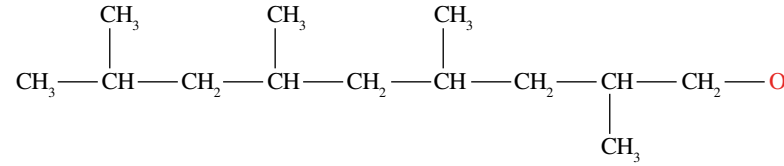
methanol

CH_3OH



butan-2-ol

$CH_3CH_2CHOHCH_3$



2,4,6,8-tetramethylnonan-1-ol

$(CH_3)_2CHCH_2CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_2OH$

FIGURE 8.4.7 Extended and condensed structural formulas of three alcohols. Each contains the hydroxyl functional group (shown in red). Note that the non-bonding electron pairs on the oxygen atom are often omitted in extended structural formulas.

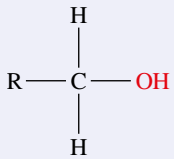
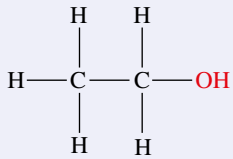
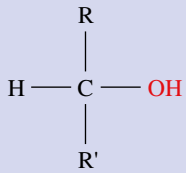
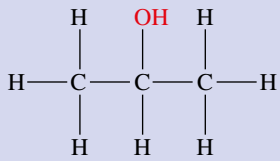
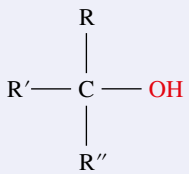
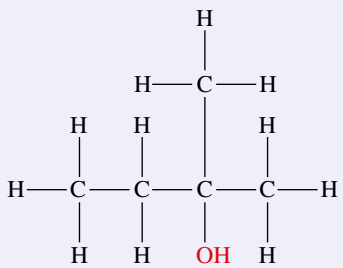
Classifying alcohols

Alcohols are classified according to the number of alkyl chains attached to the carbon bonded to the hydroxyl group. The three different types of alcohols are:

- **primary alcohols**
- **secondary alcohols**
- **tertiary alcohols**.

The definition of each type and examples are shown in Table 8.4.6. Alkyl groups are represented by the general symbols R, R' and R". This classification of alcohols as primary, secondary or tertiary is extremely important because reactions of alcohols, which are discussed in Chapter 9, differ from one class of alcohol to another.

TABLE 8.4.6 The three different types of alcohols. The hydroxyl group is shown in red.

Type of alcohol	Definition	General formula	Example
primary	The carbon atom bonded to the –OH group is only bonded to one alkyl group.		
secondary	The carbon atom bonded to the –OH group is also bonded to two alkyl groups.		
tertiary	The carbon atom bonded to the –OH group is also bonded to three alkyl groups.		

Naming alcohols

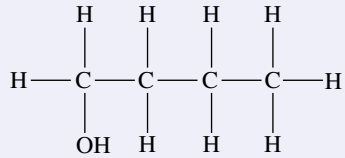
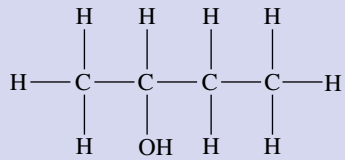
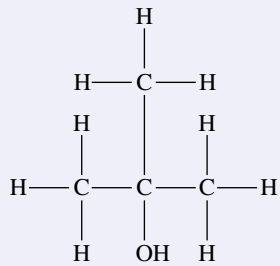
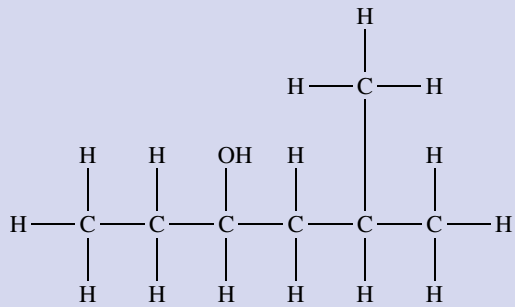
Alcohol names follow the rules used for alkanes, except that the '-e' at the end of the parent alkane's name is replaced with the suffix '-ol'.

The following rules also apply.

- Identify the parent name from the longest carbon chain containing the hydroxyl group.
- If positional isomers are possible, a number is inserted before the '-ol' to indicate the carbon to which the hydroxyl functional group is attached.
- Number the carbon chain commencing at the end closest to the hydroxyl group. In numbering the carbon chain, the hydroxyl group takes priority over any alkyl side chains, so if there is more than one numbering option, the name in which the hydroxyl group is the smallest is correct.

We can apply these rules to name the alcohols listed in Table 8.4.7 on page 252. Notice that the first three alcohols in the table are all structural isomers of $C_4H_{10}O$. The last alcohol illustrates the priority that the hydroxyl group takes over alkyl side chains when numbering the carbon chain.

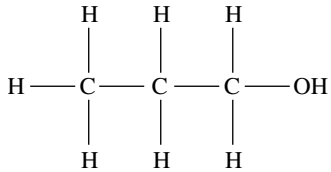
TABLE 8.4.7 Examples of naming alcohols

Name	Molecular formula	Condensed structural formula	Extended structural formula
butan-1-ol	$C_4H_{10}O$	$CH_3CH_2CH_2CH_2OH$	 This is an example of a primary alcohol.
butan-2-ol	$C_4H_{10}O$	$CH_3CHOHCH_2CH_3$	 This is an example of a secondary alcohol.
2-methylpropan-2-ol	$C_4H_{10}O$	$(CH_3)_3COH$	 This is an example of a tertiary alcohol.
5-methylhexan-3-ol	$C_7H_{16}O$	$CH_3CH_2CHOHCH_2CH(CH_3)CH_3$	 This is an example of a secondary alcohol.

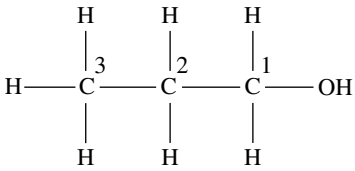
Worked example 8.4.1

IUPAC NAMING SYSTEM FOR ALCOHOLS

Use systematic naming rules to determine the name of the following alcohol.



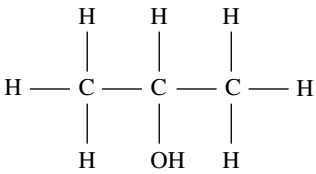
Thinking	Working
Identify the longest carbon chain in the molecule. The name of the molecule is based on this longest chain.	There are three carbon atoms in the longest chain. The name is based on propane.

Identify the functional group present and the suffix to use at the end of the molecule's name.	There is a hydroxyl group present. The molecule is an alcohol so the suffix is '-ol'.
Number the carbon atoms starting from the end closest to the hydroxyl functional group.	
Identify the position(s) and type(s) of alkyl side chains.	There are no alkyl side chains in this molecule.
Combine all components. Place the number for the position of the hydroxyl group in front of the '-ol' ending.	The name of the molecule is propan-1-ol.

➤ Try yourself 8.4.1

IUPAC NAMING SYSTEM FOR ALCOHOLS

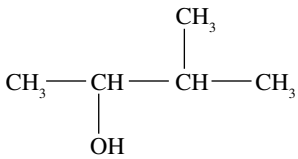
Use systematic naming rules to determine the name of the following alcohol.

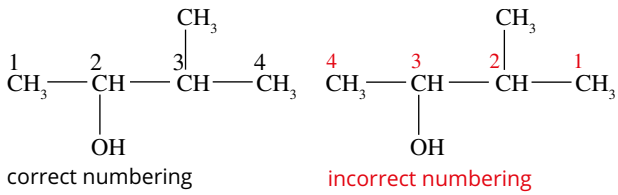


Worked example 8.4.2

NAMING ALCOHOLS THAT CONTAIN ALKYL SIDE CHAINS

Determine the systematic name for the following molecule.

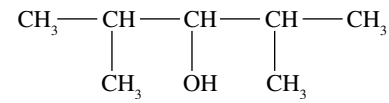


Thinking	Working
Identify the longest carbon chain in the molecule. The name of the molecule is based on this longest chain.	There are four carbon atoms in the longest chain. The name is based on butane.
Identify the functional group present and the suffix to use at the end of the molecule's name.	There is a hydroxyl group present. The molecule is an alcohol so the suffix is '-ol'.
Number the carbon atoms starting from the end closest to the functional group. Remember that the hydroxyl group takes priority over the alkyl side chains so make sure you do not number the carbon atoms starting from the wrong end.	 correct numbering incorrect numbering
Identify the position(s) and the type(s) of alkyl side chains.	There is a methyl ($-CH_3$) group on carbon number 3 so the prefix 'methyl-' will be used.
Combine all components. Place the number for the position of the alkyl side chain in front of the prefix, and the number for the position of the hydroxyl group in front of the '-ol' ending.	The name of the molecule is 3-methylbutan-2-ol.

➤ Try yourself 8.4.2

NAMING ALCOHOLS THAT CONTAIN ALKYL SIDE CHAINS

Determine the systematic name for the following molecule.



Amines

Amines are a homologous series of organic compounds that contain the **amino functional group**. In **primary amines**, the amino functional group consists of one nitrogen atom covalently bonded to two hydrogen atoms as shown in Figure 8.4.8.

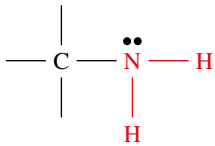


FIGURE 8.4.8 Primary amines contain the amino functional group -NH_2 (in red above). There are two non-bonding electrons on the nitrogen atom.

Amino functional groups with two hydrogens and one alkyl group are called primary amines. Amines are classified as 'primary', 'secondary' and 'tertiary' according to the number of alkyl groups attached to the nitrogen atom. Secondary and tertiary amines exist, but these compounds are not covered in this chapter. Some primary amines are shown in Figure 8.4.9.

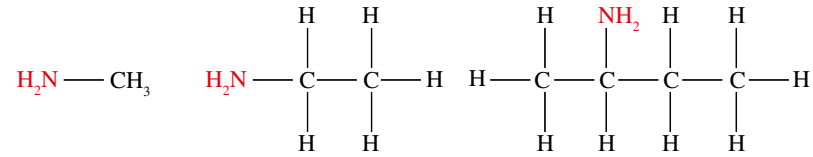


FIGURE 8.4.9 Extended and condensed structural formulas of three primary amines. The amino functional group is shown in red. Primary amines have one carbon atom bonded to the nitrogen atom.

Primary amines consist of an amino functional group in which one nitrogen atom is covalently bonded to two hydrogen atoms.

Naming amines

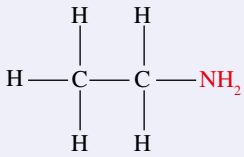
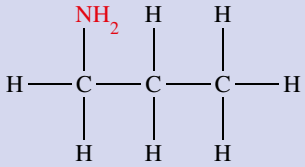
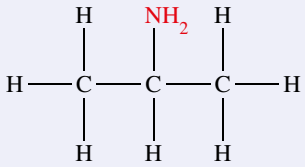
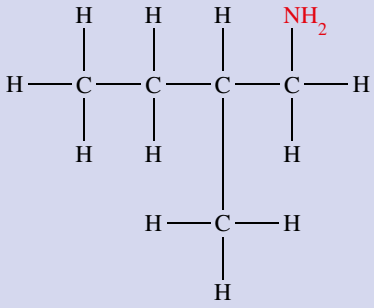
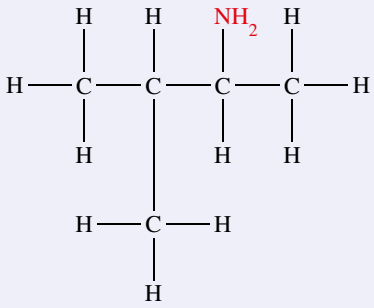
Amine names follow the rules used for alkanes, except that the '-e' at the end of the parent alkane's name is replaced with the suffix '-amine'.

The following rules also apply.

- Identify the parent name from the longest carbon chain containing the amino group.
- If positional isomers are possible, a number is inserted before the '-amine' to indicate the carbon to which the amino functional group is attached.
- Number the carbon chain commencing at the end closest to the amino group. In numbering the carbon chain, the amino group takes priority over any alkyl side chains, so if there is more than one numbering option, the name in which the amino group is the smallest is correct.

Apply these rules to understand how the amines in Table 8.4.8 are named. Note that propan-2-amine is a positional isomer of propan-1-amine and 3-methylbutan-2-amine is a positional isomer of 2-methylbutan-1-amine.

TABLE 8.4.8 Examples of naming amines

Name	Molecular formula	Condensed structural formula	Extended structural formula
ethanamine	C_2H_7N	$CH_3CH_2NH_2$	
propan-1-amine	C_3H_9N	$CH_3CH_2CH_2NH_2$	
propan-2-amine	C_3H_9N	$CH_3CH(NH_2)CH_3$	
2-methylbutan-1-amine	$C_5H_{13}N$	$CH_3CH_2CH(CH_3)CH_2NH_2$	
3-methylbutan-2-amine	$C_5H_{13}N$	$CH_3CH(CH_3)CH(NH_2)CH_3$	

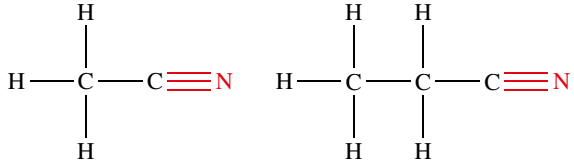
Nitriles

Nitriles are a homologous series of organic compounds that contain the **nitrile functional group**. A nitrile functional group consists of a carbon atom connected to a nitrogen atom with a triple bond, as shown in Figure 8.4.10.



FIGURE 8.4.10 Nitriles contain the nitrile functional group. There are two non-bonding electrons on the nitrogen atom.

Some examples of nitriles are shown in Figure 8.4.11. The nitrile functional group can only occur at the end of a carbon chain.



ethanenitrile
CH_3CN

propanenitrile
CH_3CH_2CN

FIGURE 8.4.11 Extended and condensed structural formulas of two nitriles. The nitrile functional group is shown in red.

Nitriles contain a nitrile functional group in which a carbon atom is covalently bonded to a nitrogen atom with a triple bond.

Naming nitriles

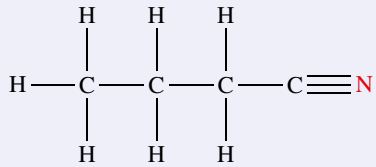
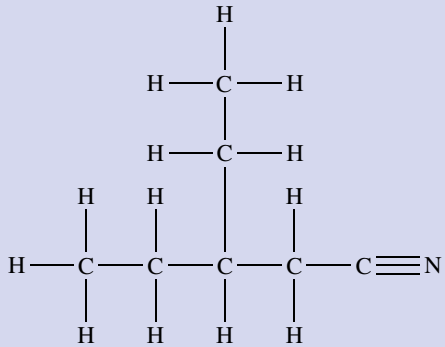
Nitrile names follow the rules used for alkanes but with the addition that the suffix '-nitrile' is added to the end of the parent alkane's name.

The following rules also apply.

- Identify the parent name from the longest carbon chain containing the nitrile group.
- Number the carbon chain so that the nitrile carbon atom is the first carbon in the chain.
- The position of the nitrile functional group does not need to be specified as it can only be on the first carbon.

Apply these rules to understand how the nitriles in Table 8.4.9 are named.

TABLE 8.4.9 Examples of naming nitriles

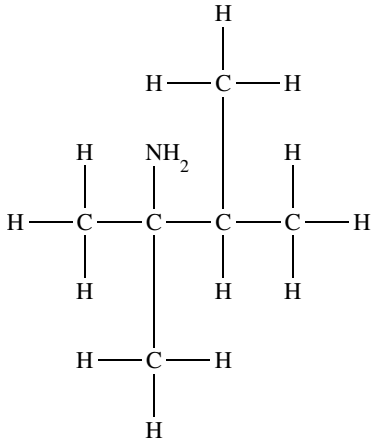
Name	Condensed formula	Structural formula
butanenitrile	$CH_3CH_2CH_2CN$	
3-ethylpentanenitrile	$CH_2CH_2CH(CH_2CH_3)CH_2CN$	

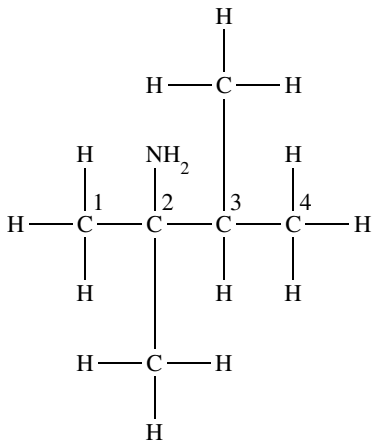
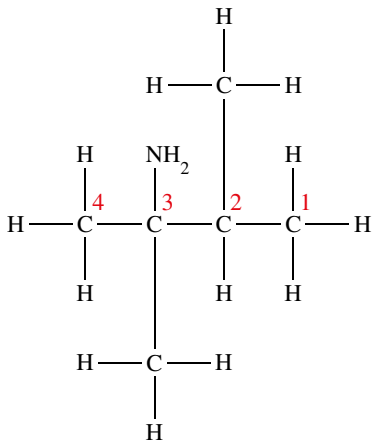
Worked example 8.4.3

CLASSIFYING AND NAMING HYDROCARBON DERIVATIVES

For the following compound, determine:

- the name of the functional group present in the compound
- the class that the compound belongs to
- the IUPAC name of the compound.



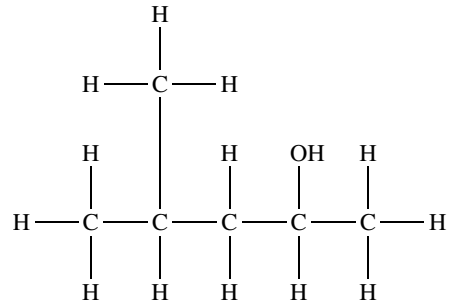
Thinking	Working
Identify the functional group that is present.	There is an amino group present.
Identify the class of compound.	The compound is an amine.
The remaining steps show how to name the compound. Identify the longest carbon chain in the molecule. Ensure the carbon containing the functional group is in this parent chain. The name of the molecule is based on this longest chain.	There are four carbon atoms in the longest chain. The name is based on butane.
Number the carbon atoms starting from the end closest to the amino functional group. Remember that the amino group takes priority over the alkyl side chains.	 correct numbering  incorrect numbering
Drop the 'e' at the end of the parent alkane's name and replace it with the suffix '-amine'. Insert a number before the '-amine' to indicate which carbon atom the amino functional group is attached to.	The parent name is butan-2-amine.
Identify the position(s) and the type(s) of alkyl side chains.	There are two methyl ($-CH_3$) groups on carbon number 2 and carbon number 3, and the amino group is on carbon number 2.
Place the numbers for the positions of each methyl group in front of the parent name and include 'di-' as a prefix.	The molecule is named 2,3-dimethylbutan-2-amine.

➤ Try yourself 8.4.3

CLASSIFYING AND NAMING HYDROCARBON DERIVATIVES

For the following compound, determine:

- the name of the functional group present in the compound
- the class that the compound belongs to
- the IUPAC name of the compound.



HYDROCARBON DERIVATIVES WITH THE CARBONYL GROUP

We will now focus on five classes of compounds which contain the carbonyl functional group. As discussed earlier in the module, a carbonyl functional group, shown in Figure 8.4.12a, consists of a carbon atom connected to an oxygen atom by a double bond. All atoms bonded to the carbon atom are in a plane and the angles between the bonds are 120°. However, for convenience, the bonds are often drawn at right angles and the non-bonding pairs of electrons are not included, as shown in Figure 8.4.12b.

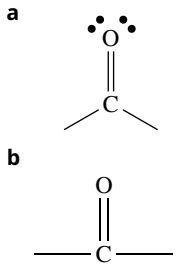


FIGURE 8.4.12 The carbonyl functional group. The non-bonding pairs of electrons shown on the oxygen atom are often not included in structural formulas.

As shown in Figure 8.4.13, the compounds containing this carbonyl group are the aldehydes, ketones, carboxylic acids, esters and amides. These compounds are prevalent in nature and they also have a wide variety of uses in industrial, pharmaceutical and cosmetic applications.

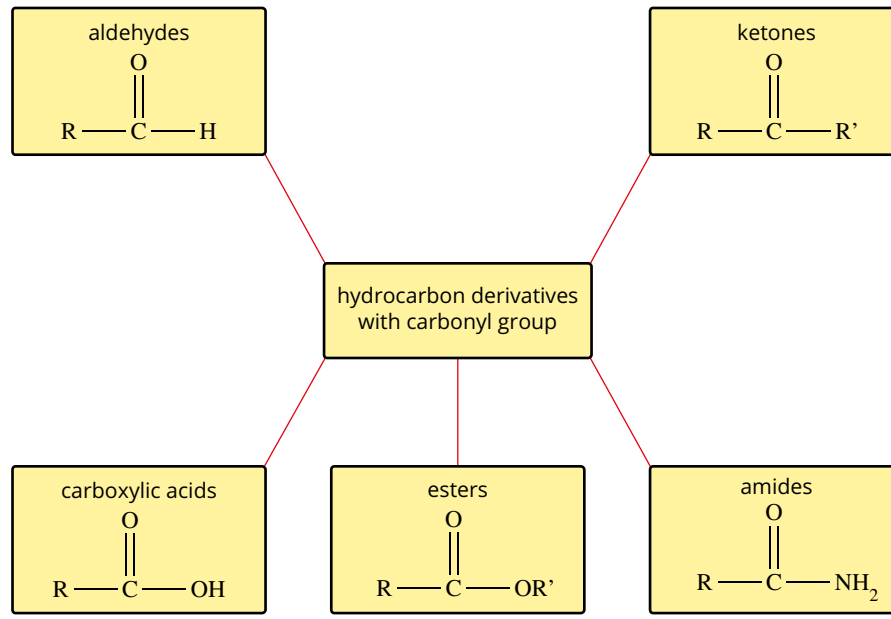


FIGURE 8.4.13 Five classes of hydrocarbon derivatives that contain the carbonyl group

Aldehydes

In aldehydes, the carbonyl group is always at the end of the hydrocarbon chain because the carbon atom of the carbonyl group is bonded to a hydrogen atom. The carbonyl functional group in an aldehyde is always written as –CHO at the end of the condensed structural formula of aldehydes.

The simplest aldehyde, HCHO, is methanal (commonly known as formaldehyde) and it is used to preserve biological specimens, including embalming human remains. The structural formulas of methanal and two other aldehydes are shown in Figure 8.4.14.

Aldehydes contain a carbonyl functional group attached to a hydrogen atom at the end of the carbon chain.

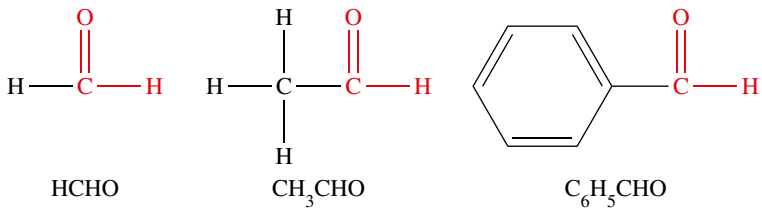


FIGURE 8.4.14 Extended and condensed structural formulas of three aldehydes. Each contains a carbonyl functional group with a hydrogen atom attached, shown in red.

Naming aldehydes

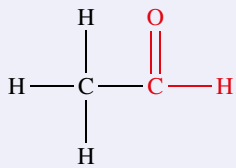
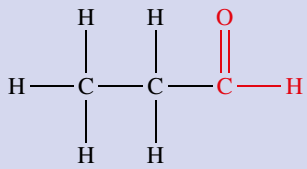
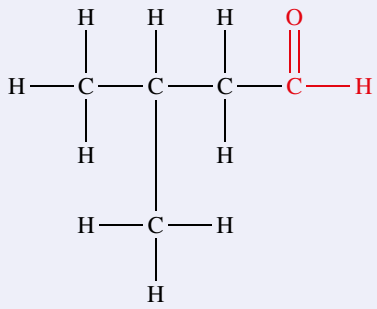
Aldehyde names follow the rules used for alkanes, except that the '-e' at the end of the parent alkane's name is replaced with the suffix '-al'.

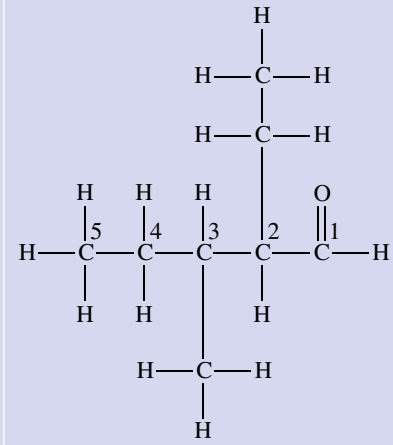
The following rules also apply.

- Identify the parent name from the longest carbon chain containing the carbonyl group.
- Number the carbon chain so that the carbonyl carbon atom is the first carbon in the chain (carbon number 1).
- The position of the carbonyl functional group does not need to be specified as it will always be on the first carbon.

Table 8.4.10 lists the names of four different aldehydes.

TABLE 8.4.10 Examples of naming aldeyhydes

Name	Molecular formula	Condensed structural formula	Extended structural formula
ethanal	C_2H_4O	CH_3CHO	
propanal	C_3H_6O	CH_3CH_2CHO	
3-methylbutanal	$C_5H_{10}O$	$CH_3CH(CH_3)CH_2CHO$	

2-ethyl-3-methylpentanal	$C_8H_{16}O$	$CH_3CH_2CH(CH_3)CH(CH_2CH_3)CHO$	

Ketones

In ketones, the carbonyl carbon is attached to two other carbon atoms. This means that the carbonyl group is never at the end of the molecule. In condensed structural formulas, the carbonyl functional group in a ketone is simply written as –CO–.

The simplest ketone, CH_3COCH_3, is commonly called acetone (its IUPAC name is propanone) and it is a useful polar organic solvent, frequently found in nail polish remover and paint thinner. Figure 8.4.15 shows the extended structural formulas of three ketones. The carbonyl group in each is highlighted in red.

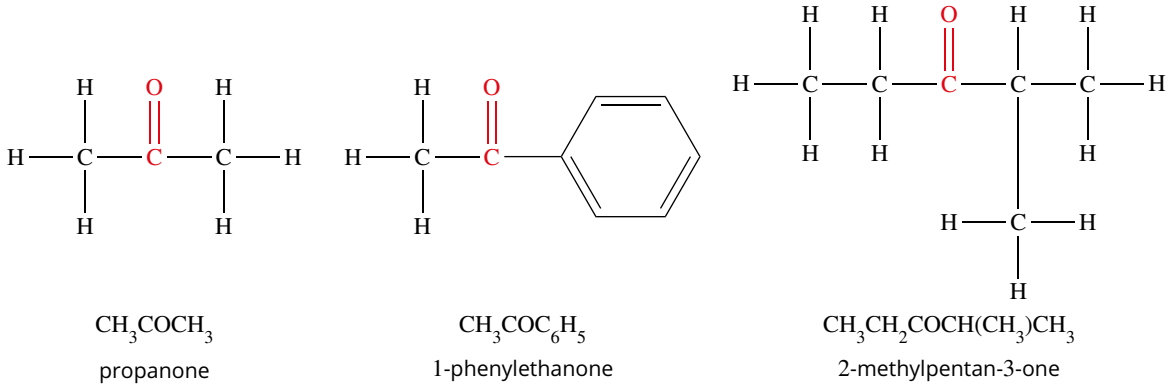


FIGURE 8.4.15 Extended and condensed structural formulas of three ketones. Each contains a carbonyl functional group (shown in red) attached to two hydrocarbon groups.

Ketones contain a carbonyl group attached to two other carbon atoms; the carbonyl group is never at the end of the carbon chain.

Naming ketones

Ketone names follow the rules used for alkanes, except that the '-e' at the end of the parent alkane's name is replaced with the suffix '-one'.

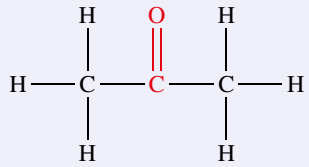
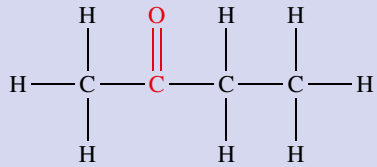
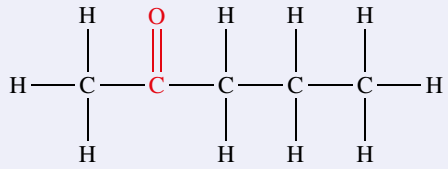
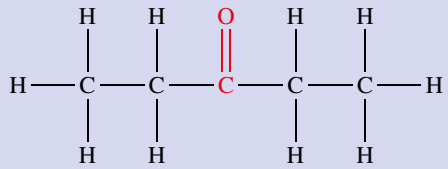
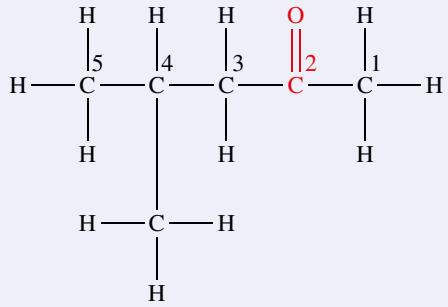
The following rules also apply.

- Identify the parent name from the longest carbon chain containing the carbonyl group.
- Number the carbon chain commencing at the end closest to the carbonyl group.
- If positional isomers are possible, use numbers to indicate the position of the carbonyl group in the molecule. This will be the case for ketones that contain five or more carbon atoms in the parent chain.

Table 8.4.11 lists the names of five different ketones. Notice that the position of the carbonyl group is not specified in the names for propanone or butanone because no positional isomers exist for either molecule; there is only one possible ketone in each case. However, pentanone, which is a ketone made up of five carbon atoms, has two positional isomers. These isomers are named pentan-2-one and pentan-3-one; the number in each name represents the position of the carbonyl group in the

molecule. It is also important to note that in 4-methylpentan-2-one, the carbonyl carbon takes priority over the methyl side chain when numbering the main carbon chain and is therefore assigned the lowest number. If the carbon chain was numbered the opposite way then the carbonyl carbon would be on carbon number 4 and the ketone would be named 2-methylpentan-4-one, which is incorrect.

TABLE 8.4.11 Examples of naming ketones

Name	Molecular formula	Condensed structural formula	Extended structural formula
propanone	C_3H_6O	CH_3COCH_3	
butanone	C_4H_8O	$CH_3COCH_2CH_3$	
pentan-2-one	$C_5H_{10}O$	$CH_3COCH_2CH_2CH_3$	
pentan-3-one	$C_5H_{10}O$	$CH_3CH_2COCH_2CH_3$	
4-methylpentan-2-one	$C_6H_{12}O$	$CH_3CH(CH_3)CH_2COCH_3$	

Carboxylic acids

Carboxylic acids are a homologous series that contain the carboxyl functional group. The carboxyl functional group (Figure 8.4.16) consists of a carbonyl group attached to a hydroxyl group.

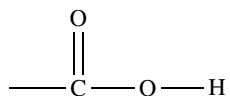


FIGURE 8.4.16 Structure of the carboxyl functional group

The **carboxyl functional group** is represented in a condensed structural formula as –COOH and is always located at one end of a hydrocarbon chain. Carboxylic acids are prevalent in nature and are also very useful in the food and pharmaceutical industries. Figure 8.4.17 on page 262 shows the extended structural and condensed structural formulas of three carboxylic acids. Methanoic acid is the simplest carboxylic acid (commonly called formic acid) and is found in some ant stings. Ethanoic acid (commonly called acetic acid) is the chief component of vinegar, and lactic acid is found in sour milk and also formed in muscles during exercise. Longer chain carboxylic acids are used in the production of soaps and other cleansing products.

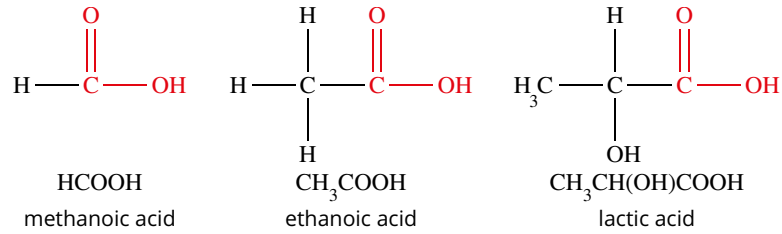


FIGURE 8.4.17 Extended structural and condensed structural formulas of three carboxylic acids. Each contains a carboxyl functional group shown in red.

Carboxylic acids contain a carboxyl functional group made up of a carbonyl group attached to a hydroxyl group. The carboxyl functional group is always located at the end of the carbon chain.

Naming carboxylic acids

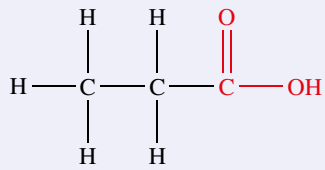
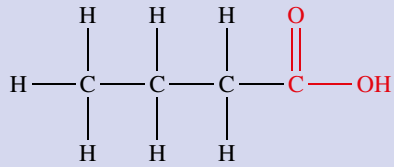
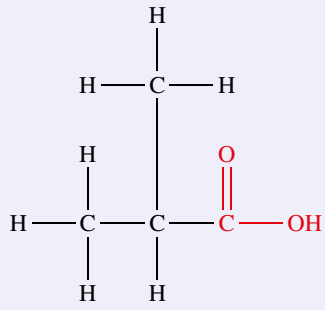
Carboxylic acids follow the rules used for alkanes, except that the '-e' at the end of the parent alkane's name is replaced with the suffix '-oic acid'.

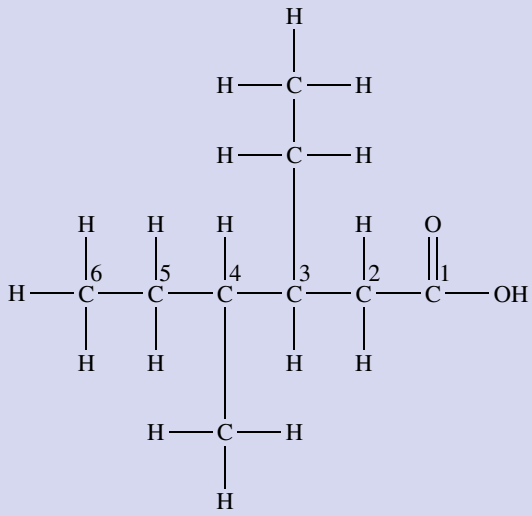
The following rules also apply.

- Identify the parent name from the longest carbon chain containing the carboxyl group.
- Number the carbon chain so that the carboxyl carbon atom is the first carbon in the chain (carbon number 1).
- The position of the carboxyl functional group does not need to be specified as it will always be on the first carbon.

Table 8.4.12 lists the names of four different carboxylic acids. Notice that butanoic acid and methylpropanoic acid are chain isomers with the molecular formula $C_4H_8O_2$.

TABLE 8.4.12 Examples of naming carboxylic acids

Name	Molecular formula	Condensed structural formula	Extended structural formula
propanoic acid	$C_3H_6O_2$	CH_3CH_2COOH	
butanoic acid	$C_4H_8O_2$	$CH_3CH_2CH_2COOH$	
methylpropanoic acid	$C_4H_8O_2$	$CH_3CH(CH_3)COOH$	

Name	Molecular formula	Condensed structural formula	Extended structural formula
3-ethyl-4-methylhexanoic acid	$C_9H_{18}O_2$	$CH_3CH_2CH(CH_3)CH(CH_2CH_3)CH_2COOH$	

Esters

Esters are a homologous series that contain a carbonyl (C=O) group attached to an oxygen that is linked to another carbon. The **ester functional group**, shown in Figure 8.4.18, is similar to a carboxyl functional group, but the hydrogen of the –OH is replaced by an alkyl group. In condensed structural formulas, the ester is usually written as –COO–.

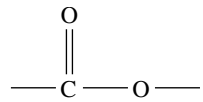
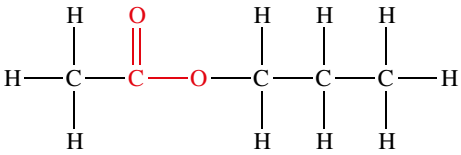


FIGURE 8.4.18 Structure of the ester functional group

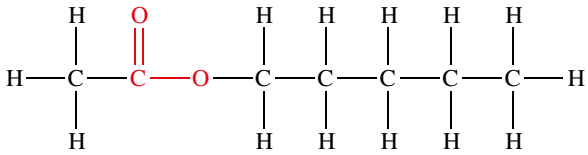
Esters are compounds that often have characteristic sweet, fruity odours. Many esters occur naturally in fruits and flowers. The distinctive and appealing odour of your favourite perfume or aftershave may well be due to esters.

Figure 8.4.19 shows the extended structural and condensed structural formulas of three esters. Propyl ethanoate smells like pears, whereas pentyl ethanoate is responsible for the odour of bananas. Acetylsalicylic acid is a very important ester; its common name is aspirin and it is used in large quantities as a painkiller.



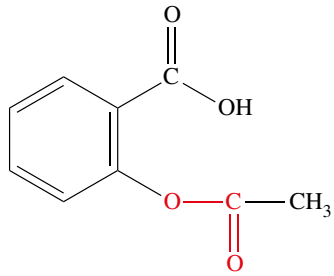
$CH_3COOCH_2CH_2CH_3$

propyl ethanoate



$CH_3COOCH_2CH_2CH_2CH_2CH_3$

pentyl ethanoate



aspirin

FIGURE 8.4.19 The structures of three different esters. The ester functional group is shown in red. It contains a carbonyl functional group attached to an oxygen atom.

Naming esters

The naming of esters tends to be a little more complex than the naming of compounds in the other homologous series that have been discussed so far. Esters are produced by the reaction of a carboxylic acid with an alcohol (this reaction will be discussed in more detail in Chapter 9). There are two parts to an ester's name and it is built up from the names of the carboxylic acid and alcohol that reacted to form it. The first word, derived from the alcohol, is based on the number of carbon atoms in the chain attached to the singly bonded (–O–). The second word of the name, derived from the carboxylic acid, is based on the number of carbon atoms in the chain containing the carbonyl group.

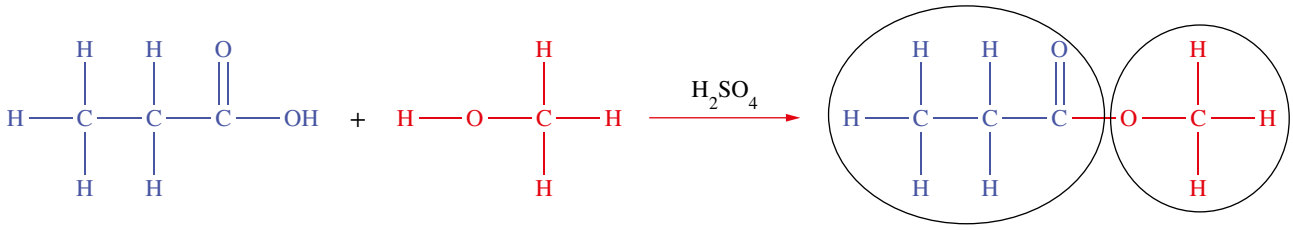
The ester functional group is similar to the carboxyl functional group except that the hydrogen of the –OH is replaced with an alkyl group.

In the example shown in Figure 8.4.20, an ester is produced from the carboxylic acid propanoic acid and the alcohol methanol.

We can determine the name of this ester using the following steps:

- The alkyl group bonded to the –O– is named first. This is the word derived from the alcohol.
- The carbonyl section of the ester makes up the second word of the name and is derived from the carboxylic acid. The name of the carboxylic acid is adapted by changing the '-oic acid' suffix to '-oate'.

Using these rules, you can work out that the name of the ester shown in Figure 8.4.20 is methyl propanoate.



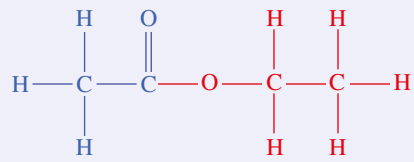
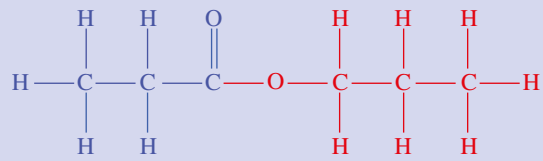
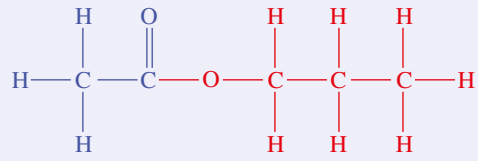
propanoic acid + methanol → methyl propanoate

$CH_3CH_2COOCH_3$

FIGURE 8.4.20 The name of an ester is derived from the names of the alcohol and carboxylic acid from which it is built.

The names and formulas of three more esters are shown in Table 8.4.13, with the part of each molecule derived from an alcohol in red and the part derived from the carboxylic acid in blue.

TABLE 8.4.13 Examples of naming esters

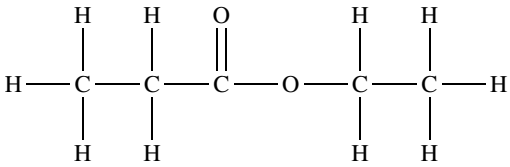
Name	Molecular formula	Condensed structural formula	Extended structural formula
ethyl ethanoate	$C_4H_8O_2$	$CH_3COOCH_2CH_3$	
propyl propanoate	$C_6H_{12}O_2$	$CH_3CH_2COOCH_2CH_2CH_3$	
propyl ethanoate	$C_5H_{10}O_2$	$CH_3COOCH_2CH_2CH_3$	

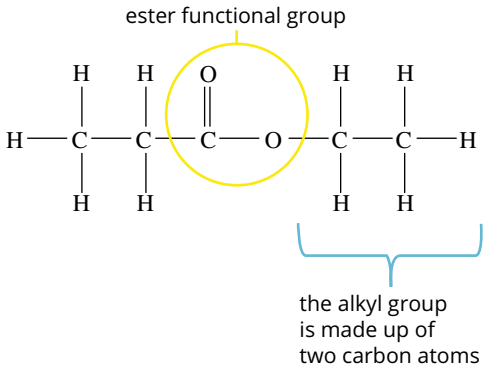
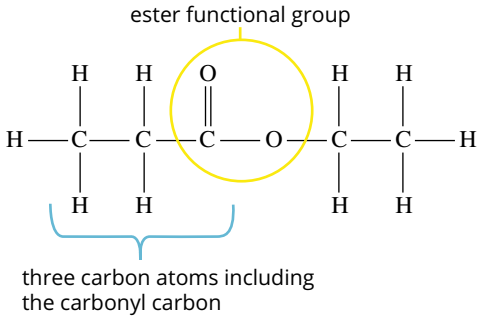
Use Worked example 8.4.4 to develop your skills in naming esters.

Worked example 8.4.4

IUPAC NAMING SYSTEM FOR ESTERS

Determine the systematic name for the following molecule.

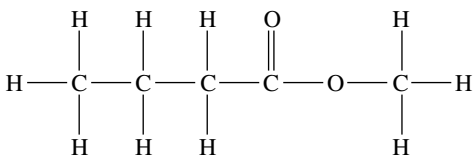


Thinking	Working
Locate the ester functional group. Identify the name of the alkyl group bonded to the –O– section of the ester functional group (this is the name derived from the alcohol). In this case the alkyl group is made up of two carbon atoms.	 The alkyl group is named ‘ethyl’. This is the first word of the ester name.
Starting from the carbonyl carbon, identify the number of carbon atoms in the chain attached to it. From the name of the corresponding carboxylic acid, replace the ‘-oic acid’ with ‘-oate’.	 There are three carbon atoms in the chain including the carbonyl carbon. The carboxylic acid with three carbon atoms is propanoic acid. From this name, change the ‘-oic acid’ suffix to ‘-oate’. This gives ‘propanoate’, which is the second word of the ester name.
Combine the two components, placing the alkyl part of the name first.	The name of the molecule is ethyl propanoate.

➤ Try yourself 8.4.4

IUPAC NAMING SYSTEM FOR ESTERS

Determine the systematic name for the following molecule.



Amides

Primary amides contain a carbonyl functional group attached to an amino functional group. They are similar to carboxyl groups, except that the –OH is replaced with $–NH_2$, as shown in Figure 8.4.21.

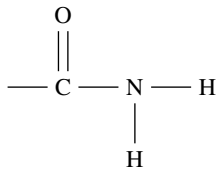
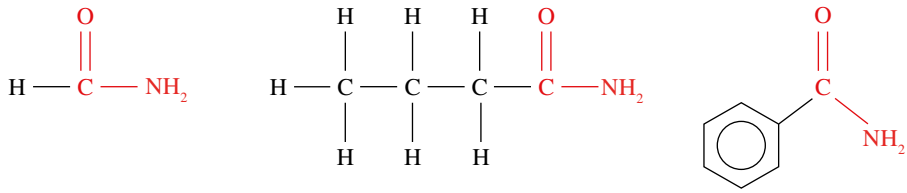


FIGURE 8.4.21 Structure of the amide functional group in a primary amide

The nitrogen atom in primary amides is bonded to two hydrogen atoms. Secondary and tertiary amides exist, but these compounds are not covered in this course. The **amide functional group** is represented in a condensed structural formula as $-CONH_2$ and is always located at one end of a hydrocarbon chain. The extended structural and condensed structural formulas of three primary amides are shown in Figure 8.4.22.



$HCONH_2$	$CH_3CH_2CH_2CONH_2$	$C_6H_5CONH_2$
methanamide	butanamide	benzanamide

FIGURE 8.4.22 Extended structural and condensed structural formulas of three amides, with the amide functional group shown in red

Amides contain a carbonyl functional group attached to an amine functional group. Primary amides have the condensed structural formula $-CONH_2$.

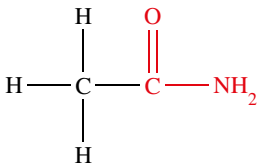


FIGURE 8.4.23 The name of an amide is derived from the name of the corresponding carboxylic acid. In this example, the amide is named ethanamide.

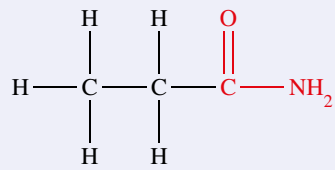
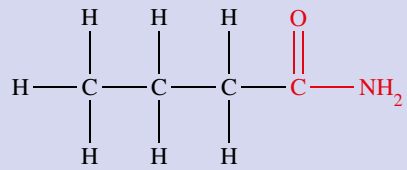
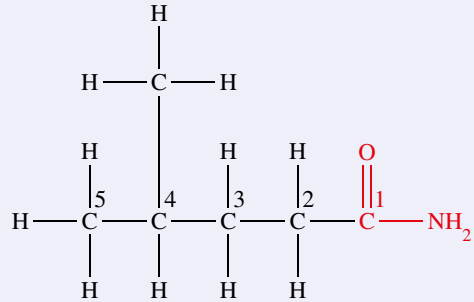
Amides are found widely in nature and are also used extensively in various industries, such as the pharmaceutical industry, the plastic industry and the paper industry.

Naming amides

Amides can be thought of as being derivatives of carboxylic acids in which the –OH group of the carboxylic acid has been replaced with an $-NH_2$ group. Amide names are therefore derived from carboxylic acids. To name an amide, take the name of the corresponding carboxylic acid and replace the '-oic acid' ending with '-amide'. The example given in Figure 8.4.23 is an amide derived from ethanoic acid. This amide is therefore named ethanamide. Note that the position of the amide functional group does not need to be specified in the name of the molecule because the carbonyl carbon will always be carbon number 1.

The names and formulas of three more amides are shown in Table 8.4.14.

TABLE 8.4.14 Examples of naming amides

Name	Molecular formula	Condensed structural formula	Extended structural formula
propanamide	C_3H_7NO	$CH_3CH_2CONH_2$	
butanamide	C_4H_9NO	$CH_3CH_2CH_2CONH_2$	
4-methylpentanamide	$C_6H_{13}NO$	$CH_3CH(CH_3)CH_2CH_2CONH_2$	

Computer modelling in drug design

Organic and biological molecules, such as proteins, can often be very large which makes it difficult to understand their three-dimensional structure and determine how they interact with other molecules. Since its inception in the latter half of the 20th century, computational molecular modelling has become increasingly important in understanding the structure of large molecules.

Current modelling programs allow scientists to construct molecules of any size and shape and to visualise and manipulate them in a three-dimensional space. Some of these programs not only enable scientists to gain a more thorough understanding of a molecule's structure and its important chemical features, but they also allow scientists to understand the mechanism by which a molecule interacts with another and predict how subsequent changes in the molecule's structure might affect its activity. This particular application has had important consequences in pharmaceutical drug design and discovery.

Professor Mark von Itzstein, shown in Figure 8.4.24, is a leading researcher and director of the Institute for Glycomics at Griffith University on the Gold Coast. Professor von Itzstein led the team that designed and developed the first anti-influenza drug, Relenza, in 1993. Influenza (more commonly known as the flu) is a highly contagious and potentially deadly disease that causes thousands of deaths every year in Australia (and many more in poorer countries). The use of Relenza and other related drugs in treating influenza has significantly contributed to reducing the severity of symptoms and preventing the spread of the disease.

Sialidase is a protein found on the surface of all types of influenza viruses and its function is to facilitate the spread of the virus in the host's body. Relenza was designed to inhibit the normal functioning of this sialidase protein.

One of the most interesting aspects about the design and subsequent development of Relenza is that computational chemistry played a primary role. Professor von Itzstein and his team used molecular modelling programs to analyse the structure of the sialidase protein and to probe its active site to fully understand how it interacts with the host cell. The active site of the sialidase consists of several different functional groups that form both intermolecular bonds and intermolecular forces of attraction with the functional groups on the host cell's protein. Using the modelling programs, Professor von Itzstein and his team were then able to build smaller molecules and predict whether they could be used to preferentially bind with the active site on the sialidase and stop it from binding



FIGURE 8.4.24 Professor Mark von Itzstein led the team that designed and developed the first anti-influenza drug, Relenza.

with the host cell. It was a long process from start to finish and Relenza, shown in Figure 8.4.25, was the result of this work. Relenza acts on sialidase by attaching itself to the active site, thus preventing the sialidase from binding to the host cell and therefore stopping the spread of the virus from infected cells to healthy cells. Figure 8.4.26 shows a computer model of Relenza's interaction with the sialidase protein.

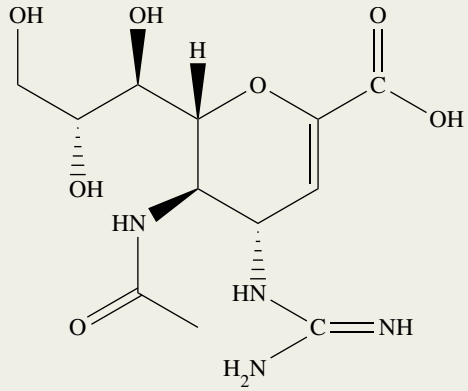


FIGURE 8.4.25 The structure of Relenza represented as a line structure. A line structure is a type of structural formula in which carbon–carbon bonds are depicted as lines and carbon–hydrogen bonds are generally not shown.

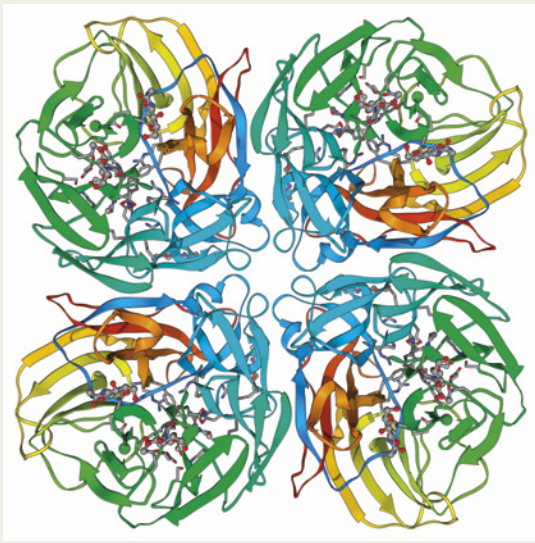


FIGURE 8.4.26 A computer model showing the interaction of Relenza with the influenza virus sialidase protein.

Because Relenza acts on a protein that is common to all types of flu viruses, it is effective against Influenza A, Influenza B, bird flu and swine flu. Professor von Itzstein's work on this drug was considered to be so important that he was one of three joint recipients of the 1996 Australia Prize alongside Dr Graeme Laver and Dr Peter Colman, whose earlier work on determining the structure of the sialidase protein was essential to the Relenza project.

Review

1. Identify the name of the influenza virus protein that Relenza targets.
2. Explain how Professor von Itzstein and his team used computer modelling programs to develop Relenza.
3. Identify why Relenza is effective against all types of flu viruses.

8.4 Review

SUMMARY

- Hydrocarbon derivatives have a hydrocarbon skeleton but contain functional groups in which one or more hydrogen atoms have been replaced with other atoms or groups of atoms that give an organic compound its characteristic properties.
- There are millions of known organic compounds but they can be organised into a relatively small number of classes (or homologous series) based on the functional groups present in their molecules.
- Haloalkanes are a homologous series derived from alkanes, in which one hydrogen atom is replaced with a halogen atom.
- Haloalkanes can be classified as primary, secondary or tertiary depending on the number of alkyl groups attached to the carbon atom bonded to the halogen atom.
- Alcohols contain a hydroxyl (–OH) functional group attached to a saturated carbon atom.
- Alcohols can be classified as primary, secondary or tertiary depending on the number of alkyl groups attached to the carbon atom bonded to the hydroxyl group.
- Primary amines contain an amino functional group that consists of a nitrogen atom covalently bonded to two hydrogen atoms.
- Haloalkanes, alcohols and primary amines can be regarded as being derived from alkanes. The name of the parent alkane is used as the basis for their names.
  - Haloalkanes are named by adding the prefix for the halogen.
  - Alcohols are named by replacing the 'e' at the end of the parent alkane with the suffix '-ol'.
  - Primary amines are named by replacing the 'e' at the end of the parent alkane with the suffix '-amine'.
  - When positional isomers exist, a number is used to specify the position of the functional group.
- The carbonyl group (–C=O) is a component of a number of functional groups.
- Aldehydes and ketones are a homologous series that contain a carbonyl group on its own.
- The carbonyl group is at the end of a hydrocarbon chain in aldehydes and within a hydrocarbon chain in ketones.
- Aldehydes are named using the suffix '-al' and ketones are named using the suffix '-one'.
- Carboxylic acids are a homologous series of molecules that contain the carboxyl group (–COOH) at the end of a hydrocarbon chain.
- Carboxylic acids are named using the suffix '-oic acid'.
- Esters are a homologous series of molecules that contain an ester group (–COO–) within the hydrocarbon chain.
- Esters have a two-word name:
  - The alkyl group bonded to the –O– is named first. This is the word of the ester that is derived from the alcohol.
  - The carbonyl section of the ester makes up the second word of the name and is derived from the carboxylic acid. The name of the carboxylic acid is adapted by changing the '-oic acid' suffix to '-oate'.
- Primary amides are a homologous series of molecules that contain the amide group ($–CONH_2$) at the end of the hydrocarbon chain.
- Amides are named as derivatives of carboxylic acids. To name an amide, take the name of the corresponding carboxylic acid and replace the '-oic acid' suffix with '-ide'.

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8.4 Review *continued*

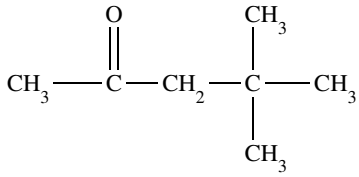
KEY QUESTIONS

Retrieval

1 **a** Define a carbonyl group.
b Identify the classes of organic compounds in which the carbonyl group is found.

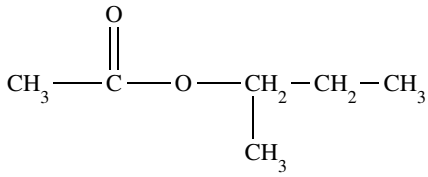
2 Identify the homologous series that each of the following molecules belongs to.

a



b $CH_3-CH_2-CH_2-OH$

c



Comprehension

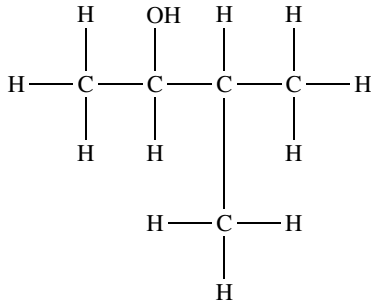
3 Describe each of the following classes of organic compounds by stating the parent molecule they are derived from and the functional group that is present in each.
a haloalkane
b alcohol

4 Draw a representation of the functional group in each of the following classes of compounds.
a aldehyde
b carboxylic acid
c ester

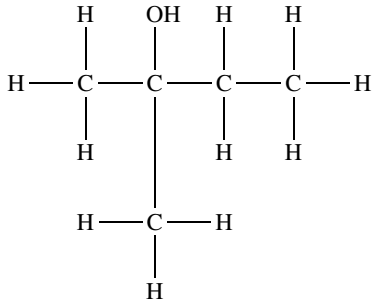
Analysis

5 Classify the following alcohols as primary, secondary or tertiary.

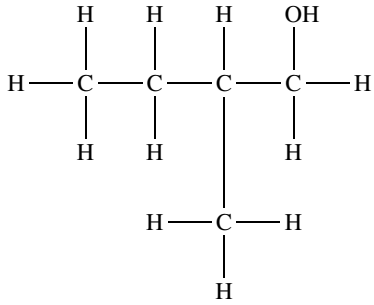
a



b



c



d 3-methylpentan-1-ol
e 3-methylpentan-3-ol

6 Analyse the names of the following organic compounds and draw a structural formula for each.
a 2,2,4-trimethylhexan-3-ol
b 3-ethylpentan-2-amine
c 3-methylbutanenitrile

7 Consider the names of the following organic compounds. Determine whether each name provides sufficient information for you to draw a specific structure. If so, draw the structure and provide the systematic name. If not, deduce what further information is required.
a bromoethane
b 2-methylpropanamine
c dimethylpropanol

8 Analyse the names of the following organic compounds and draw a structural formula for each.
a 3-ethyl-2-methylhexanal
b propyl pentanoate
c 4-methylpentanoic acid

9 Determine why the names for each of the following organic compounds are incorrect and provide the correct names.
a 2-methylbutan-3-ol
b 3-ethylhexan-4-amine

10 Analyse the names of the following organic compounds and explain why each one is incorrect.
a 2-methylbutan-1-one
b pentan-3-al
c 1-methylpropanoic acid

8.5 An overview of IUPAC nomenclature

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand that the systematic rules for naming organic compounds are determined by the International Union of Pure and Applied Chemistry (IUPAC)
- apply the IUPAC rules to systematically name organic compounds from their structures, including compounds that contain two functional groups
- draw structures for organic compounds from their systematic names, including compounds that contain two functional groups.



In the early 1960s, the International Union of Pure and Applied Chemistry (IUPAC) endorsed a common naming system for carbon compounds. These rules are regularly updated and are used worldwide to enable scientists to communicate with each other. The rules ensure that a carbon compound is given a unique name that provides useful information about its structure and distinguishes it from any isomers.

The rules specify the names for different parts of an organic molecule and may include both words and numbers to indicate locations of functional groups and alkyl side chains (for example, see Figure 8.5.1).

This module will summarise and extend your knowledge of the rules that you learnt in the previous modules for naming organic compounds. You will also learn how to name organic molecules that contain two different functional groups.

IUPAC NOMENCLATURE

IUPAC nomenclature is the term used to describe the set of rules by which chemists can name a given compound. The rules can be used in reverse to determine a structure from the IUPAC name. IUPAC names of organic molecules can be short or very long but, whether simple or complex, most IUPAC names follow the same basic pattern.

Most organic molecules can be thought of as being derived from a hydrocarbon **parent molecule**, which provides the basis for the name of the molecule. Part of the IUPAC name reflects which alkane is the parent molecule.

The IUPAC name also indicates which alkyl side chains or functional groups are present in the molecule by adding a suffix to the end of the name or a prefix to the beginning of the name. The positions of alkyl side chains and functional groups are indicated by numbers. As an example, the meaning of each part of the name 3-methylbutan-2-ol, an alcohol, is shown in Figure 8.5.2 on page 272 along with its **structural formula**.



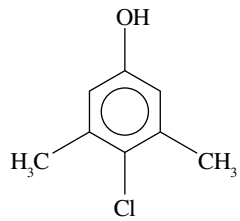


FIGURE 8.5.1 According to the IUPAC rules, the active ingredient in the antiseptic Dettol® has the name 4-chloro-3,5-dimethylphenol.

Summary of IUPAC rules for nomenclature

The following conventions are used for naming organic molecules.

- There are no spaces in a name, apart from the two-word names of esters and carboxylic acids.
- The longest carbon chain is used to derive the parent name. The longest chain must include the functional group for alkenes, alkynes, haloalkanes, alcohols, amines, aldehydes, ketones, carboxylic acids, esters, amides and nitriles.
- The functional group is indicated in the name by adding a suffix to the end of the parent name or a prefix to the beginning of the parent name.
- The names and locations of alkyl side chains and additional functional groups are also added to this parent name.

The IUPAC name indicates the parent molecule from which the name is derived and any functional groups and alkyl side chains that are present.

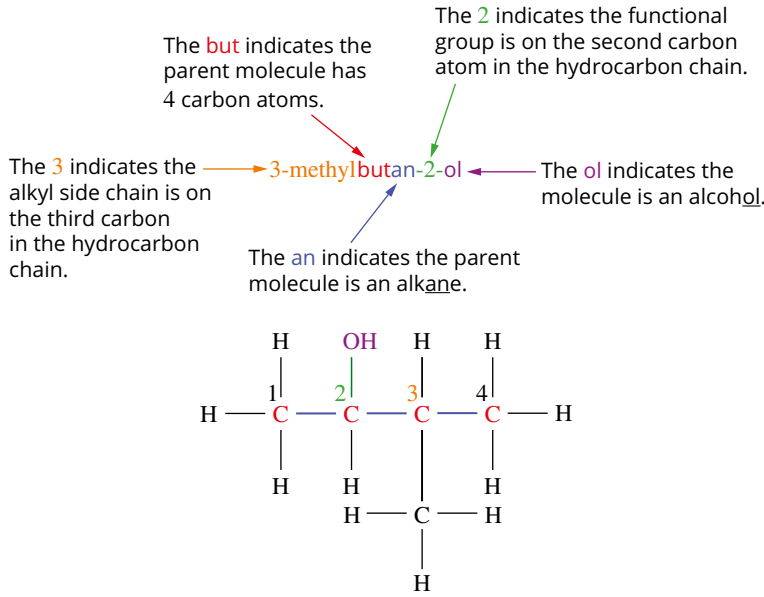


FIGURE 8.5.2 The name and extended structural formula of 3-methylbutan-2-ol. The colours of each part of the name correspond with the section of the structure that it represents.

- Numbers are used to identify the carbon atom that alkyl side chains and functional groups are attached to.
- Numbers and letters are separated by dashes.
- Numbers are separated from other numbers by commas.
- The names of alkyl side chains and additional functional groups are listed as prefixes at the beginning of a name.
- If there is more than one type of alkyl side chain or functional group to be listed at the beginning of a name, they are listed in alphabetical order.
- If there is more than one of the same type of functional group, the prefixes 'di-', 'tri-' or 'tetra-' are used. Each group is still given a number to indicate its position on the carbon chain.

The presence of a particular functional group identifies the homologous series a molecule belongs to and changes the molecule's name, as shown in Table 8.5.1.

TABLE 8.5.1 The identity, functional groups and naming conventions of the homologous series

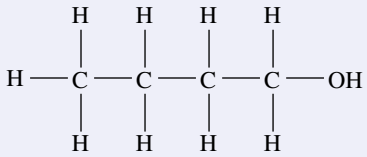
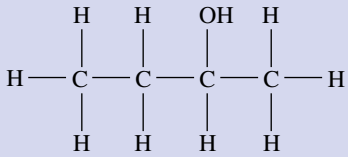
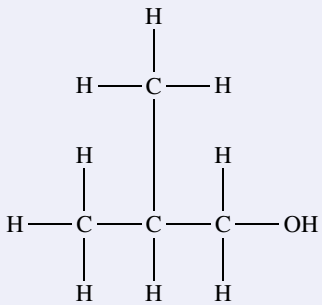
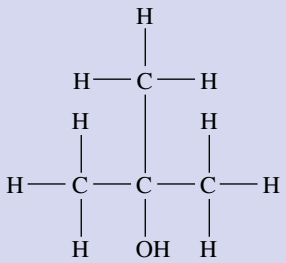
Homologous series	Functional group name	Semistructural formula	Naming convention
alkane	not applicable	not applicable	suffix '-ane'
alkene	carbon–carbon double bond	–C=C–	suffix '-ene'
alkyne	carbon–carbon triple bond	–C≡C–	suffix '-yne'
haloalkane	halo	–F, –Cl, –Br, –I	prefix 'fluoro-', 'chloro-', 'bromo-' or 'iodo-'
alcohol	hydroxyl	–OH	suffix '-ol' occasionally prefix 'hydroxy-'
amine	amino	$-NH_2$	suffix '-amine' occasionally prefix 'amino-'
nitrile	nitrile	–CN	suffix '-nitrile'
aldehyde	carbonyl (aldehyde)	–CHO	suffix '-al' occasionally prefix 'oxo-'
ketone	carbonyl (ketone)	–CO–	suffix '-one' occasionally prefix 'oxo-'
carboxylic acid	carboxyl	–COOH	suffix '-oic acid'
ester	ester	–COO–	two-word name with suffixes '-yl' and '-oate'
amide	amide	$-CONH_2$	suffix '-amide'

Naming organic molecules with a functional group and an alkyl side chain

Organic molecules with functional groups can also have alkyl side chains. The names of alkyl side chains are placed in alphabetical order in front of the parent name. The carbon chain is numbered from the end closest to the functional group to give the lowest possible number to the functional group.

This procedure is illustrated in Table 8.5.2 with the naming of the structural isomers of an alcohol with the molecular formula $C_4H_{10}O$.

TABLE 8.5.2 Names of isomers of an alcohol with the molecular formula $C_4H_{10}O$

Structure	Name
	butan-1-ol
	butan-2-ol
	2-methylpropan-1-ol
	2-methylpropan-2-ol

Naming organic compounds with two functional groups

Many organic molecules have more than one functional group. If the functional groups are the same, a multiplier ('di-', 'tri-' etc.) is used to prefix the functional group. For example, the alcohol in Figure 8.5.3 is named propane-1,2,2-triol. Note that the 'e' is not removed from the corresponding alkane name when there is more than one hydroxyl functional group.

If the molecule has different functional groups, you will need to know which one has the highest priority in order to work out what numbers and names to use.

IUPAC has designated a priority system for functional groups (Table 8.5.3 on page 274). In an organic molecule with two functional groups, the following naming conventions are used.

- The functional group with the highest priority is assigned the lowest possible number and the suffix for this functional group is used in the name.
- The lower priority functional group is indicated by a prefix or alternative name.

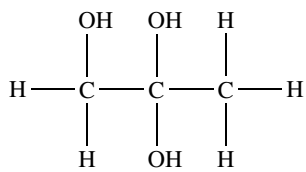


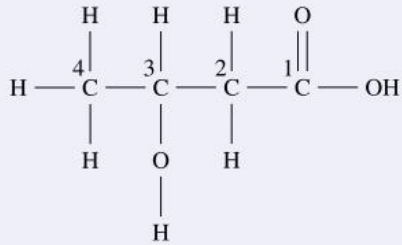
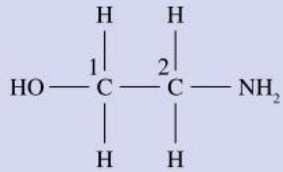
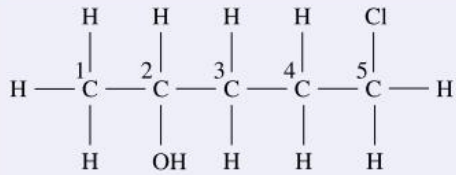
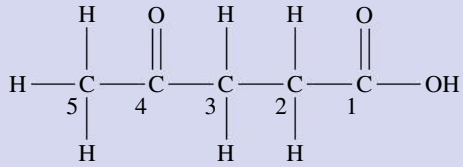
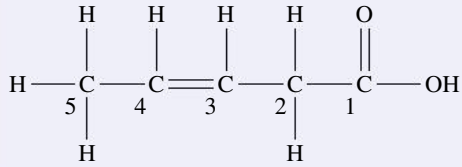
FIGURE 8.5.3 Propane-1,2, 2-triol contains three hydroxyl functional groups; its name contains the multiplier 'tri-'.

TABLE 8.5.3 IUPAC functional group priorities

Priority	Functional group	Suffix	Prefix or alternative name (when needed)
highest	carboxyl	'-oic acid'	–
	ester	'-oate'	'-R-oxycarbonyl'
	amide	'-amide'	'carbamoyl-'
	nitrile	'-nitrile'	'cyano-'
	carbonyl (aldehyde)	'-al'	'oxo-'
	carbonyl (ketone)	'-one'	'oxo-'
	hydroxyl	'-ol'	'hydroxy-'
	amino	'-amine'	'amino-'
	alkene	'-ene'	'-an-' becomes '-en-'
	alkyne	'-yne'	'-an-' becomes '-yn-'
lowest	halo	–	'halo-'

This priority system is illustrated in Table 8.5.4 with the naming of molecules with two different functional groups.

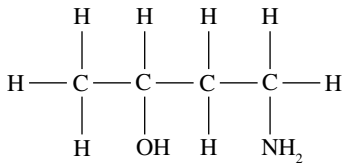
TABLE 8.5.4 Naming molecules with two different functional groups

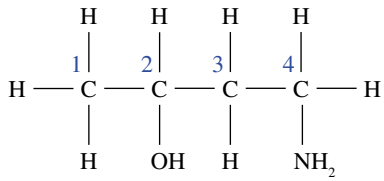
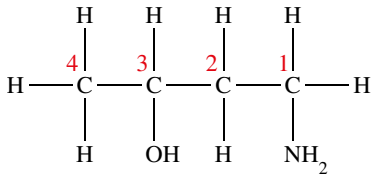
Structure	Name
	3-hydroxybutanoic acid
	2-aminoethanol
	5-chloropentan-2-ol
	4-oxopentanoic acid
	pent-3-enoic acid

Worked example 8.5.1

NAMING AN ORGANIC MOLECULE WITH TWO DIFFERENT FUNCTIONAL GROUPS

Determine the name of this molecule according to IUPAC rules.

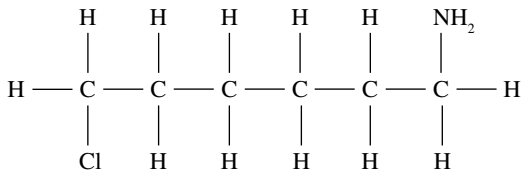


Thinking	Working
Identify the parent name by counting the longest continuous chain of carbon atoms.	There are four carbon atoms in the longest chain, so the parent name is butane.
Identify the functional groups present.	The two functional groups present are hydroxyl and amino.
Determine which functional group has the higher priority and which prefixes and suffixes to use.	The hydroxyl group has the higher priority, so the name of the molecule will end in the suffix '-ol'. The amino group has lower priority and so the prefix 'amino-' will be used.
Number the carbon chain, giving the highest priority group the lowest number possible. Take care to ensure you do not number the carbon chain the wrong way.	The hydroxyl group has the highest priority so the carbon chain should be numbered so that the carbon atom attached to the hydroxyl group has the lowest possible number.  correct numbering  incorrect numbering
Identify the number of the carbon each functional group is attached to.	The –OH is attached to carbon number 2 and $–NH_2$ is attached to carbon number 4.
Use the functional group names and carbon numbers to construct the full name.	The name of the molecule is 4-aminobutan-2-ol.

➤ Try yourself 8.5.1

NAMING AN ORGANIC MOLECULE WITH TWO DIFFERENT FUNCTIONAL GROUPS

Determine the name of this molecule according to IUPAC rules.



8.5 Review

SUMMARY

- IUPAC nomenclature is a set of rules for naming an organic compound.
- The naming of organic molecules follows a series of steps.
  - Identify the longest unbranched carbon chain to determine the parent name. The longest chain must include the functional group.
  - Number the carbon chain so that the carbon attached to the highest priority functional group has the lowest number.
  - Name functional groups by prefixes or suffixes, depending on their priority.
  - Where positional isomers are possible, insert numbers before the name of each functional group. Numbers and letters are separated by dashes.
  - If there is more than one of the same type of functional group, the prefixes 'di-', 'tri-' or 'tetra-' are used. Each group is still given a number to indicate its position on the carbon chain and the numbers are separated by commas.
  - The names of alkyl side chains are added before the parent name. Each alkyl side chain is numbered to show its position on the carbon chain. If there are more than one of the same alkyl side chain, the prefixes 'di-', 'tri-' or 'tetra-' are used. Each side chain is still given a number to indicate its position on the carbon chain and the numbers are separated by commas.
  - If there is more than one type of functional group to be listed at the beginning of the name, or there is a functional group and an alkyl side chain to be listed at the beginning of the name, they are listed in alphabetical order.
  - The name is written with no spaces, apart from the two-word names of carboxylic acids or esters.

KEY QUESTIONS

Retrieval

1 **a** State what the term 'IUPAC' stands for.
b Describe what the term 'IUPAC nomenclature' means.

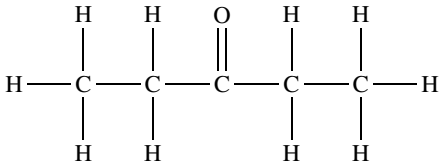
Comprehension

2 Depict the condensed and extended structural formulas of the functional group in each of the following homologous series.
a alkyne
b carboxylic acid
c aldehyde
d amide
e alcohol
f ester

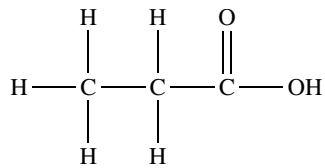
Analysis

3 Analyse the following molecules and determine their systematic names.

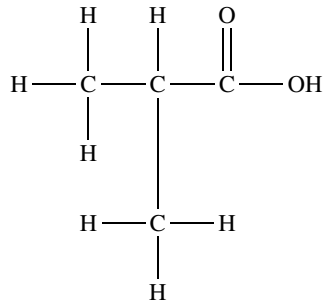
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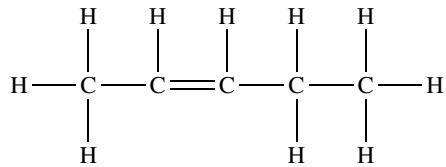
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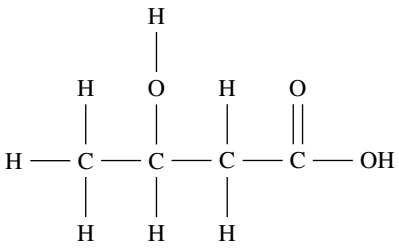


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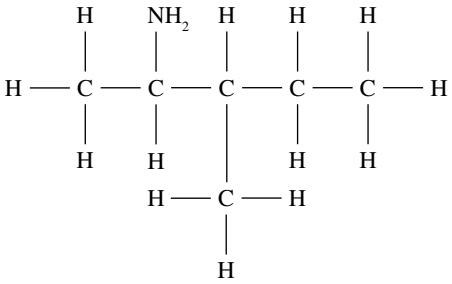


4 Analyse the following molecules and determine their systematic names.

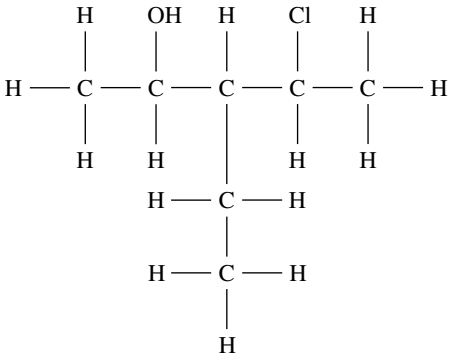
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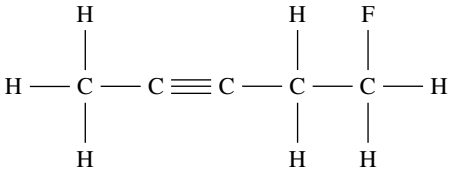
b



c



d



5 Analyse the names of the following organic compounds and draw their structural formulas.

a propan-2-ol
b 1-chlorohexane
c 2-methylbutanal
d 2,3-dimethylbutane

6 Analyse the names of the following organic compounds and draw their structural formulas.

a but-3-ynoic acid
b 4-chloropent-1-en-2-amine
c *trans*-6-bromohept-4-en-2-ol
d 3,4-diethylhex-3-ene

8.6 Boiling point change and volatility of organic compounds



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand that organic compounds display characteristic trends in their boiling points and volatility that are dependent on the functional groups present in their molecules
- describe how intermolecular forces influence the melting point, boiling point and volatility of organic compounds
- predict and explain the trend in melting point, boiling point and volatility for organic compounds that are members of the same homologous series
- predict and explain differences in boiling points and volatility between organic compounds from different homologous series
- predict and explain how molecular shape can influence boiling points of organic compounds
- predict and explain how the position of the functional group can influence boiling points of organic compounds.

The functional groups that are present in organic compounds are responsible for many of their chemical and physical properties. In this module and Module 8.7 you will focus on the effect of functional groups on physical properties such as **melting point**, **boiling point**, **solubility** and **volatility**. Differences in chemical properties will be discussed in a later chapter.

Organic compounds are made up of molecules that are held together in the liquid and solid states via attractive forces known as intermolecular forces. As you will see in this module, the boiling point and volatility of an organic compound depend upon the strength of the intermolecular forces present between its molecules in the liquid state.

You will recall that homologous series are classes of organic compounds that contain the same functional group. Members of a homologous series show a steady change in many of their physical properties. In this module, you will use your knowledge of intermolecular forces and the size of molecules to understand how and why boiling point and volatility change within homologous series.

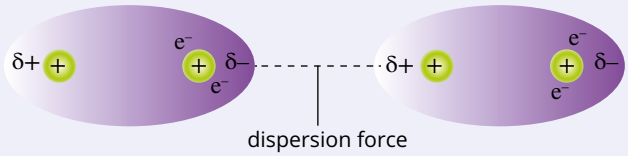
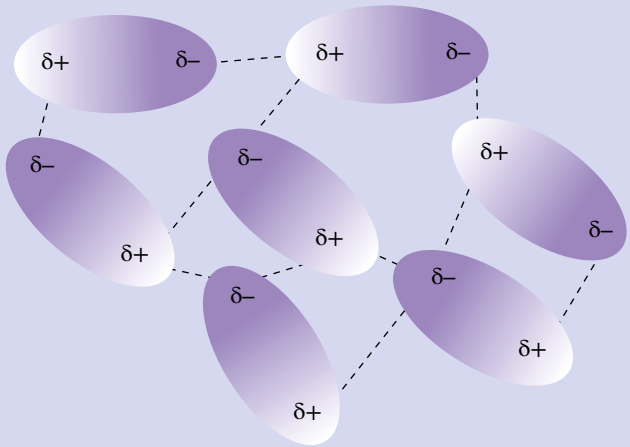
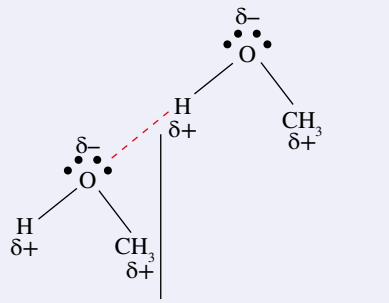
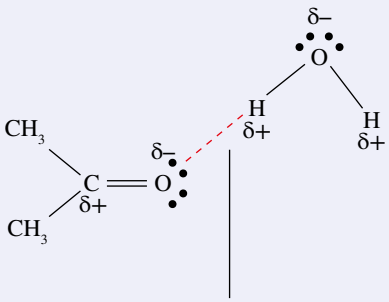
Members of different homologous series contain different functional groups and, as a result, often display very different physical properties. As you work through the module you will use your knowledge of intermolecular forces to explain the effect of different functional groups on melting point, boiling point and volatility.

BOILING POINT

Boiling occurs when molecules in the liquid state have enough energy to completely overcome the intermolecular forces holding them together. This means that organic compounds with stronger intermolecular forces will require more energy, and therefore have higher boiling points, than organic compounds with weaker intermolecular forces.

The different types of intermolecular forces and their relative strengths are summarised in Table 8.6.1 but, for a full discussion, refer to your Unit 2 notes.

TABLE 8.6.1 The different types of intermolecular forces

Intermolecular forces	Example	Description	Relative strength (when comparing molecules of a similar molecular mass)
dispersion forces		Dispersion forces occur between all molecules, no matter whether they are polar or non-polar. Dispersion forces are caused by **temporary dipoles** in the molecules that are the result of random movement of the electrons surrounding the molecules. When comparing molecules of the same molecular mass, dispersion forces are generally weaker than dipole–dipole forces and hydrogen bonding.	the weakest intermolecular forces
dipole–dipole forces		Dipole–dipole forces occur between polar molecules. They result from the attraction between the positive and negative ends of polar molecules.	stronger than dispersion forces but much weaker than hydrogen bonding
hydrogen bonding	 hydrogen bonding between methanol molecules  hydrogen bonding between water and the oxygen atom of propanone (acetone)	This is a particularly strong form of dipole–dipole force. Hydrogen bonding only occurs between highly polar molecules in which a hydrogen atom is covalently bonded to an oxygen, a nitrogen or a fluorine atom. Hydrogen bonding is the strongest type of intermolecular force.	the strongest intermolecular forces

Boiling points of hydrocarbons

Organic compounds with stronger intermolecular forces will require more energy, and therefore have higher boiling points, than organic compounds with weaker intermolecular forces.

You learnt in Module 8.2 that alkanes, alkenes and alkynes are all hydrocarbons. Molecules of hydrocarbons are **non-polar**, which means that the only intermolecular forces of attraction that exist between them in the liquid state are relatively weak **dispersion forces**. Consequently, hydrocarbons generally have lower boiling points than organic compounds of a similar molecular mass that contain **polar** functional groups. Table 8.6.2 compares the boiling points of three hydrocarbons (butane, but-1-ene and but-1-yne) with chloroethane. Butane, but-1-ene and but-1-yne all have very low boiling points; this is consistent with the fact that they are non-polar molecules and are held together in the liquid state with relatively weak dispersion forces. However, chloroethane is a member of the haloalkane homologous series and contains a polar carbon–chlorine bond. Like the hydrocarbons, chloroethane contains weak dispersion forces between its molecules but the presence of the chlorine functional group also allows **dipole–dipole intermolecular forces** of attraction to occur. Because the dipole–dipole intermolecular forces are stronger than the dispersion forces, the boiling point of chloroethane is higher than the boiling points of butane, but-1-ene and but-1-yne.

TABLE 8.6.2 A comparison of the boiling points of hydrocarbons with a haloalkane

Compound	Boiling point (°C)
butane (C_4H_{10})	−0.5
but-1-ene (C_4H_8)	−6.3
but-1-yne (C_4H_6)	−8.1
chloroethane (C_2H_5Cl)	12.5

Boiling point increases as the length of the carbon chain increases because the dispersion forces acting between the molecules get stronger.

Boiling points within a homologous series

The boiling points of compounds within a homologous series generally increase as the length of the carbon chain increases. Table 8.6.3 lists the boiling points of the first 10 members of the alkane homologous series.

TABLE 8.6.3 Boiling points of the first 10 alkanes

Alkane	Molecular formula	Boiling point (°C)
methane	CH_4	−162
ethane	C_2H_6	−89
propane	C_3H_8	−45
butane	C_4H_{10}	−0.5
pentane	C_5H_{12}	36
hexane	C_6H_{14}	69
heptane	C_7H_{16}	98
octane	C_8H_{18}	126
nonane	C_9H_{20}	150
decane	$C_{10}H_{22}$	174

You can see that the boiling points increase from methane to decane. As the carbon chain length increases, the contact surface area between the molecules also increases and the dispersion forces get stronger, as shown in Figure 8.6.1. Because the boiling points of molecular substances are determined by the strength of their intermolecular forces, the boiling points of the alkanes increase as the length of their carbon chains increase.

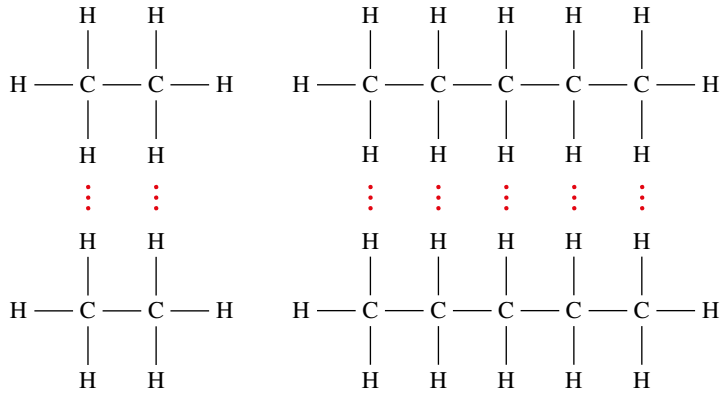


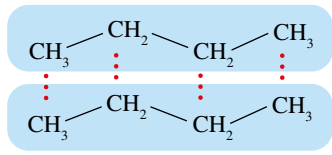
FIGURE 8.6.1 Dispersion forces are the only intermolecular forces between alkane molecules. As molecules become longer, their contact surface area increases which results in stronger dispersion forces.

The effects of branching on boiling point

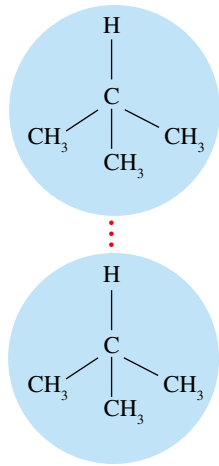
Molecular shape also influences the strength of dispersion forces and, therefore, boiling points. Straight-chain alkanes are able to fit together more closely and tend to have higher boiling points than their corresponding branched-chain isomers, which are unable to fit as closely together.

Figure 8.6.2 shows how the shapes of butane and its branched isomer 2-methylpropane influence the strength of the dispersion forces between their molecules. Butane ($CH_3CH_2CH_2CH_3$) boils at −0.5°C, whereas 2-methylpropane ($(CH_3)_3CH$) boils at −11.7°C. Although both molecules have the same molecular formula (C_4H_{10}), molecules of butane have a greater surface area and can fit together more closely, allowing more contact between the molecules and therefore forming stronger dispersion forces.

> Organic compounds made up of straight-chain molecules tend to have higher boiling points than compounds made up of branched molecules; the straight-chain molecules can fit together more closely to form stronger dispersion forces.



butane
- less compact molecule
- molecules are closer together
- boiling point –0.5°C



methylpropane
- more compact molecule
- molecules are further apart
- boiling point –11.7°C

FIGURE 8.6.2 Molecular shape affects boiling point. Dispersion forces between butane molecules are stronger than those between methylpropane molecules because butane molecules are less compact and can fit together more closely.

Boiling points of aldehydes, ketones and esters

Aldehydes, ketones and esters can be considered together because they are composed of molecules that are held together in the liquid state by dipole–dipole intermolecular forces as well as dispersion forces. Their molecules all contain a carbonyl group that is made up of a carbon–oxygen double bond. Oxygen is more electronegative than carbon, so the carbonyl group is polar. This means that molecules of aldehydes, ketones and esters contain a permanent dipole that can form dipole–dipole attractive forces with neighbouring molecules. The dipole–dipole forces that arise between ketone molecules are shown in Figure 8.6.3.

The strength of these dipole–dipole forces gives aldehydes, ketones and esters higher boiling points than hydrocarbons of a similar molecular mass. However, their boiling points are not as high as the boiling points for alcohols (the reason for this is discussed in the next part of the module). A comparison of the boiling points of members of these homologous series with that of an alkane is shown in Table 8.6.4.

TABLE 8.6.4 Comparison of boiling points of organic molecules with a similar molecular mass from different homologous series

Homologous series	Condensed structural formula	Molecular mass (amu)	Boiling point (°C)
alkane	$CH_3CH_2CH_2CH_3$	58.14	–0.5
alcohol	$CH_3CH_2CH_2OH$	60.11	97
aldehyde	CH_3CH_2CHO	58.09	48
ketone	CH_3COCH_3	58.09	56
ester	$HCOOCH_3$	60.06	32

Boiling points within the homologous series

The boiling points of aldehydes, ketones and esters increase as the carbon chain length increases. For example, Table 8.6.5 shows the boiling points of the first five members of the aldehyde homologous series. Note that methanal has a low boiling point and is a gas at room temperature. Ethanal is also a gas but propanal, butanal and pentanal are liquids.

TABLE 8.6.5 Boiling points of members of the homologous series of aldehydes

Aldehyde	Condensed structural formula	Boiling point (°C)	State at room temperature (25°C)
methanal	HCHO	–19	gas
ethanal	CH_3CHO	20	gas
propanal	CH_3CH_2CHO	48	liquid
butanal	$CH_3CH_2CH_2CHO$	75	liquid
pentanal	$CH_3CH_2CH_2CH_2CHO$	103	liquid

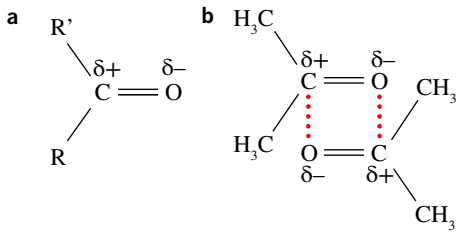


FIGURE 8.6.3 (a) A carbonyl group is polar. (b) Dipole–dipole forces between ketone molecules.

Aldehydes, ketones and esters have higher boiling points than hydrocarbons of a similar molecular mass, but lower boiling points than alcohols.

The observed increase in boiling points is due to the non-polar hydrocarbon portion or 'tail' of the molecules increasing in length, which results in increased contact surface area between the molecules and stronger dispersion forces. This trend is similar to that observed for the alkanes earlier.

Boiling points of alcohols, carboxylic acids, amines and amides

Hydrogen bonds are the strongest of the intermolecular forces and, as a result, molecules that can form hydrogen bonds generally exhibit higher boiling points. Molecules can form hydrogen bonds with neighbouring molecules when they contain an electronegative oxygen, nitrogen or fluorine atom attached to a hydrogen atom. This concept was discussed in detail in Unit 2. Alcohols, carboxylic acids, amines and amides can all form hydrogen bonds and, as shown in Table 8.6.6, they consequently have higher boiling points than alkanes of a similar molecular mass.

TABLE 8.6.6 Comparison of boiling points of compounds with different functional groups based on molecular mass

Homologous series	Compound	Formula	Molecular mass (amu)	Boiling point (°C)
alkane	butane	C_4H_{10}	58.14	−1
alcohol	propan-1-ol	C_3H_7OH	60.11	97.2
carboxylic acid	ethanoic acid	CH_3COOH	60.06	118
amine	propan-1-amine	$C_3H_7NH_2$	59.13	49
amide	ethanamide	CH_3CONH_2	59.08	210

Boiling points of alcohols

Alcohols, carboxylic acids, amines and amides have high boiling points because their molecules can form hydrogen bonds with neighbouring molecules; hydrogen bonds are the strongest of the intermolecular forces.

The higher boiling points of the alcohols are due to the presence of hydrogen bonds between neighbouring alcohol molecules. In contrast, the only intermolecular forces present between non-polar alkane molecules are much weaker dispersion forces.

Oxygen is much more **electronegative** than hydrogen (it has an electronegativity value of 3.4 compared to 2.2 for hydrogen) and the oxygen–hydrogen bond in the hydroxyl functional group is a very polar bond. Figure 8.6.4 shows hydrogen bonding occurring between the partially positive hydrogen atom on one alcohol molecule and a non-bonding electron pair on the oxygen atom of a neighbouring alcohol molecule. The presence of the hydrogen bonds results in the higher boiling points observed.

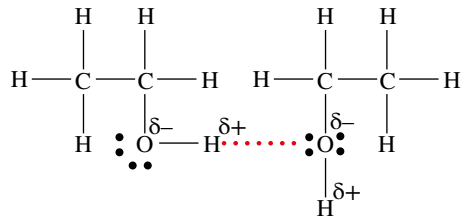


FIGURE 8.6.4 The red dotted line shows the hydrogen bond between molecules such as ethanol that contain the polar hydroxyl functional group.

Boiling points of amines and amides

The presence of highly polar nitrogen–hydrogen bonds in amine and amide molecules means that these molecules can also form hydrogen bonds. The formation of hydrogen bonds between amines and amides is illustrated in Figure 8.6.5.

In amines, the hydrogen bonds form between the non-bonding pair of electrons on the electronegative nitrogen atom and the partially positive hydrogen atom attached to the nitrogen of another amine molecule. In amides, hydrogen bonds form between the non-bonding electron pairs on the oxygen atom of one molecule and the partially positive hydrogen atom attached to the nitrogen of another amide molecule. The strength of the hydrogen bonding between molecules explains the relatively high boiling points of amines and amides when compared to hydrocarbons of a similar molecular mass.

Boiling points of carboxylic acids

Hydrogen bonding also has a marked effect on the boiling points of carboxylic acids. Figure 8.6.6 shows how two molecules of a carboxylic acid in the liquid state can form **dimers** in which two hydrogen bonds occur between the molecules and results in two molecules presenting as one.

The dimer produced is a stable species that has a molecular mass double that of the single carboxylic acid molecule. The increase in size that results from the formation of the dimer increases the strength of the dispersion forces between one dimer and its neighbours. The stronger dispersion forces combined with the hydrogen bonds between molecules results in the higher boiling points observed for carboxylic acids when compared to most other organic molecules of similar molecular masses. (Interestingly, some amides can actually have higher boiling points than carboxylic acids but the reasons for this are beyond the scope of the Queensland syllabus.) Table 8.6.7 highlights the higher boiling points of carboxylic acids compared to alcohols and ketones.

TABLE 8.6.7 Comparison of boiling points of selected carboxylic acids with alcohols and ketones

Name	Condensed structural formula	Molecular mass (amu)	Boiling point (°C)
ethanoic acid	CH_3COOH	60.06	118
propan-1-ol	$CH_3CH_2CH_2OH$	60.11	97.2
propanone	CH_3COCH_3	58.09	56.2
propanoic acid	CH_3CH_2COOH	74.09	141
butan-1-ol	$CH_3(CH_2)_2CH_2OH$	74.14	117
butanone	$CH_3COCH_2CH_3$	72.12	79.6
butanoic acid	$CH_3(CH_2)_2COOH$	88.12	164
pentan-1-ol	$CH_3(CH_2)_3CH_2OH$	88.17	138
pentan-2-one	$CH_3CO(CH_2)_2CH_3$	86.15	102

Boiling points within the homologous series

The boiling points of alcohols, amines, amides and carboxylic acids increase as molecular mass increases. Just as we have seen for the homologous series discussed earlier, as the carbon chain length increases the contact surface area between the molecules also increases and the dispersion forces get stronger; this results in higher boiling points. Figure 8.6.7 on page 284 shows the increase in boiling points within the homologous series of alcohols and carboxylic acids.

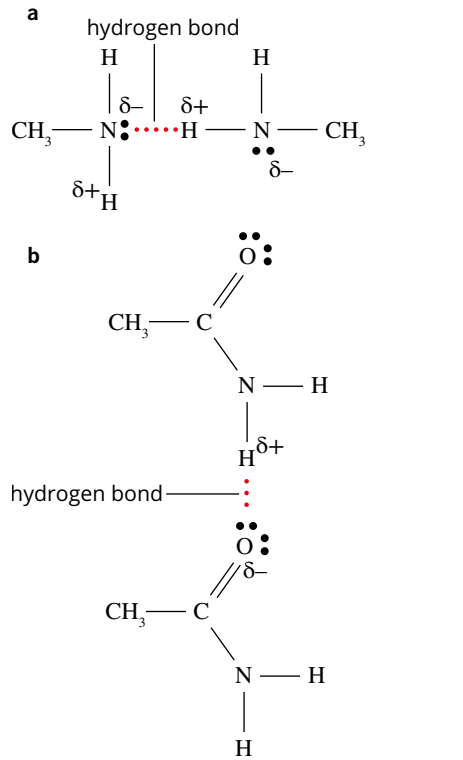


FIGURE 8.6.5 Hydrogen bonding between (a) amine molecules and (b) amide molecules

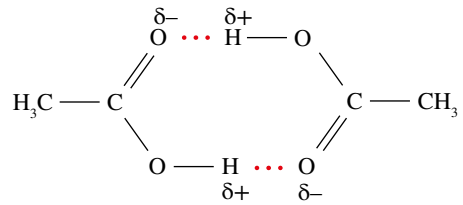
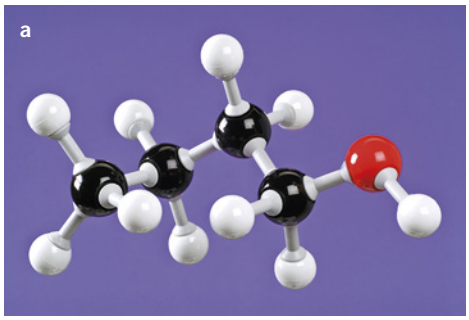
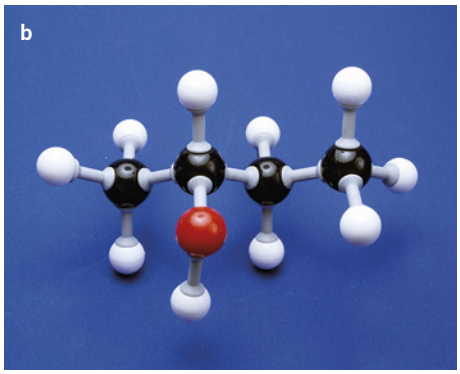


FIGURE 8.6.6 Hydrogen bonding between two ethanoic acid molecules

Carboxylic acids have particularly high boiling points due to their ability to form dimers. The dimers are stabilised by hydrogen bonds and have a molecular mass double that of a single carboxylic acid molecule. This results in stronger dispersion forces between one dimer and its neighbours.





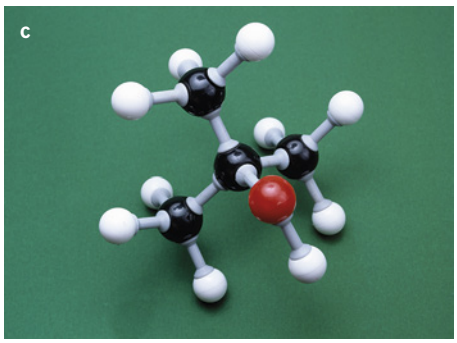


FIGURE 8.6.8 Molecular models of the three isomers of butanol: (a) butan-1-ol, (b) butan-2-ol, (c) 2-methylpropan-2-ol

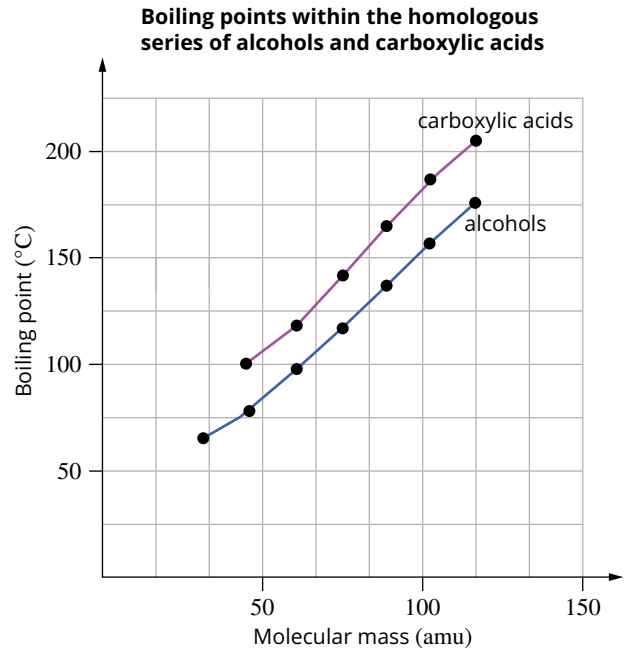


FIGURE 8.6.7 Boiling points of the alcohol and carboxylic acid homologous series with increasing molecular mass. The boiling points of the carboxylic acids are higher than the boiling points of alcohols because of their ability to form dimers, which are stabilised by hydrogen bonds between the molecules.

The effects of branching on boiling point

In the earlier discussion on the boiling points of alkanes, we saw that branched-chain isomers generally have lower boiling points than straight-chain alkanes because their molecules cannot fit as closely together, resulting in weaker dispersion forces. In the case of molecules with functional groups, in addition to the impact of branching on the strength of dispersion forces, other intermolecular forces can also be affected.

For example, in alcohols, the position of the hydroxyl group affects the hydrogen bonding. Figure 8.6.8 shows molecular models for three isomers of butanol: butan-1-ol, butan-2-ol and 2-methylpropan-2-ol. These isomers are examples of primary, secondary and tertiary alcohols, respectively.

As shown in Table 8.6.8, the boiling points of these alcohols decrease in the sequence from primary to secondary to tertiary alcohol. This is because the hydroxyl group becomes increasingly 'crowded' moving from the primary through to the secondary and tertiary isomers; the alkyl groups restrict the molecule's ability to form hydrogen bonds with other molecules.

TABLE 8.6.8 The boiling points of primary, secondary and tertiary alcohols with the formula C_4H_9OH

Alcohol	Type of alcohol	Boiling point (°C)
butan-1-ol	primary	118
butan-2-ol	secondary	100
2-methylpropan-2-ol	tertiary	82

Worked example 8.6.1

PREDICTING WHICH ORGANIC COMPOUND HAS THE HIGHEST BOILING POINT

In each of the following sets of compounds, predict which one would have the highest boiling point.

a butan-1-ol, hexan-1-ol, pentan-1-ol

b pentan-1-ol, 2-methylbutan-1-ol, 2-methylbutan-2-ol

Thinking	Working
Compare the compounds in each set and identify any relationship between them.	**a** All three compounds are members of the alcohol homologous series. They increase in carbon chain length as follows: butan-1-ol < pentan-1-ol < hexan-1-ol **b** All three compounds are structural isomers of each other.
a Determine how the boiling points change within a homologous series. **b** Determine how branched isomers and the position of the functional group affects boiling point.	**a** Boiling points increase within a homologous series. As the carbon chain length increases in size, the strength of the dispersion forces also increases and results in progressively higher boiling points. **b** Branched isomers generally have lower boiling points than straight-chain compounds for two reasons. Firstly, the dispersion forces between branched molecules are weaker than those between straight-chain molecules. Secondly, intermolecular forces formed between functional groups on neighbouring branched molecules are weaker than those formed between straight-chain molecules. This is because the surrounding alkyl groups on the branched molecules 'crowd' the functional groups and restrict their ability to form effective intermolecular forces with neighbouring molecules.
Using your understanding from above, determine which compound in each set has the highest boiling point.	**a** Hexan-1-ol has the longest carbon chain and therefore has the highest boiling point. **b** Pentan-1-ol has the highest boiling point. It is a straight-chain isomer so its molecules can fit together closely and form strong hydrogen bonds. The other two compounds are branched isomers; their alkyl groups crowd the hydroxyl functional groups and restrict the formation of hydrogen bonds between neighbouring molecules.

➤ Try yourself 8.6.1

PREDICTING WHICH ORGANIC COMPOUND HAS THE HIGHEST BOILING POINT

In each of the following sets of compounds, predict which one would have the highest boiling point.

a pentane, decane, octane

b propan-1-amine, propanone, ethanoic acid

TREND IN MELTING POINT WITHIN A HOMOLOGOUS SERIES

Similarly to the observed increase in boiling point with increasing molecular mass, the melting point within a homologous series generally increases with increasing number of carbons in the chain. However, the increase is not as regular as with the boiling point trend. For instance, in the melting points of the alkane series, shown in Table 8.6.9, the melting point of propane (–188°C) is lower than the melting point of both methane (–182°C) and ethane (–183°C).

TABLE 8.6.9 Melting points of the first 10 straight-chain alkanes

Molecule	Formula	Molecular mass (amu)	Melting point (°C)
methane	CH_4	16.05	–182.4
ethane	C_2H_6	30.08	–182.8
propane	C_3H_8	44.11	–187.6
n-butane	C_4H_{10}	58.14	–138.2
n-pentane	C_5H_{12}	72.17	–129.7
n-hexane	C_6H_{14}	86.20	–95.3
n-heptane	C_7H_{16}	100.23	–90.6
n-octane	C_8H_{18}	114.26	–58.8
n-nonane	C_9H_{20}	128.29	–53.5
n-decane	$C_{10}H_{22}$	142.32	–29.6

While melting point generally increases as the length of the carbon chain increases (because the dispersion forces acting between the molecules get stronger), the irregular nature of the trend is a result of differences between odd- and even-numbered carbon chains. As a solid, the even-numbered carbon chains (n = 2, 4, 6 etc.) pack tighter. This means that the intermolecular forces that need to be overcome are stronger and thus require more energy to separate them as the compounds melt.

As with the homologous series of alkanes, the alcohols, shown in Table 8.6.10, also show an increasing melting point as the number of carbons in the chain increases. However, as with the alkanes the first three alcohols do not fit the trend perfectly.

TABLE 8.6.10 Melting points of the first eight straight-chain primary alcohols

Molecule	Formula	Molecular mass (amu)	Melting point (°C)
methanol	CH_3OH	32.05	–97.6
ethanol	C_2H_5OH	46.08	–114.1
1-propanol	C_3H_7OH	60.11	–126.1
1-butanol	C_4H_9OH	74.14	–89.8
1-pentanol	$C_5H_{11}OH$	88.17	–78.9
1-hexanol	$C_6H_{13}OH$	102.20	–44.6
1-heptanol	$C_7H_{15}OH$	116.23	–34.0
1-octanol	$C_8H_{17}OH$	130.26	–15.5

The situation with the alcohols is more complicated as the temperature at which the substance melts is not just dependent upon the strength of the intermolecular forces but also how the solid packs together as some favourable intermolecular interactions may be decreased when as a solid due to steric hindrance which may be less problematic in the more freely moving molecules in the liquid state. Steric hindrance will not be discussed further as it is beyond the scope of this course.

The strength of the intermolecular forces in the alcohol series is related to the hydrogen bonding between neighbouring hydroxyl groups; therefore, the addition of the CH_2 group does not significantly increase the overall intermolecular force between the neighbouring molecules.

VOLATILITY

Organic compounds that are liquids at room temperature are described as being volatile if they evaporate easily; this means that the liquid readily forms a **vapour**. We can often detect volatile organic compounds by their smell. For example, perfumes and air fresheners contain esters that give off a pleasant smell. Nail varnish remover often contains propanone (acetone) which has a very pungent smell. Many volatile organic compounds give off vapours that can be harmful to our health so it is important to be aware of the hazards associated with using them.

The volatility of an organic compound depends upon the strength of its intermolecular forces in the liquid state. A volatile organic compound contains weak intermolecular forces of attraction which are easily overcome so the liquid readily evaporates. Recall that the process of evaporation is different to boiling because evaporation can occur across a range of temperatures, whereas boiling occurs at one specific temperature. However, the boiling point of a compound and its volatility are directly related. Compounds with low boiling points contain weak intermolecular forces and are therefore more volatile than compounds with higher boiling points which contain stronger intermolecular forces.

Organic compounds that contain weak intermolecular forces evaporate more easily and are therefore more volatile than organic compounds that contain strong intermolecular forces.

Volatility is also related to **vapour pressure**. Recall that the vapour pressure of a liquid is the pressure exerted by a vapour in equilibrium with its liquid in a closed container (this was discussed in detail in Chapter 12 of *Pearson Chemistry 11 Queensland Student Book*). Volatile compounds evaporate more readily and therefore have a higher vapour pressure than non-volatile compounds.

Volatility of hydrocarbons

As discussed earlier in the module, hydrocarbons are non-polar and can only form dispersion forces. Small hydrocarbons that are liquids at room temperature are held together with relatively weak dispersion forces; consequently, they are highly volatile and have low boiling points. As the length of the carbon chain increases within a homologous series, the dispersion forces get stronger resulting in the compounds becoming less volatile and having higher boiling points. Consider the first 10 members of the homologous series of alkanes. As shown in Table 8.6.3 on page 280, the boiling points increase as the carbon chain increases in length. Methane, ethane, propane and butane are gases at room temperature but pentane through to decane are liquids; these liquid alkanes range from being highly volatile to volatile and then semivolatile, depending on the length of their carbon chain.

Volatility of haloalkanes, aldehydes and ketones

Haloalkanes, aldehydes and ketones are all polar compounds and those that are liquids at room temperature are held together with dipole–dipole forces as well as dispersion forces. As discussed earlier in the module, dipole–dipole forces are stronger than dispersion forces when comparing molecules of a similar molecular mass or carbon chain length. As a result, haloalkanes, aldehydes and ketones are not as volatile as hydrocarbons and have higher boiling points, as shown in Table 8.6.11.

Just as we saw with the hydrocarbons, as the carbon chain length of the compounds increases, the volatility decreases because the dispersion forces become stronger.

Volatility of alcohols and carboxylic acids

Alcohols and carboxylic acids are much less volatile and have higher boiling points than hydrocarbons, haloalkanes, aldehydes and ketones of a similar molecular mass; this can be seen in Table 8.6.11. The lower volatility and higher boiling points of alcohols and carboxylic acids are due to the relatively strong hydrogen bonding that exists between their molecules in the liquid state. Carboxylic acids are the least volatile out of the two classes because, as discussed earlier, they form dimers, which effectively doubles their molecular mass and increases the strength of the dispersion forces acting between their molecules.

TABLE 8.6.11 Comparison of boiling points of polar compounds with an alkane

Homologous series	Compound	Formula	Molecular mass (amu)	Boiling point (°C)
alkane	butane	C_4H_{10}	58.14	−1
haloalkane	chloroethane	C_2H_5Cl	64.52	12.5
aldehyde	propanal	C_3H_6O	58.09	48
ketone	propanone	C_3H_6O	58.09	56
alcohol	propanol	C_3H_8O	60.11	97
carboxylic acid	ethanoic acid	$C_2H_4O_2$	60.11	118

As seen with the other classes of organic compounds, when the carbon chain length of the compounds increases, volatility decreases due to the dispersion forces becoming stronger.

8.6 Review

SUMMARY

- The melting and boiling points of organic molecules are determined by intermolecular forces. Dispersion forces are always present and there may also be dipole–dipole forces or hydrogen bonds.
- The only forces of attraction between molecules of the alkane, alkene and alkyne homologous series are dispersion forces.
- Molecules of haloalkanes are attracted to each other by dipole–dipole forces in addition to dispersion forces.
- Molecules of aldehydes, ketones and esters have polar carbonyl functional groups and are attracted to each other by dipole–dipole forces.
- Molecules of alcohols, carboxylic acids, amines and amides contain functional groups that can form hydrogen bonds with other molecules.
- When comparing molecules of a similar molecular mass in different homologous series, it is generally true that their melting points and boiling points increase in the following order: alkanes < alkenes < alkynes < aldehydes < ketones < esters < alcohols < carboxylic acids < amines < amides. Carboxylic acids and amides tend to have the highest boiling points.
- The strength of dispersion forces between molecules depends on the size and shape of the molecules.
- When comparing molecules from the same homologous series, boiling points increase as the carbon chain length increases. This is because the longer carbon chains can form stronger dispersion forces between neighbouring molecules.
- When comparing molecules from the same homologous series, melting points generally increase as the carbon chain length increases. This is because the longer carbon chains can form stronger dispersion forces between neighbouring molecules; however, the packing of the molecules in the solid phase can greatly influence the trend, especially for compounds that contain between one and three carbon atoms.
- Straight-chain molecules are able to fit together more closely and tend to have higher boiling points than their corresponding branched-chain isomers, which are unable to fit as closely together.
- The position of functional groups within molecules can also affect boiling points. If surrounding alkyl groups prevent functional groups between neighbouring molecules from approaching each other closely enough, then the intermolecular forces formed between them will not be as effective and will result in lower boiling points.
- Organic compounds that are liquids at room temperature are described as being volatile if they evaporate easily.
- A volatile organic compound contains weak intermolecular forces of attraction that are easily overcome so the liquid readily evaporates.
- Small hydrocarbons that are liquids at room temperature are highly volatile because their molecules are held together with only relatively weak dispersion forces.
- Haloalkanes, aldehydes and ketones are not as volatile as hydrocarbons of a similar molecular mass because they have dipole–dipole forces of attraction holding their molecules together in addition to dispersion forces.
- Alcohols and carboxylic acids are much less volatile than hydrocarbons and haloalkanes, aldehydes and ketones of a similar molecular mass due to the relatively strong hydrogen bonding that exists between their molecules.
- For all organic compounds, as their carbon chain length increases, their volatility decreases because the dispersion forces between their molecules become stronger.

continued over page

8.6 Review *continued*

KEY QUESTIONS

Retrieval

1 State the intermolecular forces of attraction that exist between molecules of alkanes, alkenes or alkynes.

2 State what is meant when a liquid is described as being volatile.

Comprehension

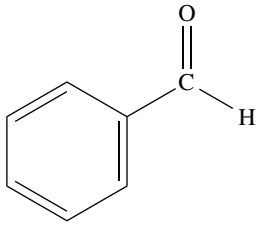
3 Construct a diagram that shows the dipole–dipole forces that exist in the liquid state between molecules of ethanal (CH_3CHO).

4 Explain why a small, non-polar organic compound like pentane is volatile.

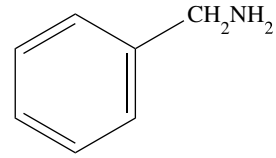
Analysis

5 Pentane, 2-methylbutane and 2,2-dimethylpropane are structural isomers with a molecular formula of C_5H_{12}. Classify these compounds in order of increasing boiling point. Explain your order.

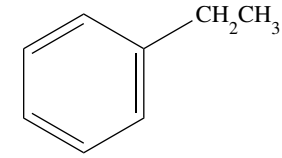
6 Analyse the structural formulas of the three organic compounds below. Classify them in order of increasing boiling point.



benzaldehyde



benzylamine



ethylbenzene

7 The following compounds are liquids at room temperature and have a similar molecular mass. Classify them in order of increasing volatility and explain your order.
butan-1-ol, pentane, butanal

8 Classify the following alkanes in order of increasing volatility and explain your order.
hexane, octane, decane

9 The table below shows the results obtained in a series of experiments to determine the boiling points of various organic compounds.

Experiment	Organic compound	Molecular mass (amu)	Boiling point (°C)
1	CH_3CHO	44.06	20.5
	CH_3CH_2OH	46.08	78.0
	HCOOH	46.03	102
2	$CH_3(CH_2)_2CHO$	72.12	74.8
	$CH_3(CH_2)_2CH_2OH$	74.14	119
	CH_3CH_2COOH	74.09	139
3	$CH_3(CH_2)_4CHO$	100.18	129
	$CH_3(CH_2)_4CH_2OH$	102.20	157
	$CH_3(CH_2)_3COOH$	102.15	152

a Analyse the data and draw conclusions about the boiling points of these organic compounds.

b Identify any anomalies in the results (i.e. identify any results that you would not expect; these results may be due to an experimental error).

c Explain your answers to parts **a** and **b**.

10 An ester can be made via the reaction of an alcohol with a carboxylic acid. The process is called esterification. Because the reaction does not go to completion there is always an equilibrium mixture of reactants and products at the end. The esters can be purified by refluxing and distilling the components of each reaction mixture. The following table shows the boiling points of the reactants and products of several esterification reactions.

Alcohol	Boiling point (°C)	Carboxylic acid	Boiling point (°C)	Ester	Boiling point (°C)
methanol	64.5	methanoic acid	101	methyl methanoate	31.5
ethanol	78.5	propanoic acid	141	ethyl propanoate	99.1
butan-1-ol	117	ethanoic acid	118	butyl ethanoate	126

Analyse the data in the table and identify the ester whose purification process would:

a result in it being the first component collected in the distillation process

b result in it being the last component collected in the distillation process

c be the most difficult to distinguish between the three components in the distillation process.

11 Vapour pressure can be used as a measure of an organic compound's volatility. Consider the vapour pressures (in kilopascals, KPa) for four organic compounds listed as A, B C and D in the table below.

Compound	Vapour pressure (KPa)
A	3850
B	214
C	68.4
D	6.11

a Using your understanding of the relationship between vapour pressure and volatility, classify the compounds in order of increasing volatility.

b In no particular order, the four organic compounds are pentane, ethane, butane and heptane. Determine which letter matches each compound in the table. Explain your answer.

c Predict how the volatility of ethanol would compare with the volatility of the compounds listed in the table.

d Using your understanding of the relationship between vapour pressure and volatility, predict how the vapour pressure of ethanol would compare with the vapour pressures of the alkanes listed in the table.

12 a Using the data provided in the following table, predict the melting point of 1-chlorodecane ($C_{10}H_{21}Cl$).

b Explain the trend in melting points for the haloalkanes from 1-chlorobutane to 1-chlorododecane.

Molecule	Formula	Molecular mass (amu)	Melting point (°C)
chloromethane	CH_3Cl	50.49	–97.5
chloroethane	C_2H_5Cl	64.52	–136.0
1-chloropropane	C_3H_7Cl	78.55	–122.8
1-chlorobutane	C_4H_9Cl	92.58	–123.0
1-chloropentane	$C_5H_{11}Cl$	106.61	–98.8
1-chlorohexane	$C_6H_{13}Cl$	120.64	–93.9
1-chloroheptane	$C_7H_{15}Cl$	134.67	–69.4
1-chlorononane	$C_9H_{19}Cl$	162.73	–39.2
1-chloroundecane	$C_{11}H_{23}Cl$	190.79	–16.7
1-chlorododecane	$C_{12}H_{23}Cl$	204.82	–9.1

8.7 Solubility of organic compounds



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- describe how intermolecular forces influence the solubility of organic compounds
- predict and explain the trend in solubility (in both water and non-polar solvents) for organic compounds that are members of the same homologous series
- predict and explain differences in solubility (in both water and non-polar solvents) between organic compounds from different homologous series.

In the previous module, you learnt that members of a homologous series of organic compounds show a steady change in their boiling points and volatility, which is reflective of the strength of the dispersion forces between their molecules. You also learnt that members of different homologous series often display very different boiling points and vary in their volatility because their molecules are held together by different intermolecular forces. In this module, you will focus on one more physical property, solubility. Just as you observed for boiling point and volatility, you will see that the trends observed for solubility, both within the same homologous series and across different homologous series, are dependent on the strength of the intermolecular forces that can be formed.

SOLUBILITY

The intermolecular forces present in an organic compound have an important effect on its solubility. The different types of intermolecular forces and their relative strengths were covered in Unit 2. Recall that dispersion forces are generally the weakest intermolecular forces; while they are present between all molecules, they are the only intermolecular forces that exist between non-polar molecules. Dipole–dipole forces are stronger than dispersion forces and occur between polar molecules. Hydrogen bonds are the strongest intermolecular forces and only occur between highly polar molecules in which a hydrogen atom is covalently bonded to an oxygen, a nitrogen or a fluorine atom.

In general, a solute will dissolve in a **solvent** that has similar intermolecular forces. In the first step of the dissolving process, energy is required to break the intermolecular forces in both the pure solute and pure solvent. Energy is then released when new intermolecular forces form between the solute and solvent. A solute will only dissolve in a solvent if the energy released in the formation of the new solute–solvent intermolecular forces compensates for the energy required to break the solute–solute and solvent–solvent intermolecular forces in the first place.

Many organic compounds are **insoluble** in water and, when mixed together, form two visible layers, such as when oil is mixed with water (Figure 8.7.1). The solubility of an organic compound in water is dependent on two main factors, namely the functional group present in the compound (due to its interaction with the water molecules) and the length of the hydrocarbon portion of the chain. These factors determine the strength of the intermolecular forces that can be formed with the water molecules, which in turn, determines whether the compound will be soluble.



FIGURE 8.7.1 When oil is mixed with water, two visible layers are formed with the oil floating on top of the water.

As shown in Figure 8.7.2, water molecules are polar and are held together by hydrogen bonds, which are particularly strong intermolecular forces of attraction. When solutes dissolve in water, a relatively large amount of energy is required to break these hydrogen bonds between the water molecules. Organic compounds are therefore more likely to dissolve if their functional groups are able to form similar hydrogen bonds with the water molecules; this is because the energy released when the new hydrogen bonds form compensates for the energy required when the hydrogen bonds between the water molecules are broken in the first place.

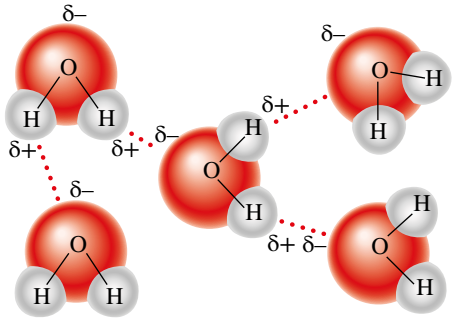


FIGURE 8.7.2 Water molecules are held together by hydrogen bonds.

Solubility of hydrocarbons

The non-polar nature of alkanes, alkenes and alkynes makes them insoluble in water. If they were to dissolve, they could only form weak dispersion forces with the water molecules. The energy released on the formation of these dispersion forces would not be enough to compensate for the much larger amount of energy that would be required to break the hydrogen bonds between the water molecules in the first place. As as a result, the two substances remain separate and do not mix. For example, when hexane is added to water, it simply forms a layer on top of the water; the two liquids do not mix and the hexane floats on top of the water because it is less dense than water. Liquids that do not mix are said to be **immiscible**.

Crude oil is a mixture of many different compounds. Most of these compounds are hydrocarbon compounds of varying lengths. While there are some alkenes in crude oil, many of the hydrocarbons are alkanes. Because alkanes are generally less dense than water, when crude oil spills occur at sea the crude oil floats on the surface, forming a thick insoluble layer. As the oil layer is moved by the waves of the sea, the oil can spread over many hundreds of square kilometres. The presence of the thick oil layer can have disastrous consequences for marine and bird life. Oil that reaches the shore, like the oil spill shown in Figure 8.7.3, has catastrophic effects on beaches and wildlife.

In general, a solute will dissolve in a solvent if it has similar intermolecular forces.



FIGURE 8.7.3 Oil spills at sea can contaminate shorelines and are very difficult to clean due to the lack of solubility of the oil in the water. Other non-polar solvents or physical methods are required to disperse or remove the oil.

Solubility of hydrocarbons in organic solvents

Hydrocarbons readily dissolve in non-polar solvents such as other hydrocarbons or symmetrical haloalkanes (for example, pentane is soluble in octane and tetrachloromethane). This is because the energy required to break the relatively weak dispersion forces between the solvent molecules is low and similar to the energy released when solute–solvent molecules interact. Figure 8.7.4 on page 294 depicts the process of pentane dissolving in hexane. Both are non-polar liquids and only contain dispersion forces; they mix easily because of their similar intermolecular

forces. The energy that is required to break the pentane–pentane and octane–octane dispersion forces in the pure liquids is compensated for by the similar amount of energy that is released when the new pentane–octane dispersion forces form. The liquids are described as being **miscible**; that is, they are soluble in each other.

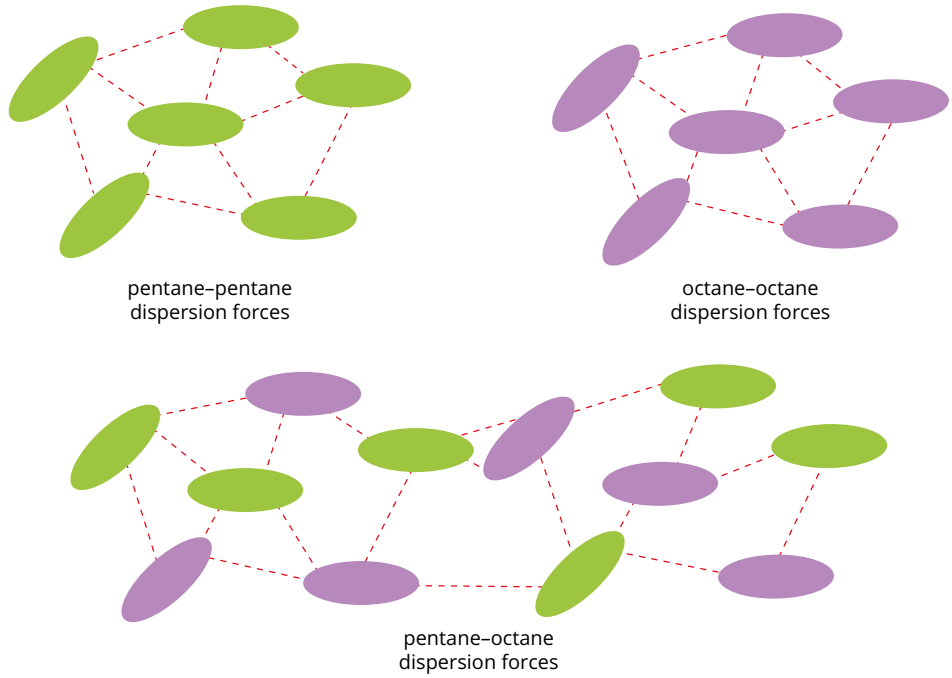


FIGURE 8.7.4 Pentane dissolves in octane. Both molecules are non-polar and are attracted to each other by dispersion forces.



FIGURE 8.7.5 White spirit contains a mixture of alkanes. It is a useful solvent for other non-polar liquids.

Many commercial cleaning agents contain non-polar liquids that are useful for removing oil stains. White spirit is a mixture of alkanes and other hydrocarbons obtained by the refining of crude oil. White spirit is a useful cleaning agent because it can dissolve other non-polar liquids, such as oils and greases. It is used as a solvent in aerosols and in the home as a degreasing solvent. White spirit is also used for cleaning paintbrushes and as a general cleaning agent (Figure 8.7.5).

Solubility of haloalkanes, aldehydes and ketones

As a result of the polar halogen–carbon bond in haloalkanes, haloalkanes are slightly more soluble than hydrocarbons in water. However, the solubility is still very low because the overall influence of the dipole–dipole interactions is small. The influence of the halogen decreases as the length of the carbon chain increases. Many haloalkanes are denser than water and, unlike the hydrocarbons, these liquids settle to form a layer on the bottom when added to water.

Molecules of aldehydes and ketones cannot form hydrogen bonds with themselves. However, Figure 8.7.6 shows how hydrogen bonds can form between a lone pair of electrons on the oxygen atom of the carbonyl group and the partially positive hydrogen atoms in water molecules. The strength of this interaction is enough to make small aldehydes and ketones quite soluble in water.

Hydrocarbons are insoluble in polar solvents such as water, but soluble in non-polar solvents such as other hydrocarbons or symmetrical haloalkanes.

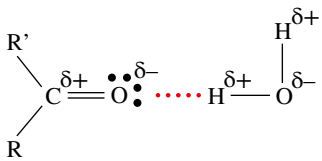


FIGURE 8.7.6 Hydrogen bonds form between the partial negatively charged electron pair on the oxygen atom in a carbonyl group and the partial positively charged hydrogen atom in a water molecule.

Solubility in the homologous series

The solubility of aldehydes and ketones in water decreases with increasing length of the carbon chain. While the carbonyl group of the aldehyde or ketone can form hydrogen bonds with water molecules, the hydrocarbon 'tail' cannot. Only dispersion forces could form between this non-polar part of the chain and the water molecules, but they are not strong enough to break the hydrogen bonds between the water molecules in the first place; consequently, as chain length increases and the hydrocarbon portion of the molecule gets bigger, aldehydes and ketones become less soluble.

Table 8.7.1 shows the solubilities in water of the first five members of the homologous series of aldehydes. The smaller aldehydes are very soluble but as the hydrocarbon chain gets longer, the solubilities quickly decrease.

TABLE 8.7.1 Solubility of aldehydes in water

Aldehyde	Condensed structural formula	Number of carbon atoms	Solubility
methanal	CH_2O	1	very soluble
ethanal	CH_3CHO	2	very soluble
propanal	CH_3CH_2CHO	3	soluble
butanal	$CH_3CH_2CH_2CHO$	4	slightly soluble
pentanal	$CH_3CH_2CH_2CH_2CHO$	5	slightly soluble

Small aldehydes and ketones are soluble in water because they can form hydrogen bonds between their carbonyl group and the hydrogen atoms on the water molecules. As the aldehydes and ketones get bigger and the non-polar hydrocarbon portion of the molecules gets longer, their solubility in water decreases.

Solubility in organic solvents

Aldehydes and ketones become more soluble in organic solvents as they get larger. Organic solvents, such as hexane, benzene and toluene, are non-polar. The increased solubility in these non-polar solvents is due to the longer hydrocarbon chains being able to form stronger dispersion forces with the non-polar solvents.

Solubility of alcohols and carboxylic acids

Small alcohols and carboxylic acids dissolve well in water because hydrogen bonds can form between the polar functional groups of their molecules and adjacent water molecules. While the energy required to break the hydrogen bonds in the pure solute (alcohol or carboxylic acid) and pure solvent (water) is relatively large, the release of energy when new hydrogen bonds form between the solute and solvent compensates for this; as a result, small alcohols and carboxylic acids are highly soluble in water.

As depicted in Figure 8.7.7a, when alcohols dissolve in water, hydrogen bonds form between the partially positive hydrogen atoms of the hydroxyl groups (–OH) and the lone pairs of electrons on the oxygen atoms of adjacent water molecules. There is also attraction between the partially positive hydrogen atoms within water molecules and the lone pairs of electrons on the hydroxyl groups of the alcohol molecules. This is how ethanol dissolves in water in alcoholic drinks, such as beer and wine.

When carboxylic acids dissolve in water, hydrogen bonding occurs between water molecules and both the C=O group and the –OH group, making these compounds more soluble than alcohols in water; this is depicted in Figure 8.7.7b.

Solubility in the homologous series

The smaller alcohols, methanol and ethanol, dissolve readily in water. As the carbon chain increases in length and the alcohols get bigger, their solubility in water decreases. Just as we saw for aldehydes and ketones, this is because the alcohol's non-polar hydrocarbon 'tail' gets longer, reducing the amount of hydrogen bonding that can occur between the alcohol and water molecules, so the alcohols become less soluble. Figure 8.7.8 on page 296 shows the solubility of three alcohols decreasing as their carbon chain length increases.

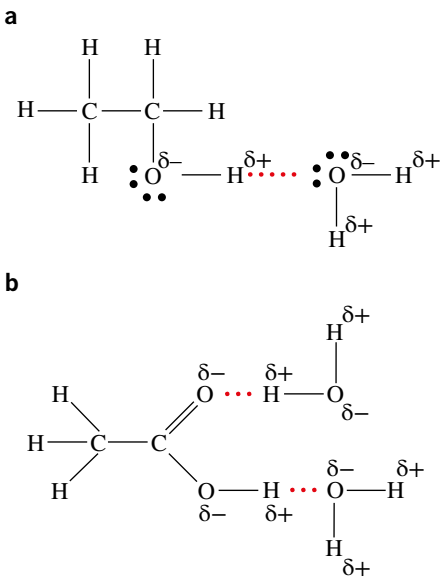


FIGURE 8.7.7 (a) Hydrogen bonding between water molecules and an ethanol molecule (b) Carboxylic acids are more soluble in water than alcohols because hydrogen bonding occurs between the water molecules and both the carbonyl group (C=O) and the hydroxyl group (–OH).

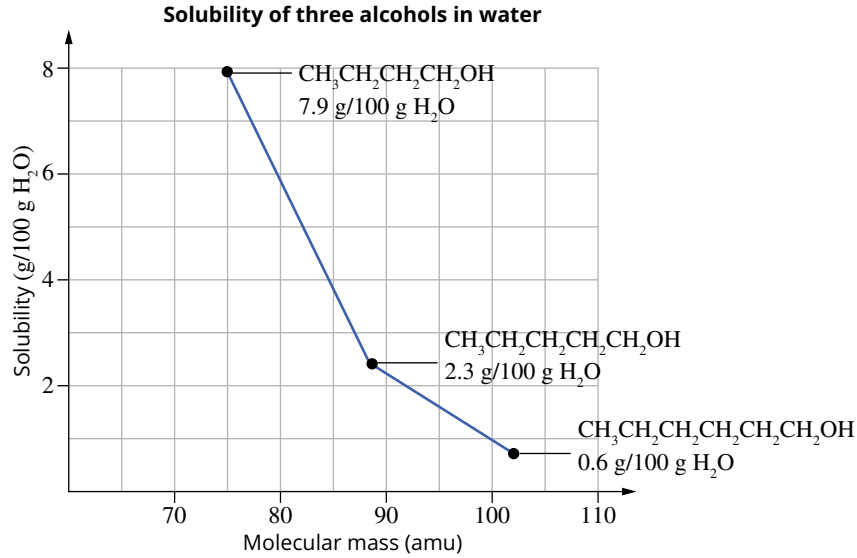


FIGURE 8.7.8 The solubility of alcohols in water decreases with increasing chain length. This trend is also observed for other polar organic compounds such as aldehydes, ketones and carboxylic acids.

Small alcohols and carboxylic acids are highly soluble in water because they can form hydrogen bonds with the water molecules. Carboxylic acids are generally more soluble in water than alcohols because hydrogen bonding can occur on two sites of the carboxylic acid molecules (the C=O and –OH) compared to just the one on alcohol molecules (the –OH).

Like the alcohols, the solubility of the carboxylic acids decreases as the acids increase in size. While the first four members of the carboxylic acid homologous series are highly soluble in water, only the first two members of the alcohol series are highly soluble. This relates to the fact that carboxylic acids can form hydrogen bonds between water molecules with their carbonyl group as well as their hydroxyl group. Being able to form more strong hydrogen bonds benefits the solubility. Table 8.7.2 shows the solubility of the first 10 members of the carboxylic acid homologous series.

TABLE 8.7.2 Solubility of carboxylic acids in water

Name	Condensed structural formula	Number of carbon atoms	Solubility (g per 100 g H_2O)
methanoic acid	HCOOH	1	unlimited
ethanoic acid	CH_3COOH	2	unlimited
propanoic acid	CH_3CH_2COOH	3	unlimited
butanoic acid	$CH_3(CH_2)_2COOH$	4	unlimited
pentanoic acid	$CH_3(CH_2)_3COOH$	5	5.0
hexanoic acid	$CH_3(CH_2)_4COOH$	6	1.1
heptanoic acid	$CH_3(CH_2)_5COOH$	7	0.25
octanoic acid	$CH_3(CH_2)_6COOH$	8	0.07
nonanoic acid	$CH_3(CH_2)_7COOH$	9	0.03
decanoic acid	$CH_3(CH_2)_8COOH$	10	0.015

Solubility in organic solvents

In contrast to their solubility in water, alcohols become more soluble in organic solvents as they get larger. This is because organic solvents, such as hexane, benzene and toluene, are non-polar. Only relatively non-polar alcohols with long hydrocarbon chains dissolve well in non-polar solvents.

Small alcohols such as ethanol, which are very soluble in water, do not dissolve as well in organic solvents. The dispersion forces between their hydrocarbon chains and the solvent are not strong enough to disrupt the hydrogen bonds that hold the alcohol molecules together. Therefore, the alcohol molecules do not separate and disperse throughout the solvent.

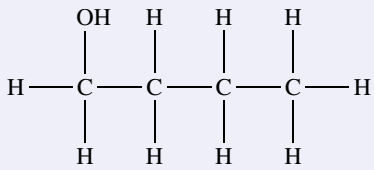
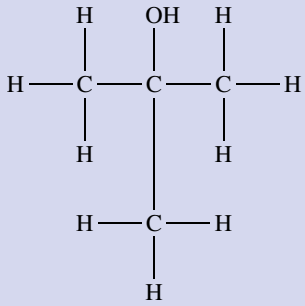
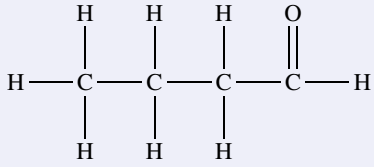
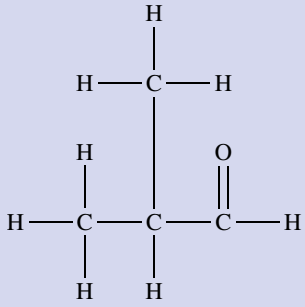
The solubilities of carboxylic acids in organic solvents show similar trends to those of alcohols.

Solubility and molecular shape

The solubility of organic compounds can also be affected by molecular shape. Branched compounds are generally more soluble in water than the corresponding straight-chain compounds. For example, as shown in Table 8.7.3, 2-methylpropan-2-ol is more soluble in water than butan-1-ol and 2-methylpropanal is more soluble than butanal. As discussed in Module 8.6, branched molecules have a smaller contact surface area and, in the pure liquid, they do not fit as closely together as straight-chain molecules. Consequently, the dispersion forces between their molecules are weaker; when the compound is added to water, these weaker dispersion forces enable the molecules to separate from each other more easily and mix with the water molecules.



TABLE 8.7.3 A comparison of the solubilities of straight-chain and branched alcohols

Compound	Molecular formula	Structural formula	Solubility in water at 20°C
butan-1-ol	$C_4H_{10}O$		soluble
2-methylpropan-2-ol	$C_4H_{10}O$		highly soluble
butanal	C_4H_8O		slightly soluble
2-methylpropanal	C_4H_8O		soluble

Worked example 8.7.1

CLASSIFYING ORGANIC COMPOUNDS IN TERMS OF THEIR SOLUBILITY IN WATER

Classify the following compounds in order of their increasing solubility in water. propanoic acid, pentane and butanal	
Thinking	**Working**
Compare the compounds and identify any relationship between them.	Propanoic acid, pentane and butanal are members of different homologous series. However, they all have a similar molecular mass so any difference in their solubility would be due to their different functional groups and how those groups interact with water molecules.
Identify the class of each compound.	Propanoic acid is a carboxylic acid. Pentane is an alkane. Butanal is an aldehyde.
Compare the general solubilities of each class of compounds.	Alkanes are non-polar and are therefore insoluble in water. Aldehydes are polar; small aldehydes can dissolve in water because their carbonyl groups can form hydrogen bonds with water molecules. Carboxylic acids are generally more soluble than other organic compounds because they have two sites on their molecules that can hydrogen bond to water molecules.
Determine how the solubilities of the listed compounds change and order them in terms of increasing solubility.	Propanoic acid would be more soluble than butanal in water. Pentane would not be soluble at all. The order, in terms of increasing solubility in water, is therefore: pentane (not soluble) < butanal < propanoic acid

➤ Try yourself 8.7.1

CLASSIFYING ORGANIC COMPOUNDS IN TERMS OF THEIR SOLUBILITY IN WATER

Classify the following compounds in order of their increasing solubility in water.
ethanol, butan-1-ol and hexan-1-ol

8.7 Review

SUMMARY

- The non-polar nature of alkanes, alkenes and alkynes makes them insoluble in water. The relatively weak dispersion forces that they form with the water molecules are not strong enough to compensate for the energy required to break the hydrogen bonds between the water molecules.
- Hydrocarbons readily dissolve in non-polar solvents, such as other hydrocarbons, because they can form similar dispersion forces with the solvent molecules.
- Haloalkanes are slightly more soluble in water than hydrocarbons because of the polar halogen–carbon bond, but their solubility is still very low.
- Small aldehydes and ketones are soluble in water because they can form hydrogen bonds with the water molecules.
- Small alcohols and carboxylic acids dissolve well in water because hydrogen bonds can form between the polar functional groups of the molecules and adjacent water molecules.
- When carboxylic acids dissolve in water, hydrogen bonding occurs between water molecules and both the C=O group and the –OH group, making these compounds more soluble than alcohols in water.
- Aldehydes, ketones, alcohols and carboxylic acids become less soluble in water and more soluble in organic solvents as the length of their carbon chain increases. This is because the non-polar hydrocarbon part of their molecules becomes longer, making them less able to form hydrogen bonds with water but more able to form dispersion forces with organic solvents.
- Branched compounds of aldehydes, ketones, alcohols and carboxylic acids are more soluble in water than the corresponding straight-chain compounds. This is because, in the pure liquid, branched compounds contain weaker dispersion forces which can be more easily overcome when the compound is mixed with water.

KEY QUESTIONS

Retrieval

1 Recall the two factors that affect the solubility of organic compounds.

Comprehension

2 Explain why hydrocarbons are insoluble in water but soluble in non-polar solvents, such as other hydrocarbons.

Analysis

3 Predict whether each of the following pairs of compounds would be miscible or immiscible.
- **a** pentane and pent-1-yne
- **b** hex-2-ene and water
- **c** 2-bromopropane and 2-chlorobutane

4 Propan-1-ol, ethanoic acid and chloromethane have a similar molecular mass. Categorise the three compounds in order of:
- **a** increasing solubility in water
- **b** increasing solubility in hexane.

5 Analyse the compounds ethanol and pentan-1-ol and determine why ethanol is more soluble in water than pentan-1-ol, but pentan-1-ol is more soluble in hexane than ethanol.

6 Predict which compound you would expect to be more soluble in water: butan-1-ol or butanoic acid. Explain your answer.

7 The solubilities in water of three ketones are given in the table below.

Ketone	Condensed structural formula	Solubility in water at room temperature (mg/mL)
propanone	CH_3COCH_3	1000
butanone	$CH_3COCH_2CH_3$	223
pentan-2-one	$CH_3COCH_2CH_2CH_3$	43

- **a** Compare the solubilities of propanone and pentan-2-one and deduce an explanation for the observed difference.
- **b** Predict how the solubility of 3-methylbutan-2-one would compare with pentan-2-one.

Modelling the structure of organic compounds



Research and planning

Aim

- To examine the bonding, shape and nomenclature of a number of organic molecules with common functional groups.
- To investigate the concept of structural isomers and geometric isomers.

Rationale (scientific background to the experiment)

Physical representation of the bonding and structure of organic molecules enables scientists to identify:

- similarities and differences in the classes of organic compounds
- the various isomerisms that can occur—structural and geometric isomers.

Through this modelling practical, you should recognise the limitations within the models scientists use to describe the various structures seen in the classes of organic compounds.

Timing

Up to 90 minutes—depending on the number of models constructed.

Materials

- molecular model building kit for constructing the molecules listed in Parts A and B of the method section

Method

Risk assessment

Assessment of risks include chemical hazards and physical hazards. Before you commence this practical activity, you must conduct a risk assessment. Complete the template in your skills and assessment book or download it from your eBook.

Part A—Functional groups

For each of the molecules listed below complete the following steps.

1 Construct a three-dimensional model.
2 Draw the three-dimensional model.
3 Write the semistructural formula.
4 Draw the structural formula.

Complete your answers in the Part A results table.

i alkanes: methane, butane
ii alkenes: ethene, propene, but-1-ene, but-2-ene
iii haloalkanes: chloromethane, 1,2-dichloroethane
iv alcohols: ethanol, butan-2-ol
v amines: methanamine, propan-1-amine
vi nitriles: ethanenitrile, hexanenitrile
vii aldehydes: methanal, 2-methylbutanal
viii ketones: butanone, pentan-3-one
ix carboxylic acids: methanoic acid, propanoic acid
x esters: methyl ethanoate, hexyl propanoate
xi amides: ethanamide, 3-methylbutanamide

Part B—Isomers

For each of the molecules listed below complete the following steps.

1 Construct a three-dimensional model.
2 Draw the structural formulas of all possible isomers.
3 Write the IUAC (systematic) names for each isomer where possible.

Complete your answers in the Part B results table.

i 1,1-dichloroethene
ii pentane
iii butanol
iv 4-hydroxybutanoic acid

Variables

i Independent: the functional groups.
ii Dependent: the bonding ability of the molecule.

Analysing

Raw data

1 Record your observations in the following table.

PART A RESULTS

Molecule	Draw your model	Semistructural formula	Structural formula
methane			
butane			
ethene			
propene			
but-1-ene			
but-2-ene			
chloromethane			
1,2-dichloroethane			
ethanol			
butan-2-ol			
methanamine			
propan-1-amine			
ethanenitrile			
hexanenitrile			
methanal			
2-methylbutanal			
butanone			
pentan-3-one			
methanoic acid			
propanoic acid			
methyl ethanoate			
hexyl propanoate			
ethanamide			
3-methylbutanamide			

PART B RESULTS

Molecule	Draw your model	Structural formula	Systematic name
dichloroethane			
pentane			
butanol			
hydroxybutanoic acid			

Processed data

2 State what type of bonding is present within the molecules.

3 Complete the following table naming the functional groups present in the molecules constructed in Part A.

Homologous series	Functional group present
alkanes	
alkenes	
haloalkanes	
alcohols	
amines	
nitriles	
aldehydes	
ketones	
carboxylic acids	
esters	
amides	

Reflect and check that your data analysis demonstrates these characteristics

- ☐ Effective investigation of phenomena is demonstrated by the collection of sufficient and relevant raw data.
- ☐ Accurate application of algorithms, visual and graphical representations of data is demonstrated by appropriate processing and presentation of data to aid the analysis and interpretation of data.

Analysis

4 Explain the difference between a structural isomer and a geometric isomer. From the models that you have built in Part B, draw an example of each type of isomer.

Reflect and check that your analysis demonstrates these characteristics

- ☐ Systematic and effective analysis of evidence is demonstrated by a thorough and appropriate error analysis.
- ☐ Systematic and effective analysis of evidence is demonstrated by a thorough identification of relevant trends, patterns and relationships.
- ☐ Insightful and valid interpretation of evidence is demonstrated by drawing a valid and defensible conclusion based on the analysis.

Interpreting and communicating

Conclusion

1 **a** State your conclusion. Explain how the alkane has changed structurally and chemically because of the presence of the functional group.

b Explain the evidence you have collected that leads you to this conclusion.

Evaluation

2 Assess your analysis and conclusion. Identify whether the modelling of the different homologous series provided an effective and efficient method of determining the differences in the homologous series.

Improvements

3 Critique the experiment. If you were to repeat the experiment, identify the steps that you would do differently. Discuss the following in your answer:

a Analyse how you would change the methodology to help improve the accuracy of the results.

b Evaluate how accurately you performed the tasks and the skills that you need to improve on in your technique.

c Explain how the collection of data could be improved or uncertainty reduced.

Reflect and check that your evaluation demonstrates these characteristics

- ☐ Critical evaluation of processes is demonstrated by a discussion of the reliability and validity of the experimental process supported by evidence such as the quality of the data (as quantified in the error analysis).
- ☐ Critical evaluation of the conclusion is demonstrated by a discussion of the veracity of the conclusions with respect to the error analysis and limitations or sufficiency of the data.
- ☐ Insightful evaluation of processes and conclusions is demonstrated by a suggestion of improvements or extensions to the experiment which are logically derived from the analysis of the evidence.

Chapter review

08

KEY TERMS

alcohols
aldehydes
alkanes
alkenes
alkyl side chain
alkynes
amides
amide functional group
amines
amino functional group
benzene
boiling point
bond energy
bond strength
carbonyl functional group
carboxyl functional group
carboxylic acids
chain isomers
cis-isomer
cis-trans isomers
condensed structural formula
crude oil
cyclic molecule
cycloalkanes
cyclohexane
delocalised
delocalised electrons
dimers
dipole–dipole intermolecular forces
dispersion forces
electronegative
electronic configuration
ester
ester functional group
extended structural formula
functional group
geometric isomers
halo functional group
haloalkane
halogen
homologous series
hydrocarbons
hydrocarbon skeleton
hydrogen bonds
immiscible
insoluble
International Union of Pure and Applied Chemists (IUPAC)
isomers
IUPAC nomenclature
ketones
melting point
miscible
molecular formula
nitriles
nitrile functional group
non-polar
optical isomer
organic chemistry
parent alkane
parent molecule
petroleum
polar
positional isomers
primary alcohol
primary amides
primary amines
primary haloalkane
saturated molecule
secondary alcohol
secondary haloalkane
solubility
solvent
stem name
stereoisomers
structural formulas
structural isomers
temporary dipoles
tertiary alcohol
tertiary haloalkane
tetrahedral
trans-isomer
unsaturated molecule
valence electrons
valence number
vapour
vapour pressure
volatility

KEY QUESTIONS

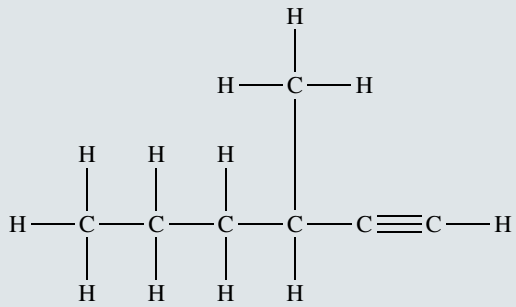
Retrieval

1 Determine which molecular formula indicates a non-cyclic alkane.
- **A** C_3H_6
- **B** C_5H_8
- **C** C_6H_6
- **D** C_7H_{16}

2 Identify which statement about isomers is incorrect.
- **A** Isomers can have very different chemical and physical properties.
- **B** There are two main types of isomers: structural isomers and stereoisomers.
- **C** Isomers can have different molecular formulas as long as they contain the same type of atoms.
- **D** Isomers are molecules that have the same molecular formula but a different arrangement of atoms.

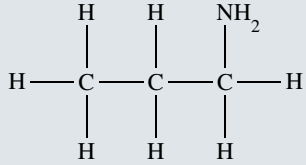
3 Identify the functional group present in alcohols.
- **A** hydroxyl
- **B** carbonyl
- **C** carboxyl
- **D** halogen

4 Identify which class of compounds the following molecule belongs to.



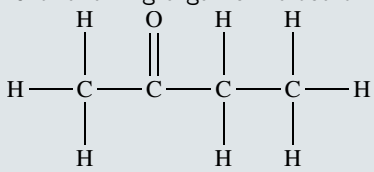
- **A** an alkane
- **B** an alkene
- **C** an alkyne
- **D** cyclohexane

5 Identify the class of compound and the functional group present in the following organic molecule.



A class = amine, functional group = amino
B class = ketone, functional group = carbonyl
C class = ester, functional group = carboxylate
D class = amide, functional group = carboxamide

6 Identify the class of compound and the functional group present in the following organic molecule.



A class = ketone, functional group = carbonyl
B class = alcohol, functional group = hydroxyl
C class = aldehyde, functional group = carbonyl
D class = carboxylic acid, functional group = carboxyl

7 Identify what the 'pent' part of the name 2-methylpent-2-ene refers to.
A The molecule is an alkene.
B The double bond is on carbon number 5.
C The molecule contains an alkyl side chain.
D The parent molecule contains five carbon atoms.

8 Identify which statement about boiling points of organic compounds is false.
A Molecular shape affects the boiling points of organic compounds.
B Organic compounds that contain weak intermolecular forces have high boiling points.
C The boiling points of alkanes generally increase as the length of the carbon chain increases.
D The boiling points of organic compounds are dependent on the functional groups present in the compounds.

9 Identify which one of the following statements is true.
A A volatile compound contains weak intermolecular forces of attraction and evaporates easily.
B A volatile compound contains strong intermolecular forces of attraction and evaporates easily.
C A volatile compound contains weak intermolecular forces of attraction and does not evaporate easily.
D A volatile compound contains strong intermolecular forces of attraction and does not evaporate easily.

10 Identify which one of the following statements about the solubility of organic compounds is false.
A Hydrocarbons dissolve well in water.
B Small alcohols and carboxylic acids dissolve well in water.
C A solute will dissolve in a solvent that has similar intermolecular forces.
D Organic compounds that are insoluble in water often dissolve well in organic solvents.

11 Define the following terms.
a structural isomers
b stereoisomers

12 The IUPAC name of an organic compound indicates which functional group is present in the molecule by adding a suffix to the end of the name. For each of the following classes of compounds, state the suffix that would be used.
a alcohol
b amine
c ketone
d carboxylic acid

13 State how the boiling points of compounds within a homologous series change as the length of the carbon chain increases.

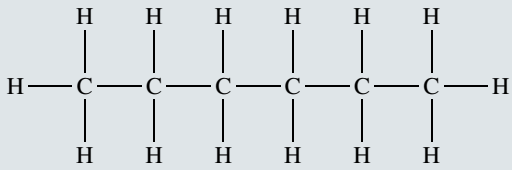
Comprehension

14 Represent the alkane heptane using its condensed molecular formula.

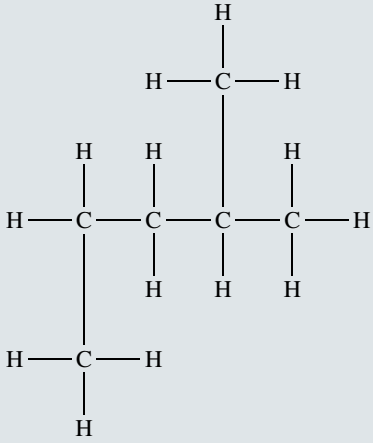
15 The condensed structural formula of 2-methylbutane is $CH_3CH(CH_3)CH_2CH_3$. Draw its corresponding extended structural formula.

16 The structural formulas of three hydrocarbons are shown below. Represent them with their systematic names.

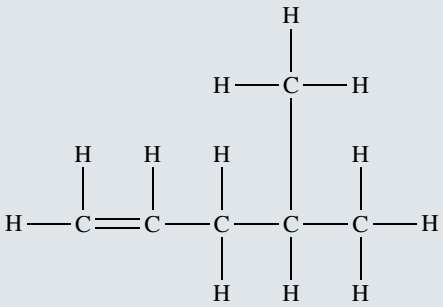
a



b



c



17 The following relates to the hydrocarbon with the molecular formula C_3H_4.
- **a** Identify the class of compounds to which the hydrocarbon belongs.
- **b** Draw the extended structural formula of this hydrocarbon.
- **c** State the hydrocarbon represented by this structural formula.

18 Draw the following:
- **a** *trans*-1,2-dichloroethene
- **b** *cis*-1,2-dichloroethene

19 Draw the *cis*- and *trans*-isomers of hex-3-ene.

20 Describe:
- **a** an aldehyde
- **b** carboxylic acid.

21 Draw an extended structural formula for an ester with four carbon atoms and circle the ester functional group. (Hint: there is more than one possible answer.)

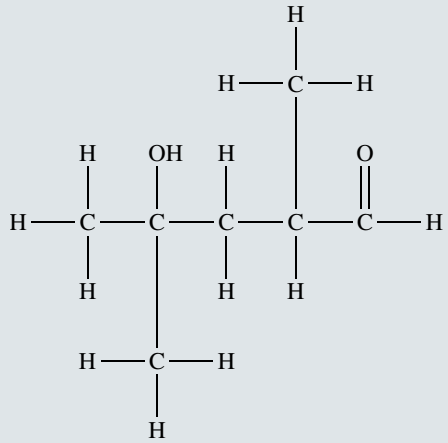
22 Describe the features of the following IUPAC names and explain what information they provide.
- **a** 3-methylpentanamine
- **b** octan-4-ol
- **c** 2-methylhexan-3-one

Analysis

23 Compare the boiling points of octane and ethane and explain why octane has a higher boiling point than ethane.

24 Compare the solubility in water of carboxylic acids and alkanes and explain why carboxylic acids are more soluble than alkanes.

25 Determine the condensed structural formula for the following organic molecule by analysing its extended structural formula.

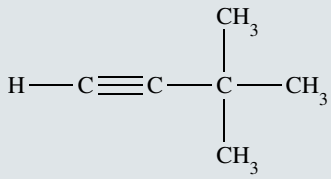


26 Determine the extended structural formula for the following organic compound by analysing its condensed structural formula.
$CH_3CH(CH_3)CO(CH_2)_3NH_2$

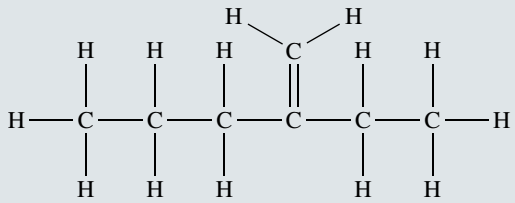
27 Analyse the systematic names of the following alkanes and draw their extended structural formulas and corresponding condensed structural formulas.
- **a** 2,2,3-trimethylpentane
- **b** 4-ethyl-2-methylhexane

28 Analyse the structural formulas of the following alkenes and alkynes and determine their systematic names.

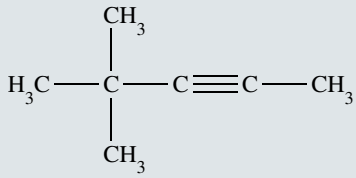
a



b



c



29 Analyse the systematic names of the following hydrocarbons and draw their extended structural formulas.
- **a** 2,3-dimethylpent-2-ene
- **b** 5,5-dimethylhex-2-ene
- **c** 3-ethylhex-3-ene

30 Explore and discuss the following statements.

a The hydrocarbon 2-methylbut-2-yne does not exist.

b The hydrocarbon 2,2-dimethylbut-1-ene does not exist.

c Prop-1-ene is usually just named propene but it is more correct to use the name but-1-ene rather than butene.

31 Analyse the following incorrect names for three unsaturated hydrocarbons. For each, discuss what is wrong with the name and determine the correct name.

a 2,2-dimethylpent-5-ene

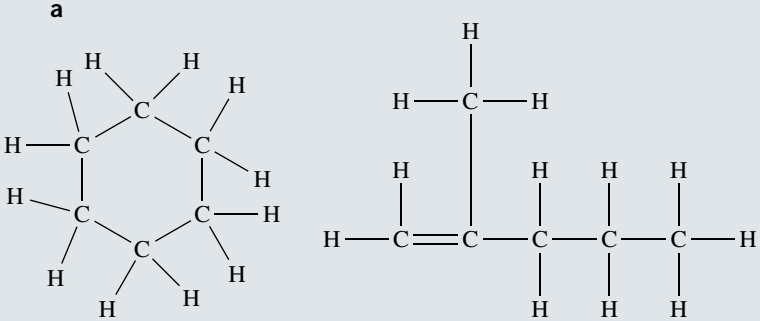
b 1-methylbut-2-ene

c 3-methylbut-2-ene

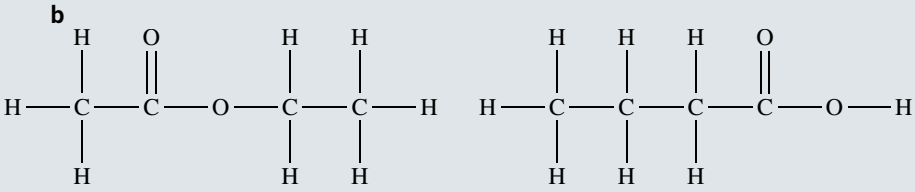
32 Determine all of the possible structural isomers for the organic compound with the molecular formula C_4H_9Cl. Draw the structural formulas for the isomers and deduce which compounds are positional isomers and which are chain isomers.

33 For each of the following pairs of compounds, determine whether the molecules are structural isomers, identical or unrelated.

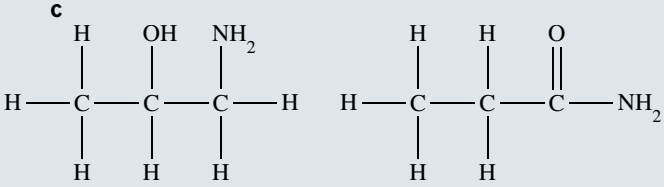
a



b



c



34 Determine in which of the following alkenes *cis-trans* isomers would be possible. Draw and name the *cis-trans* isomers.

a $H_2C{=}CHCH_2CH_3$

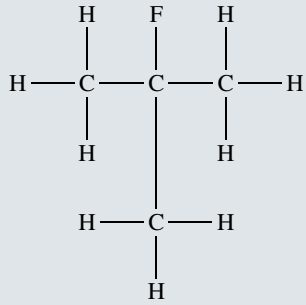
b $H_3CHC{=}CHCH_3$

c $H_3CHC{=}CHCl$

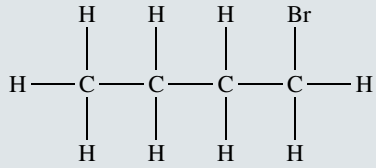
d $(H_3C)_2C{=}C(CH_3)_2$

35 Classify the following haloalkanes as primary, secondary or tertiary.

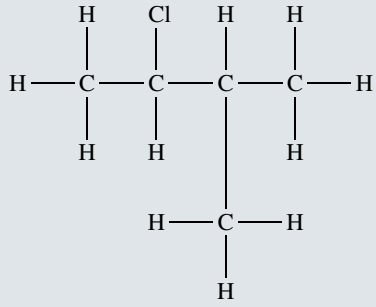
a



b



c



36 Determine the structural formulas for the aldehyde and ketone that have a molecular formula of C_3H_6O.

37 Determine the names of the following compounds from their condensed structural formulas.

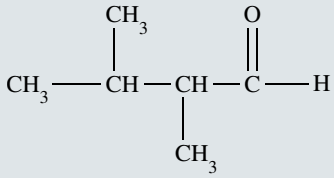
a $CH_3CHOH(CH_2)_3CH_3$

b $CH_3CH_2CH(CH_3)COOH$

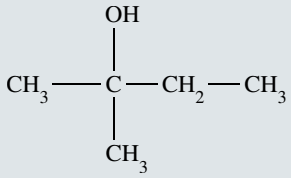
c $CH_3COCH(CH_3)CH_2CH_3$

38 Determine the names of the following compounds from their extended structural formulas.

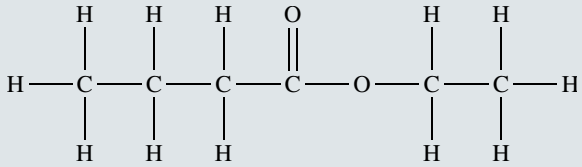
a



b



c



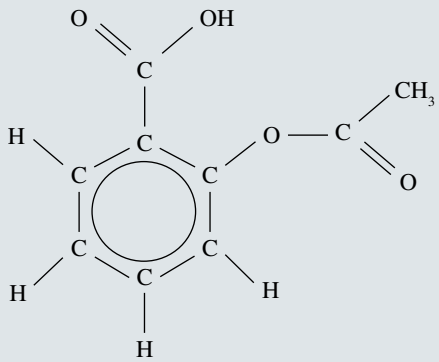
39 Analyse the names of the following organic compounds and determine their structural formulas.

a 2-methylpropanamide

b 4-ethyl-2-methylhexan-3-one

c 3-methylbutanenitrile

40 The image below shows the structure of aspirin (acetylsalicylic acid).



a Identify the ester functional group in the structure of aspirin.

b Determine the structure of the alcohol and carboxylic acid that reacted together to produce aspirin.

41 Analyse the following information and draw an isomer that corresponds to the specification in each part of the question.

a An aldehyde that is a structural isomer of pentan-2-one.

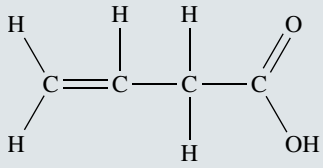
b A secondary alcohol that is a structural isomer of butan-1-ol.

c A cyclic compound that consists of six carbon atoms in a ring and is a structural isomer of hex-2-ene.

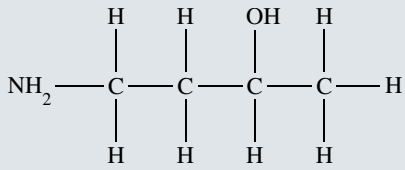
d An alkene that is a structural isomer of but-1-ene.

42 Determine the names of each of the following organic compounds.

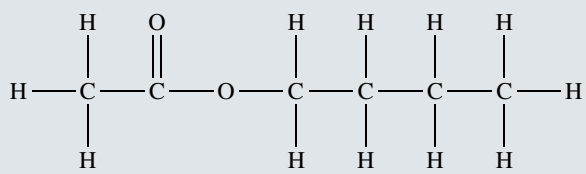
a



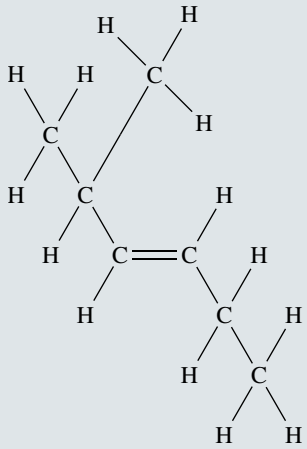
b



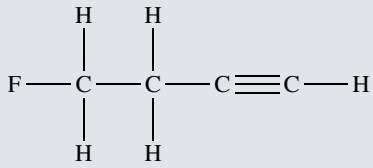
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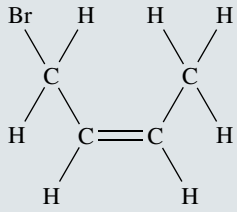
d



e



f



43 Determine the structural formula of:

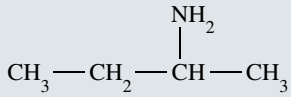
a ethyl propanoate

b *cis*-oct-4-enoic acid

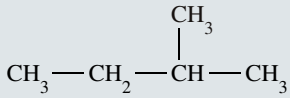
c 3-methylbutan-1-amine.

44 Classify the following compounds in order of increasing boiling point. Explain your order.

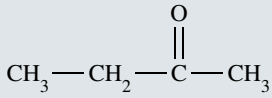
A



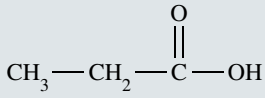
B



C



D



45 Explore how and why the amount of branching present in a compound affects its boiling point. Provide an example to illustrate your explanation.

46 Classify the following compounds in order of increasing boiling point.

a $CH_3CH(CH_3)CH(CH_3)CH_2CH_2OH$

b $CH_3(CH_2)_5CH_2OH$

c $CH_3CH(CH_3)CH_2CH_2CH_2CH_2OH$.

47 Analyse the compounds $CH_3CH_2CH_3$, CH_3CH_2OH and CH_3CHO. Determine which compound:

a has the highest boiling point

b is the most volatile

c has the highest vapour pressure.

48 Explain why, when comparing the effect of functional groups on the boiling points of different homologous series, it is important to compare molecules with a similar molecular mass.

49 The boiling points for some of the members of the homologous series of alkanes are given in the table below.

Alkane	Molecular formula	Boiling point (°C)
methane	CH_4	–162
ethane	C_2H_6	–89
propane	C_3H_8	
butane		–0.5
pentane		
hexane		
heptane		
octane		125
nonane		
decane		174

a Complete the 'Molecular formula' column of the table.

b Plot a graph of boiling point against the number of carbon atoms.

c Draw a line of best fit through the points.

d Alkane X (a straight-chain alkane) boils at 98°C. State the likely identity of this alkane.

e Alkane Y (also a straight-chain alkane) boils at –42°C. State the likely identity of this alkane.

f Deduce where on the graph the boiling point of 2-methylbutane would lie.

50 Determine whether each of the following pairs of compounds would be either miscible or immiscible with each other.

a hexane and hex-2-yne

b pentane and pent-1-ene

c pent-1-yne and water

d 3-bromobutane and 3-chloropentane

51 Analyse the compounds CH_3OH, $CH_3(CH_2)_3OH$ and $CH_3(CH_2)_6OH$.

a Classify the compounds in order of increasing solubility in water.

b Explain your answer to part **a**.

c Classify the compounds in order of increasing solubility in hexane.

d Explain your answer to part **c**.

Knowledge utilisation

52 An organic chemist concludes that an unknown haloalkane with a molecular formula of $C_5H_{11}Cl$ contains a tertiary chlorine atom. Determine a possible structure and name for this organic compound.

53 Determine the two structural isomers for the organic compounds with molecular formula $C_3H_6O_2$. Draw and name them. Analyse their structures and discuss how their boiling points would differ.

54 An unknown organic compound was analysed in the laboratory and was found to be highly soluble in water and to have a very high boiling point of 163°C. It was found that the compound had a molecular mass of 85.1 amu, was made up of carbon, hydrogen and oxygen, and contained a carbonyl group. Assess the information given and determine a possible structure and name for this organic compound.

55 Intermolecular bonding can greatly affect the boiling point of a molecule.

a Research and design an experiment that will enable you to create a list of increasing boiling points of organic molecules. Your list should include alkanes, alkenes, alkynes, haloalkanes, alcohols, amines, aldehydes, ketones, carboxylic acids, esters, amides and nitriles.

b Deduce the increasing boiling point list from the organic molecules.

c Explain why, in terms of bonding, you would see this order.

OPTIONAL: Adapt your experiment to explore how the presence of *cis-trans* isomers or two functional groups within the molecule might change the boiling point.

CHAPTER

09 Chemical properties and reaction pathways

The versatility of the carbon atom forms the basis for carbon chemistry, also called organic chemistry. It is, however, the functional groups that determine the chemical reactivity of these molecules. These groups increase the chemical reactivity compared to that of alkanes. They are 'value-added extras' that are evident in characteristic chemical properties and functions of carbon-based compounds. In Chapter 8 you learnt about the effect functional groups have on physical properties such as boiling point, solubility and volatility. In this chapter, you will understand more about the chemical reactions of the different classes of organic compounds and how chemists synthesise products by manipulating the conditions and reagents of known reaction pathways.

Syllabus subject matter

Topic 1 • Properties and structure of organic materials

■ ORGANIC REACTIONS AND REACTION PATHWAYS

- appreciate that each class of organic compound displays characteristic chemical properties and undergoes specific reactions based on the functional group present; these reactions, including acid–base and oxidation reactions, can be used to identify the class of the organic compound
- understand that saturated compounds contain single bonds only and undergo substitution reactions, and that unsaturated compounds contain double or triple bonds and undergo addition reactions
- determine the primary, secondary and tertiary carbon atoms in halogenoalkanes and alcohols and apply IUPAC rules of nomenclature
- describe, using equations:
  - oxidation reactions of alcohols and the complete combustion of alkanes and alcohols
  - substitution reactions of alkanes with halogens
  - substitution reactions of haloalkanes with halogens, sodium hydroxide, ammonia and potassium cyanide
  - addition reactions of alkenes with water, halogens and hydrogen halides
  - addition reactions of alkenes to form poly(alkenes)
- recall the acid–base properties of carboxylic acids and explain, using equations, that esterification is a reversible reaction between an alcohol and a carboxylic acid
- recognise the acid–base properties of amines and explain, using equations, the reaction with carboxylic acids to form amides
- recognise reduction reactions and explain, using equations, the reaction of nitriles to form amines and alkenes to form alkanes
- recognise and explain, using equations, that:
  - esters and amides are formed by condensation reactions
  - elimination reactions can produce unsaturated molecules and explain, using equations, the reaction of haloalkanes to form alkenes

- understand that organic reactions can be identified using characteristic observations and recall tests to distinguish between:
  - alkanes and alkenes using bromine water
  - primary, secondary and tertiary alcohols using acidified potassium dichromate (VI) and potassium manganate (VII)
- understand that the synthesis of organic compounds often involves constructing reaction pathways that may include more than one chemical reaction
- deduce reaction pathways, including reagents, conditions and chemical equations, given the starting materials and the product.

SCIENCE AS A HUMAN ENDEAVOUR

Use of organochlorine compounds as insecticides: Organochlorine compounds, such as DDT, chlordane and lindane, were identified as powerful insecticides in the 1950s because their structure makes them chemically unreactive.

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9.1 Understanding the reactivity of organic compounds

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand aspects of functional groups that change the chemical characteristics of a hydrocarbon
- understand key laboratory tests that identify certain classes of organic chemicals.

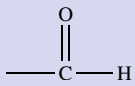
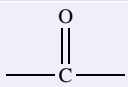
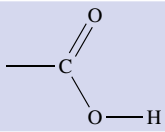
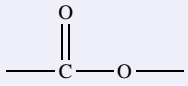
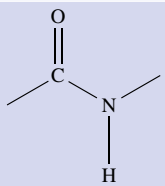


The four valence electrons of the carbon atom are a starting point for building a diverse range of organic compounds. The carbon 'backbone' may contain single, double and triple bonds between carbon atoms, bonded hydrogen atoms, as well as an array of new atoms formed into functional groups (as described in Chapter 8). These functional groups bring features such as high or low electronegativity, charged clouds in the form of non-bonding electrons and areas that are protected by high bond stability. Therefore, each class of organic compound exhibits common chemical characteristics that are identified through the reactions of their functional groups. It is important to remember that the class is the name of the group and the functional group is their common and characteristic group of atoms. Some strategies for determining the presence of these groups are outlined in this module.

CLASSES OF ORGANIC COMPOUNDS AND THEIR FUNCTIONAL GROUPS

In Chapter 8 you learnt about the many organic compound classes. You can review these by referring to Table 9.1.1. They are defined by their functional group.

TABLE 9.1.1 Key classes of organic compounds

Class	Functional group	General formula
alkane	C–C	R
alkene	C=C	R=R´
alkyne	C≡C	R≡R´
alcohol	–OH	ROH
haloalkane	–X (X = F, Cl, Br, I)	RX
aldehyde		RCHO
ketone		RCOR'
carboxylic acid		RCOOH
ester		RCOOR'
amide		RCONHR
nitrile	–C ≡ N	RCN
amine	$-NH_2$	$R-NH_2$

The class is the name of a group of similar molecules, and the functional group is their common and characteristic group of atoms.

CHEMICAL PROPERTIES RESULTING FROM FUNCTIONAL GROUPS

Hydrocarbons of the alkane family have a limited range of chemical reactivity. This range increases when functional groups are present. The chemical properties of molecules containing functional groups are diverse because different functional groups allow particular reactions to occur.

Effects of polar bonds

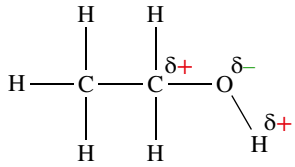


FIGURE 9.1.1 Polar bonds in ethanol

Alkane molecules are non-polar due to the tetrahedral arrangement of bonds around each carbon atom. Also, there is an insignificant difference in electronegativity of atoms (0.4) in a carbon–hydrogen bond. When a functional group containing an atom of higher electronegativity, such as nitrogen, oxygen or a halogen, is attached to a carbon, there is unequal sharing of the electrons in the bond resulting in the formation of a **polar bond**. Carbon has an electronegativity of 2.6, and oxygen has an electronegativity of 3.4. Therefore, the difference in the electronegativity values of C and O (0.8) means that the C–O bond is polar, as shown in Figure 9.1.1. This polarity allows many possible electrostatic charge interactions with other molecules and has myriad consequences for both physical and chemical properties (refer to Chapter 8 for information about physical properties).

Smaller hydrocarbons exhibit large changes in character; however, larger molecules will still have significant non-polar properties due to the non-polar 'tail' as shown in Figure 9.1.2. A simple way to look at this is with the addition of an OH functional group. When the molecule is small, the polarity of the OH tail is very influential (Figure 9.1.1) but as the chain length of the alcohol increases, the polar influence of the OH functional group lessens (Figure 9.1.2). This means that ethanol is very soluble in water but octanol has low solubility in water ($0.3\,g\,L^{-1}$).

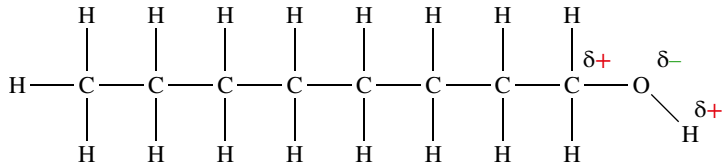


FIGURE 9.1.2 Polar bonds in octanol

Another example of a polar functional group is the carboxyl group (–COOH group) in carboxylic acids. In these molecules, both the C–O single bond and the C=O double bond are polar. This unequal sharing of electrons weakens the O–H covalent bond in the functional group of the acid. In water, carboxylic acids dissociate, as shown in Figure 9.1.3, as a result of the polarity of the COOH group.

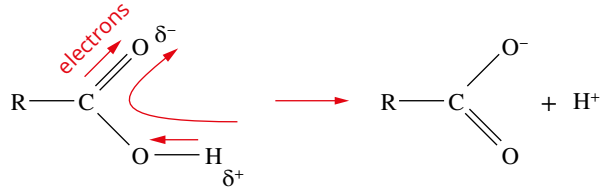


FIGURE 9.1.3 Dissociation of a carboxylic acid

Effects of non-bonding electrons

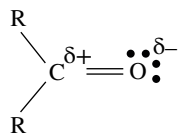


FIGURE 9.1.4 The non-bonding electrons of the carbonyl group in this ketone molecule contribute to the substantial dipole in this ketone.

Carbon atoms in organic molecules always form four covalent bonds. In saturated molecules, these are tetrahedrally arranged single bonds, and they use all carbon's valence electrons. This provides a stable structure free from charge imbalances. Atoms in functional groups often have valence electrons that do not take part in covalent bonding, known as non-bonding electrons. Elements common in functional groups are nitrogen, oxygen and halogens. These atoms have one, two and three pairs of non-bonding electrons, respectively. This means that, in addition to the oxygen atom being more electronegative than carbon, they cause a localised area of partial negative charge in the molecule, as shown in Figure 9.1.4. This creates a dipole in the region of the carbon atom.

Species that have a positive charge or an area of partial positive charge are called electrophiles (meaning 'electron-liking'). They react with electron-rich areas. Species that have a negative charge or area of partial negative charge are called nucleophiles (meaning 'nucleus-liking'). Electrostatic charge interactions between these species form the basis for many organic chemistry reactions, in particular the addition of electron-rich groups to the C atom in the carbonyl group. Their strength is often great enough to overcome activation energies associated with reactions. A more detailed study of the mechanism behind these organic reactions is outside the scope of the syllabus.

Effects of double and triple bonds

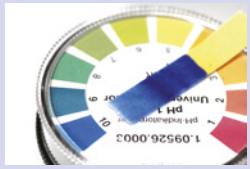
In alkenes and alkynes, the electrons in the double and triple bonds often take part in chemical reactions. The most common of these are addition reactions; for example the reaction of an alkene (unsaturated) with hydrogen to form an alkane (saturated). These reactions are explained in Module 9.2.

The same type of conversion of an alkyne to an alkane via an addition reaction is more difficult to complete. A reason for this is that greater energy is required to break a triple bond. The bond energy of the C=C double bond is 614 kJ mol^{-1} and the bond energy of the C≡C is 839 kJ mol^{-1}. The greater the bond energy, the greater the energy required to break the bond. Addition reactions involving the breaking of the C≡C can occur if a suitable **catalyst** is used. These types of reactions are described in Module 9.2.

TESTING FOR CLASSES OF ORGANIC COMPOUNDS

Laboratory testing can identify classes of organic compounds. By eliciting reactions involving both the functional group and a coloured compound, different classes of organic compound can be easily distinguished by a colour change. Examples of these tests are shown in Table 9.1.2. Three key examples are determination of organic acids and bases using a pH indicator, determination of an alkene, and determination of primary, secondary and tertiary alcohols.

TABLE 9.1.2 Summary of some tests for classes of organic compounds

Class detected	Test	Result	Chemical process
carboxylic acids	add to water and test for pH		Dissociation of the acid and release of H^+ into solution; refer to Module 9.1
amines	add to water and test for pH		ionisation of the base and release of OH^- into solution; refer to Module 9.1
alkenes	add bromine water; a colour change from brownish-red to colourless indicates an alkene		two bromine atoms are added to the molecule at the position of the double bond; refer to Module 9.2
1°, 2° and 3° alcohols	add acidified potassium dichromate (or potassium permanganate) and heat; a colour change from yellow to green is observed for 1° and 2° but not 3° tertiary alcohols		1° alcohols will react to form carboxylic acids, 2° alcohols will react to form ketones and 3° alcohols will not react; refer to Module 9.3

Unsaturated compounds cause a colour change to bromine water.

No change is observed with saturated compounds.

Primary and secondary alcohols cause a colour change to acidified potassium dichromate.

No change is observed with tertiary alcohols.

Determination of organic acids and bases using a pH indicator

The strong polarity of the carboxylic acid functional group will result in easy dissociation of the molecule when added to water. This means that H^+ is released into solution. By using universal indicator, or by adding a carbonate, the presence of aqueous H^+ can be detected.

Amines are organic bases that react with hydrogen ions and so result in a greater concentration of OH^- ions in solution. A pH indicator will reveal a high pH for an amine in solution.

Determination of an alkene

The presence of a C=C double bond in alkenes compared to saturated alkanes is detected using bromine water. The brownish-red bromine solution will become colourless in the presence of an alkene. Two bromine atoms are added in the position of the double bond which is converted to a single bond (Figure 9.1.5). This reaction is described further in Module 9.2. Nowadays the use of bromine in the laboratory is limited due to its hazardous nature. More commonly the presence of a double bond is determined using potassium permanganate which decolourises from purple in the presence of a double bond.

Potassium permanganate is also known as potassium manganate(VII)

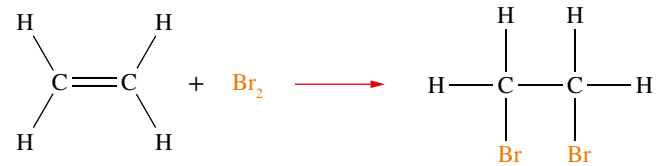


FIGURE 9.1.5 Determination of an alkene using bromine solution

Determination of primary, secondary and tertiary alcohols

You will recall from Module 8.4 that in primary, secondary and tertiary alcohols (commonly represented as 1°, 2° and 3° alcohols respectively) the hydroxyl group is positioned in different parts of the molecule, as shown in Figure 9.1.6. This results in changes to the molecule's reactivity. By using a strong oxidising agent such as acidified potassium dichromate ($H^+/K_2Cr_2O_7$), or potassium permanganate ($H^+/KMnO_4$), alternate colour changes are observed. 1° alcohols will react to form an aldehyde and then be further oxidised to a carboxylic acid (colour change from yellow to green); 2° alcohols will react to form a ketone but not react further to the carboxylic acid (colour change from yellow to green); and 3° alcohols will not react (solution remains yellow). These oxidation reactions are further explained in Module 9.3.

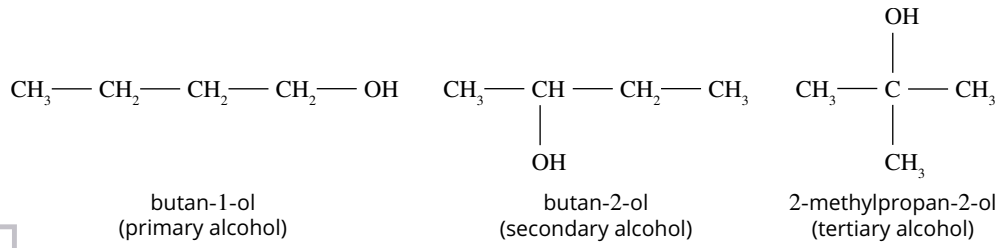


FIGURE 9.1.6 Examples of 1°, 2° and 3° alcohols showing the different positions of the hydroxyl group (–OH)

WS 4.1.6 PA 4.1.1

9.1 Review

SUMMARY

- Organic compounds are grouped into classes. Each class is characterised by a common functional group.
- Reactivity in organic molecules is conferred by the functional groups present and these reactions can be used to identify classes.
- Highly electronegative atoms in functional groups cause bond polarity and areas of partial negative and positive charge.
- A polar bond, non-bonding electrons and electrons in double and triple bonds are areas of charge disparity in molecules that attract oppositely charged species, often leading to a chemical reaction.
- A molecule containing a carboxylic acid group will exhibit a low pH in water, and a molecule containing an amine group will exhibit a high pH in water.
- A molecule containing a carbon–carbon double or triple bond will turn bromine water from brownish-red to colourless.
- A molecule containing a hydroxyl group as a 1° or 2° alcohol can be oxidised by an oxidising agent, whereas a 3° alcohol cannot be oxidised.

KEY QUESTIONS

Retrieval

1 Use Table 9.1.1 on page 311 to identify how many classes of organic compounds shown contain:

a oxygen

b nitrogen

c a halogen.

Comprehension

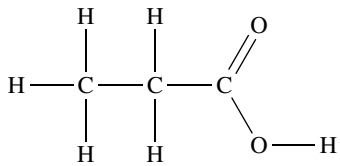
2 Determine which pH would be higher between ethanoic acid solution and ethylamine. Provide a reason for your answer.

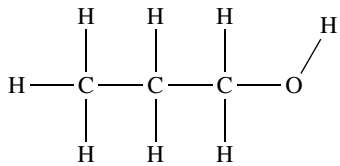
3 A sample known to contain an alcohol does not react (produces no colour change) with acidified potassium dichromate. Draw a possible structure for this alcohol molecule.

4 Two alcohols, propanol and decanol, are placed in separate test tubes containing water and then stirred. Explain why after several minutes the liquids in one test tube separate into two distinct layers but this does not happen in the other test tube.

Analysis

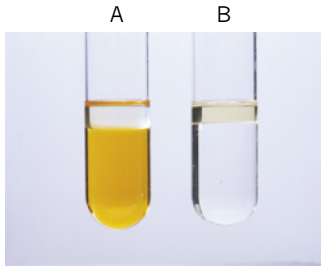
5 Determine what test/s you would perform to identify the following compounds.





6 Two samples of cooking oil containing either a saturated or unsaturated fat were added to test tubes containing bromine water.

Explain how your observations can help you determine which sample is olive oil and which is coconut oil.



9.2 Chemical reactions of alkanes, haloalkanes and alkenes



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand that alkanes and alkenes undergo combustion
- understand that alkanes undergo substitution reactions with halogens (Reaction 1)
- understand that haloalkanes undergo substitution reactions with halogens (Reaction 2), cyanide ions (Reaction 3), ammonia (Reaction 4) and hydroxide ion (Reaction 11)
- understand that alkenes undergo addition reactions with hydrogen (Reaction 5, also known as reduction), halogens (Reaction 6), water (Reaction 7) and hydrogen halides (Reaction 8)
- understand that alkenes undergo addition polymerisation reactions to form polymers (Reaction 10)
- recognise that addition of a hydrogen halide to an alkene (Reaction 8) can be reversed—this is called an elimination reaction (Reaction 9)
- recognise the specific reactions of alkanes and alkenes that require certain conditions to proceed
- explain organic chemistry reactions using chemical equations and structural formulas.

The simpler hydrocarbons such as alkanes, haloalkanes and alkenes undergo chemical change in several key ways. The reactions discussed here are **substitution reactions** (reacting atom(s) are exchanged for others in the molecule), **addition reactions** (atom(s) are added to the molecule), **elimination reactions** (a pair of atoms in the molecule are removed and a double bond formed) and **combustion**. These reactions are driven by forces integral to polar bonds, multiple covalent bonds and non-bonding pairs (described in Module 9.1); however, the mechanism of each reaction is outside the scope of the syllabus and so will not be discussed here. The reactions described in this module are introduced in Figure 9.2.1.

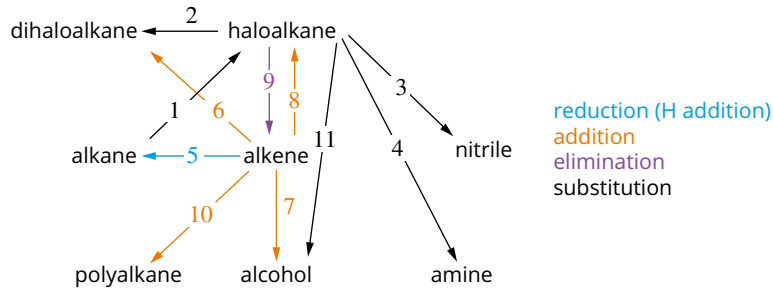


FIGURE 9.2.1 Reactions described in this module

A summary of the **reaction pathways** described in this module is shown in Figure 9.2.2. This diagram shows chemical structures and reaction conditions for reactions of alkanes, haloalkanes and alkenes.

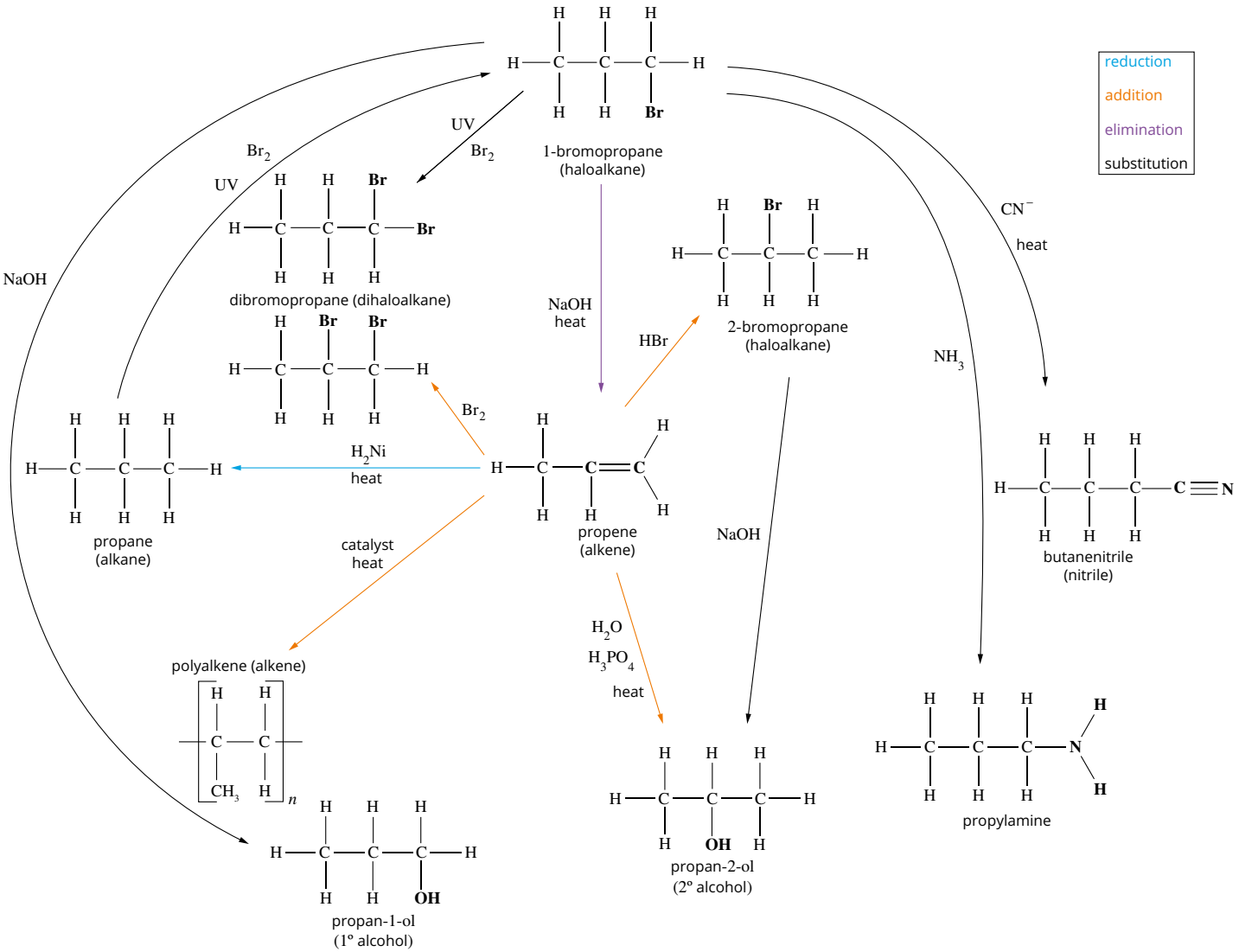


FIGURE 9.2.2 Chemical structures and reaction conditions for reactions of alkanes, haloalkanes and alkenes. Note that addition reactions of alkenes must follow Markovnikov's rule and therefore the major product of addition to an alkene is a secondary structure (secondary haloalkane or secondary alcohol) not a primary structure. Functional groups are shown in bold.

COMBUSTION OF ALKANES

A reaction of alkanes that has great significance to our society is combustion. As fuels, any member of the alkane class can provide energy. For example, the alkane mixture known as crude oil provides:

- smaller molecules such as methane and propane for use as gas fuels
- octane, nonane and decane as major components of petroleum
- larger molecules ($C_{10}H_{22}$ to $C_{15}H_{32}$) for use as diesel fuels.

Alkanes react with oxygen to produce carbon dioxide and water and significant amounts of energy. It is an exothermic **oxidation–reduction reaction**. If the supply of oxygen is plentiful, the products of combustion will be carbon dioxide and water. This is known as **complete combustion** and is represented by the following balanced reaction:

$$C_x H_y(g) + (x + y/4)\ O_2(g) \rightarrow xCO_2(g) + y/2\ H_2O(g) + \text{energy}$$

Combustion and fuels (including incomplete combustion) are explained in Unit 1. Figure 9.2.3 shows natural gas (primarily methane) undergoing complete combustion in a Bunsen burner when the air holes are open. The equation for the complete combustion of methane is:

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



FIGURE 9.2.3 Methane undergoes complete combustion in a Bunsen burner when the air holes are open.

Octane is a major component of petroleum. The balanced reaction for the complete combustion of octane is:

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

SUBSTITUTION REACTIONS OF ALKANES

A substitution reaction occurs when an atom or functional group in a molecule is replaced or 'substituted' by another atom or group.

Alkanes are saturated hydrocarbons and undergo substitution reactions with halogens, such as chlorine and bromine, to produce haloalkanes. At room temperature and in the dark, a reaction vessel containing a mixture of an alkane such as methane and chlorine gas will not react. For the substitution reaction to occur, the reaction must be initiated by ultraviolet (UV) light.

The reaction between methane and chlorine in the presence of UV light is given by the equation:

$$CH_4(g) + Cl_2(g) \xrightarrow{\text{UV light}} CH_3Cl(g) + HCl(g)$$

For each molecule of chlorine gas (Cl_2) that reacts, a hydrogen atom on the alkane is replaced by a chlorine atom.

Chemists write the general equation for an alkane reacting with chlorine in shorthand form as:

$$RH + Cl_2 \xrightarrow{\text{UV light}} RCl + HCl$$

For all general equations, R represents an **alkyl group**.

Chloromethane is the substitution product of this reaction. As the reaction proceeds, the chloromethane product may continue to react with another chlorine molecule. If this occurs, dichloromethane (CH_2Cl_2, a dihaloalkane) is produced.

$$RCl + Cl_2 \rightarrow RCl_2 + HCl$$

If enough chlorine is available, further reactions can result in all four hydrogen atoms of the original methane molecule being substituted by chlorine atoms, as seen in Figure 9.2.4. The different substituted products have different boiling points so they may be separated from one another by **fractional distillation**.

Substitution reactions of alkanes using excess chlorine gas can result in a mixture of chloroalkane products with varying levels of substitution.

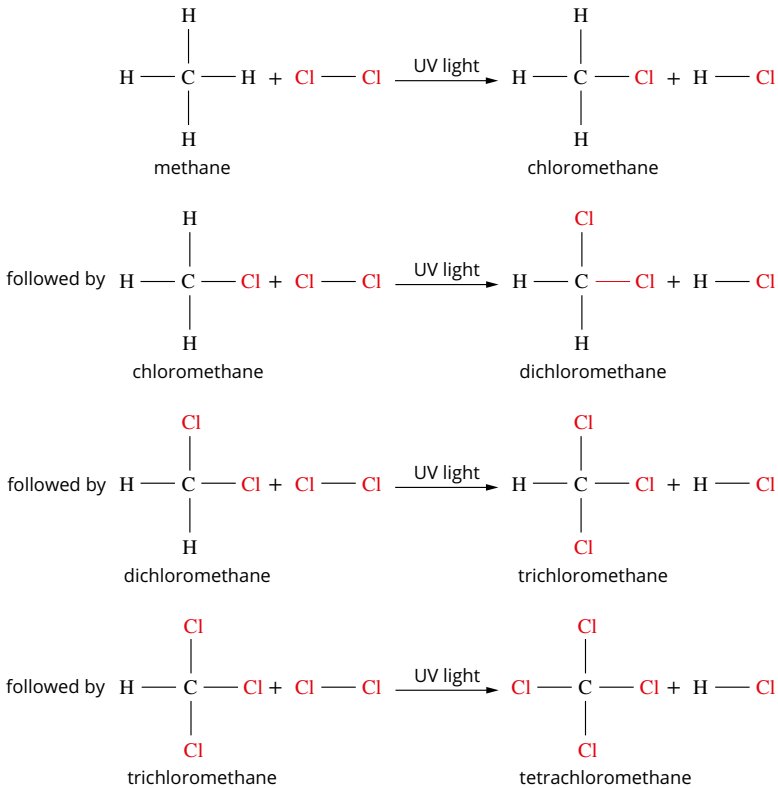


FIGURE 9.2.4 Substitution reactions of methane and chlorine

Substitution reactions of haloalkanes

In haloalkanes, the large electronegativity difference between halogen and carbon atoms means that the carbon–halogen bond is polar. This makes the bond weaker than one without a dipole. Species such as another halogen ion, a cyanide ion (CN^-), ammonia or hydroxide ion (OH^-) can be substituted for the halogen in the polar bond. The new organic product is a different haloalkane, a nitrile, or an amine, respectively. For example, in the reaction shown below, a bromine atom takes the place of the chlorine atom in the haloalkane. Because the chlorine atom of the chloroalkane has been replaced, this is a substitution reaction:

$$KBr + CH_3Cl \rightarrow CH_3Br + KCl$$

Potassium cyanide and sodium cyanide also react with haloalkanes in substitution reactions. The product of these reactions is a nitrile. The general equation for the formation of a nitrile by substitution with potassium cyanide or sodium cyanide is:

$$RCl + CN^- \xrightarrow{\text{heat}} RCN + Cl^-$$

In this substitution reaction, a haloalkane is heated with a solution of potassium cyanide or sodium cyanide in ethanol. The halogen is replaced by a cyano group (–C≡N) and a nitrile is produced. The solution must be anhydrous as the presence of water will allow –OH to be substituted rather than –CN. This reaction is biologically significant because it serves to lengthen the carbon backbone. This means that smaller molecules can be made into larger ones. Importantly, a new atom is also added, nitrogen, meaning that the molecule now has a key part of the basic structure of an amino acid. Proteins are polymers composed of many amino acid monomers. In this way, the substitution reaction using CN^- may contribute to protein synthesis.

Ammonia also reacts with haloalkanes in substitution reactions. The product of these reactions is an amine. The general equation for the formation of an amine by substitution with ammonia is:

$$RCl + NH_3 \longrightarrow RNH_2 + HCl$$

Figure 9.2.5 shows the reaction of chloroethane with ammonia. The substitution reaction does not require a catalyst and produces ethanamine as the product. The production of propan-2-amine by reaction of 2-chloropropane with ammonia is also shown. Other haloalkanes containing fluorine, bromine and iodine also undergo substitution reactions with ammonia to produce the corresponding amines.

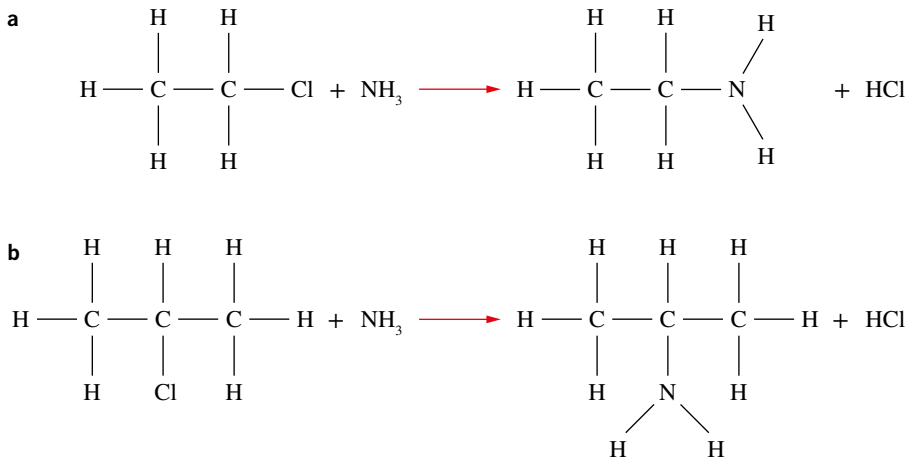


FIGURE 9.2.5 (a) Reaction of chloroethane with ammonia produces ethanamine. (b) Reaction of 2-chloropropane with ammonia produces propan-2-amine.

Sodium hydroxide also reacts with haloalkanes in substitution reactions. The product of these reactions is an alcohol. The general equation for the formation of an alcohol by substitution of a haloalkane with hydroxide is:

$$RCl + NaOH \rightarrow ROH + NaCl$$

A substitution reaction occurs when an atom or functional group in a molecule is replaced by another atom or group.

In the presence of sodium hydroxide or potassium hydroxide, a haloalkane can undergo the substitution reaction or, when heat is applied, an elimination reaction is favoured. This means that for the same reactants, a haloalkane and sodium hydroxide, changing the conditions of the reaction will alter the products. Lower temperatures favour a substitution reaction (producing an alcohol) and higher temperatures favour elimination (producing an alkene). The elimination reaction is favoured when the reaction is done in ethanol not water. Tertiary haloalkanes usually undergo elimination and primary haloalkanes usually undergo substitution in the presence of sodium hydroxide solution. Table 9.2.1 list the factors that influence substitution or elimination.

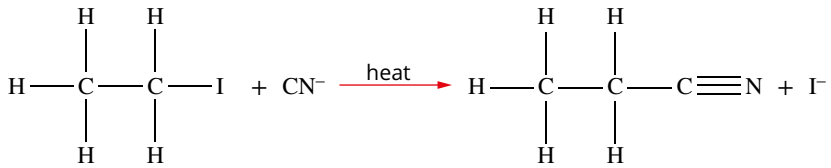
TABLE 9.2.1 Factors influencing substitution or elimination

Substitution or elimination	
Type of haloalkane	
primary	mainly substitution
secondary	both substitution and elimination
tertiary	mainly elimination
Solvent	
water	encourages substitution
ethanol	encourages elimination
Temperature	
heat	encourages elimination
Sodium hydroxide concentration	
high	encourages elimination

Worked example 9.2.1

DEDUCING A SUBSTITUTION REACTION

Construct the chemical equation and the structural formulas for the substitution reaction between potassium cyanide and iodoethane.

Thinking	Working
Identify the reacting organic molecule.	iodoethane (CH_3CH_2I)
Identify the inorganic reactant.	cyanide ion CN^-
Recall reactions of haloalkanes and identify the reacting species (refer to Figure 9.2.2 on page 317).	Haloalkanes can undergo substitution reactions with KBr, NH_3, CN^- and OH. So the reacting species is likely to be CN^- on the inorganic reactant and I on iodoethane.
Substitute the two reacting species.	$CH_3CH_2I + CN^- \xrightarrow{\text{heat}} CH_3CH_2CN + I^-$
Draw the structural formulas.	

➤ Try yourself 9.2.1

DEDUCING A SUBSTITUTION REACTION

Construct the chemical equation and the structural formulas for the substitution reaction between ammonia and bromoethane.

A haloalkane can undergo a substitution reaction to form a dihaloalkane, an amine, a nitrile or an alcohol.

ADDITION REACTIONS OF ALKENES

The carbon–carbon double covalent bond in alkenes has a significant effect on the chemical properties of the homologous series. Alkenes are generally more reactive compounds, reacting more readily and with more chemicals than alkanes, which contain only single bonds. The reactions of alkenes usually involve the addition of a small molecule to the double bond of the alkene. These reactions are called addition reactions.

During addition reactions:

- two reactant molecules combine to form one product molecule
- the C=C double bond becomes a C–C single bond
- an unsaturated compound becomes saturated
- the atoms of the small molecule adding to the alkene are 'added across the double bond', so that one atom or group from the molecule forms a bond to each of the carbon atoms in the double bond.

A typical addition reaction is shown in Figure 9.2.6. X_2 designates any halogen molecule.

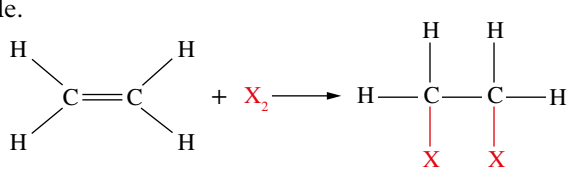


FIGURE 9.2.6 The addition reaction between an alkene and molecule X_2

When ethene reacts with a small molecule, each atom of the molecule forms a covalent bond to a carbon atom in the double bond. The double bond becomes a single bond. Unlike substitution reactions, there is no inorganic product formed. All the atoms in the reactants end up in the final product.

An addition reaction occurs when a small molecule is added to the double bond of the alkene, converting the double bond to a single bond.

Four different types of addition reactions of alkenes are explained in detail below.

Reaction of alkenes with hydrogen—reduction of alkenes

Alkenes react with hydrogen gas in the presence of a metal catalyst, such as nickel, to form alkanes. This reaction converts an unsaturated molecule to a saturated one. The reaction shown in Figure 9.2.7 is the addition reaction of ethene and hydrogen gas to produce ethane.

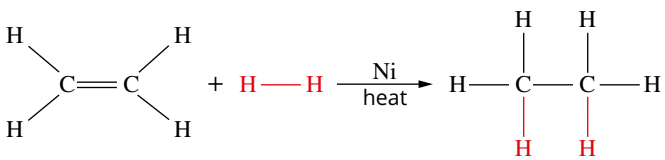


FIGURE 9.2.7 Addition reaction of ethene with hydrogen to form the corresponding saturated alkane, ethane

The activation energy for the reaction is too high for the reaction to proceed at room temperature without a catalyst. Metals such as nickel, palladium and platinum are used as catalysts, and the reaction is usually heated. This reaction is often called a reduction reaction because hydrogen atoms are added.

The triple bond in alkyne molecules can be converted to three single bonds by the addition of hydrogen atoms. This is also a reduction reaction; however, it requires a strong metal catalyst and high temperatures to proceed. This is due to the greater stability of the triple bond compared to a double bond. An example of an addition reaction is the reduction of butyne:

$$CH_3–C{\equiv}C–CH_3 + 2H_2 \xrightarrow[\text{heat}]{\text{Ni}} CH_3–CH_2–CH_2–CH_3$$

Reaction of alkenes with halogens

Figure 9.2.8 shows the reaction of ethene with bromine to form 1,2-dibromoethane. The halogens add across the double bond of the molecule, so in the product there is one bromine atom attached to each carbon atom.

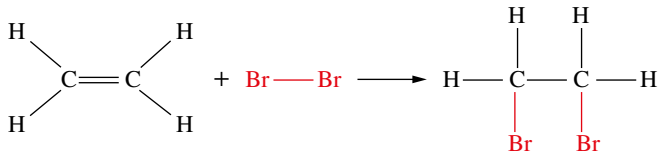


FIGURE 9.2.8 Addition reaction of ethene with bromine



FIGURE 9.2.9 Immiscible layers of bromine water and alkane (left) and bromine water and alkene (right). This image shows the liquids re-separated after mixing. The alkene reacts with the coloured bromine and the solution loses colour (right). The test tube on the left shows that when an alkane is added to aqueous bromine, no addition reaction occurs and so the colour of the dissolved bromine remains.

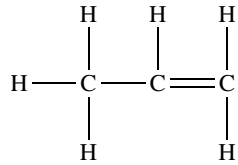
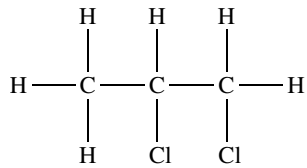
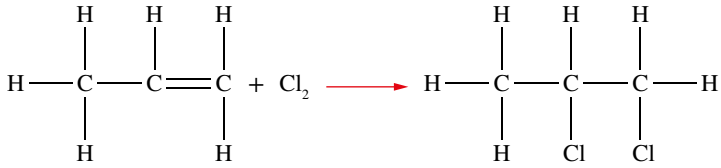
This reaction proceeds at room temperature without a catalyst. Other halogens such as Cl_2 and I_2 also undergo addition reactions with alkenes to form the corresponding di-substituted haloalkanes.

Bromine is often used as a test for the presence of a carbon–carbon double bond due to the ease and speed with which it reacts with an alkene. As described in Module 9.1, the brownish-red colour of the bromine quickly disappears when it is mixed with an alkene. Figure 9.2.9 demonstrates this test, showing the alkane in the test tube on the left and the alkene on the right. Note that the hydrocarbons are non-polar liquids and so are clearly visible as the upper layer in each test tube.

Worked example 9.2.2

DESCRIBING ADDITION REACTIONS OF ALKENES

Describe the addition reaction between propene and chlorine by constructing the chemical equation and structural formulas.

Thinking	Working
Identify the alkene and double bond where addition will occur.	CH_3CHCH_2 
Identify the molecule to be added.	Cl_2
Deduce the product by adding a halogen to the two carbons of the double bond.	$CH_3CHClCH_2Cl$ 
Construct the chemical equation.	$CH_3CHCH_2 + Cl_2 \rightarrow CH_3CHClCH_2Cl$
Draw the structural formulas. 	

➤ Try yourself 9.2.2

DESCRIBING ADDITION REACTIONS OF ALKENES

Describe the addition reaction (also a reduction reaction) between but-1-ene and iodine gas by constructing the chemical equation and structural formulas.

Reactions of alkenes with water

Alkenes react with water under specific conditions to form the corresponding alcohol. For example, ethanol can be produced by an addition reaction of ethene and water, using a catalyst and heat to increase the rate of the reaction. Figure 9.2.10 shows the addition reaction of steam and ethene, using a phosphoric acid catalyst. This reaction is used extensively in industry for the production of ethanol.

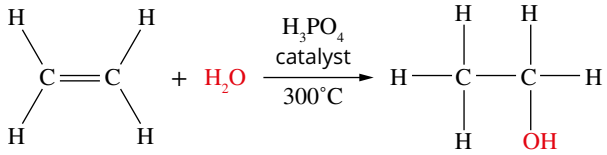


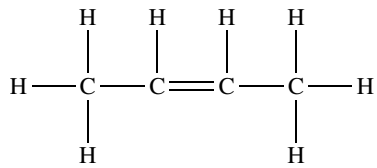
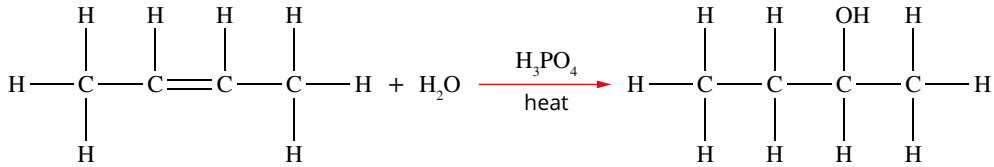
FIGURE 9.2.10 Addition reaction of ethene with water in the presence of a phosphoric acid catalyst and heat

The reaction is carried out at 300°C. The gaseous reactants are passed over a solid bed of the catalyst and gaseous ethanol is formed. In the addition reaction, water is 'added' across the double bond. The reaction is used for the commercial manufacture of ethanol because it is a one-step process that uses little energy, apart from initial heating. The heterogeneous (solid-gas) nature of the reaction system means it is easy for manufacturers to remove the product from the reaction mixture, leaving the catalyst intact.

Worked example 9.2.3

DESCRIBING THE PRODUCTION OF ALCOHOL FROM AN ALKENE

Draw the structural formula of the alcohol produced by the reaction of water and but-2-ene.

Thinking	Working
Identify the organic reactant and double bond where addition occurs.	$CH_3CHCHCH_3$ 
Identify the inorganic reactant.	H_2O
Recall the addition reaction of butene and water (OH and H are added, one to each carbon atom of the double bond; reaction occurs in the presence of phosphoric acid and heat).	$CH_3CHCHCH_3 + H_2O \rightarrow CH_3CH_2CHOHCH_3$
Draw the structural formulas.	

➤ Try yourself 9.2.3

DESCRIBING THE PRODUCTION OF ALCOHOL FROM AN ALKENE

Draw the structural formula of the alcohol produced by the reaction of water and ethene.

Reactions of alkenes with hydrogen halides

Another small molecule that can be added across the double bond of an alkene is a hydrogen halide. For example, but-2-ene reacts with hydrogen chloride, a hydrogen halide, in an addition reaction. Figure 9.2.11 shows the reaction of but-2-ene with hydrogen chloride to produce a single product, 2-chlorobutane. In this reaction, a hydrogen atom adds to one of the carbon atoms in the carbon–carbon double bond and a halogen atom adds to the other carbon atom.

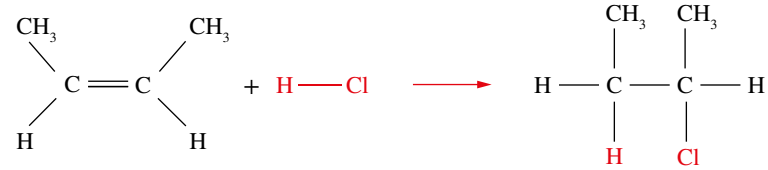


FIGURE 9.2.11 The addition reaction of but-2-ene with hydrogen chloride produces 2-chlorobutane

However, as Figure 9.2.12 shows, when you react hydrogen chloride with an asymmetrical alkene such as but-1-ene, two products are possible.

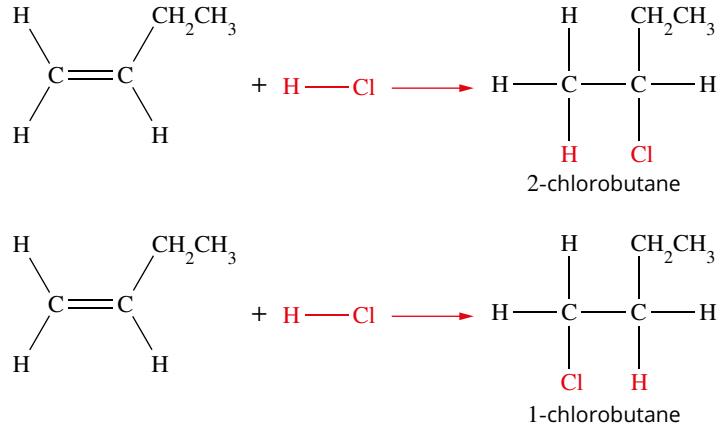


FIGURE 9.2.12 Addition reaction of but-1-ene with hydrogen chloride. Two isomers are possible as products.

The addition reaction can produce two isomers. In one product, the hydrogen atom from the hydrogen chloride molecule has been added to the (C1) carbon atom in the carbon–carbon double bond at the end of the but-1-ene molecule. In the other product, the hydrogen atom has been added to the (C2) carbon atom at the other end of the carbon–carbon double bond.

When you react an asymmetrical alkene such as but-1-ene with an asymmetrical reactant, isomers are produced. More of one isomer is usually produced than the other. The greater formation of one isomer can be predicted using **Markovnikov's rule**. While it is important to be able to accurately determine which isomer is favoured, the mechanism is outside the scope of the syllabus.

Markovnikov's rule states that, during the addition of HX or H_2O to an asymmetrical alkene, hydrogen adds to the carbon atom of the double bond that has the greater number of hydrogens attached. In Figure 9.2.12, as the double bond between carbon number 1 and carbon number 2 becomes a single bond, atoms are added to both carbon number 1 and carbon number 2. However, carbon number 1 has two hydrogen atoms compared to the single hydrogen atom attached to the carbon number 2 carbon atom; therefore the hydrogen will add to carbon number 1. This means that the other atom, the halogen, must be added to carbon number 2. Then, the main product of the addition of HCl to but-1-ene will be 2-chlorobutane (Figure 9.2.12 top isomer), not 1-chlorobutane (Figure 9.2.12 lower isomer).

Markovnikov's rule states that, in the addition of HX or H_2O to an alkene, hydrogen adds to the carbon atom of the double bond that has the greater number of hydrogens attached.

Worked example 9.2.4

USING MARKOVNIKOV'S RULE TO IDENTIFY PRODUCTS OF ADDITION TO AN ASYMMETRICAL ALKENE

Describe the reaction and products of the addition reaction of pent-1-ene with hydrogen bromide.	
Thinking	**Working**
Identify the organic molecule containing a double bond.	$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3$ C1 C2 C3 C4 C5
Identify the small molecule to be added.	HBr
Identify the number of hydrogen atoms attached to each carbon atom at the double bond (carbon number 1 and carbon number 2), and determine which carbon atom has the most hydrogens.	Carbon number 1 has two hydrogen atoms, while carbon number 2 has one hydrogen atom.
Add the hydrogen atom of HBr to the carbon with the most hydrogens, and the bromine atom from the HBr to the other carbon (Markovnikov's rule).	Hydrogen adds to carbon number 1. Bromine adds to carbon number 2. $CH_3CHBrCH_2CH_2CH_3$ is produced.
Construct the reaction equation.	$CH_2CHCH_2CH_2CH_3 + HBr \rightarrow CH_3CHBrCH_2CH_2CH_3$
Draw the structural formulas.	

➤ Try yourself 9.2.4

USING MARKOVNIKOV'S RULE TO IDENTIFY PRODUCTS OF ADDITION TO AN ASYMMETRICAL ALKENE

Describe the addition reaction of hydrogen chloride and 2-methylbut-2-ene.

Addition reactions of alkenes to form poly (alkenes)

Polyethene is an example of a **polymer** ('many units'). Polymers are very long molecules formed from the linking of a large number of small molecules, called **monomers** ('one unit'). Polyethene is formed from the reaction of thousands of ethene monomer molecules. The reaction, shown in Figure 9.2.13, is an example of an **addition polymerisation** process. Several thousand ethene monomers usually react to make one molecule of polyethene. Large square brackets around the repeating unit, and the subscript *n*, are used to simplify the drawing of long polymer molecules. The value of *n* varies with each polymer molecule but the average molecular chain formed may contain around 20 000 carbon atoms.

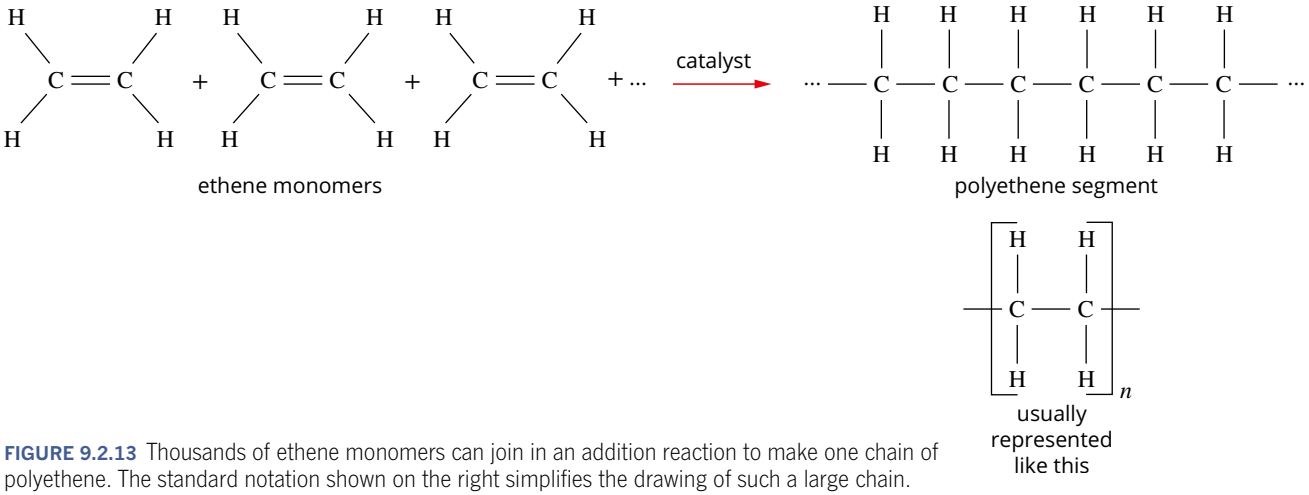


FIGURE 9.2.13 Thousands of ethene monomers can join in an addition reaction to make one chain of polyethene. The standard notation shown on the right simplifies the drawing of such a large chain.

Note that the empirical formula of each monomer is the same as that of the polymer, since there are no other products in addition polymerisation reactions. When ethene polymerises, the double bonds break and new covalent bonds are formed between carbon atoms on nearby monomers. The polyethene formed does not contain any double bonds.

Other alkenes react in a similar way. For example, propene forms polypropene and butene forms polybutene. Polymers are further explained in Chapter 13.

ELIMINATION REACTIONS OF HALOALKANES

Addition reactions can be reversed. This reaction is called an elimination reaction because the haloalkane loses two atoms (one hydrogen and one halogen) and regains a double bond. This can be seen in Figure 9.2.14.

In elimination reactions, a hydrogen is removed from one carbon atom and a halogen is removed from another carbon atom. This means that an unsaturated molecule is derived from a saturated molecule. This reaction requires a strong base such as sodium hydroxide and heat to proceed. At lower temperatures a substitution reaction is favoured.

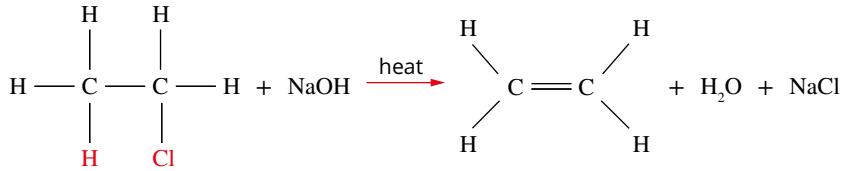
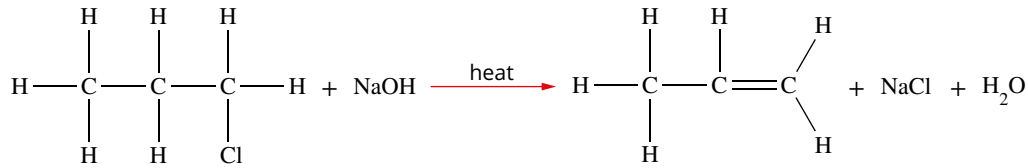


FIGURE 9.2.14 Reaction of chloroethane with sodium hydroxide to give ethene

Worked example 9.2.5

PRODUCTS OF AN ELIMINATION REACTION OF A HALOALKANE USING SODIUM HYDROXIDE

Identify the product of an elimination reaction of 1-chloropropane and sodium hydroxide.	
Thinking	**Working**
Identify the reactants in the reaction.	$CH_3CH_2CH_2Cl$ and NaOH
Recall the elimination process (at high temperature) and identify the adjacent carbon atoms that each lose an atom. A Cl atom and an H atom are removed. Water and NaCl are produced.	$CH_3CHHCH_2Cl + NaOH \rightarrow CH_3CHCH_2 + NaCl + H_2O$
Draw the structural formulas. 	

➤ Try yourself 9.2.5

PRODUCTS OF AN ELIMINATION REACTION OF A HALOALKANE USING SODIUM HYDROXIDE

Identify the product of an elimination reaction of 1-bromobutane and sodium hydroxide.

SCIENCE AS A HUMAN ENDEAVOUR

Use of organochlorine compounds as insecticides

The organochlorine compounds DDT, chlordane and lindane are synthetic organic halogen compounds produced by direct halogenation of hydrocarbons and by addition reactions to alkenes and alkynes. Figure 9.2.15 shows their chemical structure. After initial use during World War II, they have been used as pesticides since the 1950s and have been responsible for dramatic decreases in the incidence of insect-borne diseases (typhus, malaria, yellow fever and dengue fever) and increases in crop yields.

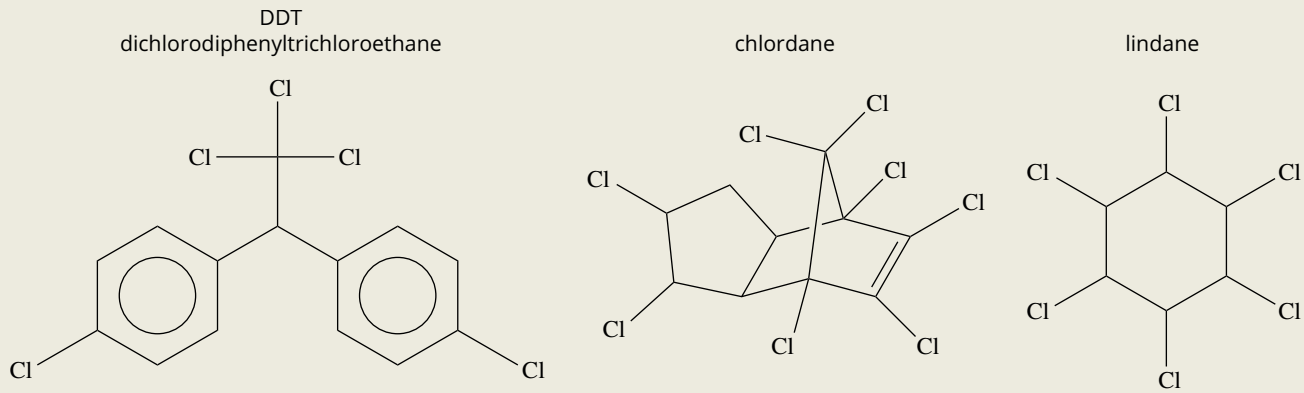


FIGURE 9.2.15 Chemical structure of dichlorodiphenyltrichloroethane, chlordane and lindane

These compounds have remarkable stability in the environment and in body systems and are described as persistent organic pollutants (POPs). Although they contain halogen functional groups these groups are resistant to the substitution and elimination reactions described in Module 9.2. Their stability is due to the presence of phenyl or other ring structures. These reduce the polarity of the carbon–halogen bond significantly, and charge interactions with other molecules also lessen. Therefore, the carbon–halogen bond resists hydrolysis and photolytic degradation, and the lack of charged regions makes the molecule non-polar.

The persistence of POPs in nature is also related to their hydrophobicity resulting in their accumulation in the fatty tissues of animals. After their use became widespread, evidence emerged that the compounds were being biomagnified (transferred through food chains in increasing concentrations). Biomagnification can cause health issues for predator species because their diet consists of tissue from prey in which a POP has accumulated. Higher levels of DDT are associated with fragile eggshells and reproductive abnormalities in birds.

At a high enough dosage, DDT has been shown to have some detrimental effects on vertebrates, including humans. Symptoms of DDT toxicity include apprehension, headache, anorexia, nausea, hyper-excitability, muscle fibrillation, respiratory arrest, coma and death. For this reason, and the apparent development of resistant insects, its use was scaled back by the early 1970s. In 1995, the United Nations identified POPs as an issue requiring global action, resulting in a range of organochlorine compounds being banned for agricultural use worldwide under the Stockholm Convention in 2001. However, some organochlorine compounds are still licensed for use under strict guidelines in areas where certain diseases, including newer pathogens such as Zika virus and aggressively spreading species such as fire ants, are a substantial threat.

Review

1. State two characteristics of POPs that contribute to detrimental effects in nature.
2. Explain how the structure of the DDT molecule causes its negative impact(s).
3. If you were an Environmental Protection Authority (EPA) officer investigating POP pollution, state which parts of an ecosystem you would test for signs of this pollution.

9.2 Review

SUMMARY

- Alkanes and alkenes burn in the presence of oxygen to produce carbon dioxide and water.
- Alkanes are generally unreactive but they can undergo substitution reactions with halogens in the presence of ultraviolet light to produce haloalkanes.
- Haloalkanes undergo substitution reactions with:
  - haloalkanes to produce a different haloalkane or a dihaloalkane
  - cyanide ions to produce a nitrile
  - ammonia to produce amines
  - sodium hydroxide at low temperature to produce alcohol and a salt.
- Alkenes are unsaturated hydrocarbons. They undergo addition reactions to produce saturated compounds.
- Alkenes undergo addition reactions with:
  - hydrogen and a metal catalyst to produce alkanes (this reaction is also known as a reduction reaction)
  - halogens to produce dihaloalkanes
  - water and a phosphoric acid catalyst at high temperature to produce alcohols
  - hydrogen halides to produce haloalkanes. Under typical conditions, asymmetrical alkenes add the hydrogen to the carbon that already has more hydrogen atoms (Markovnikov's rule).
- The addition of a hydrogen halide to an alkene can be reversed using a strong base such as sodium hydroxide and high temperature—this is called an elimination reaction.
- Both substitution and elimination reactions involve the removal of small molecules from the original molecule, thus producing more than one product.
- Alkenes require a catalyst to undergo addition polymerisation reactions to form polymers composed of carbon–carbon single bonds.

KEY QUESTIONS

Retrieval

1 State the products of the following reaction and balance the chemical equation:

$C_2H_4(g) + 3O_2(g) \rightarrow$ …….. (g) + ……. (g)

2 Name the products formed when ethene reacts with:
- **a** hydrogen chloride
- **b** chlorine
- **c** water in the presence of phosphoric acid catalyst and heat
- **d** hydrogen in the presence of a metal catalyst and heat.

3 Name the organic products formed when each of the following pairs of compounds react.
- **a** bromoethane and ammonia
- **b** 2-chlorobutane and sodium hydroxide at high temperature
- **c** pentene and water in the presence of a strong acid catalyst

4 Construct a balanced chemical equation to show the complete combustion of the following alkanes. Remember to include the states of the reactants and products.
- **a** gaseous methane
- **b** liquid hexane

Comprehension

5 Represent each of the following reactions with a balanced chemical equation.
- **a** gaseous propene bubbled into bromine solution
- **b** gaseous but-2-ene reacted with steam in the presence of a phosphoric acid catalyst

6 Construct balanced equations to represent all stages in the formation of carbon tetrachloride from methane and chlorine.

7 Use structural formulas to construct equations and name the products of the reactions of:
- **a** but-2-ene with hydrogen bromide.
- **b** but-1-ene with chlorine

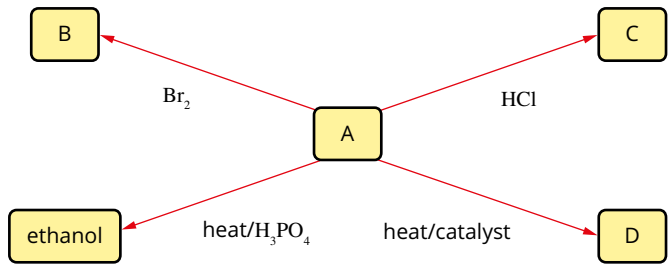
8 Explain the difference in reactivity of alkenes and alkanes with bromine water.

9 Explain the two possible reaction products when but-1-ene is heated with phosphoric acid and water and why they are not produced in equal amounts.

10 Use structural formulas to construct equations and name the products for the following reactions.
- **a** hexane and bromine gas in UV light (assuming a single molecule of bromine reacts)
- **b** bromoethane and sodium hydroxide
- **c** 1-chloropentane and potassium cyanide

Analysis

11 Identify A—D using the information shown in the reaction diagram below.



9.3 Reactions of compounds containing oxygen and nitrogen atoms

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand that oxidation of primary, secondary or tertiary alcohols results in different products depending on the position of the hydroxyl group (Reactions 1, 2 and 3)
- predict and identify the products of oxidation of alcohols from the alcohol type
- explain that combustion is another oxidation reaction of alcohols
- recognise that amines are produced by reduction of nitriles (Reaction 4)
- describe and explain that carboxylic acids undergo a condensation reaction with alcohols in the presence of an acid catalyst to produce esters (Reaction 5)
- identify the products of ester hydrolysis (Reaction 6)
- recognise that a condensation reaction occurs when a carboxylic acid reacts with an amine to form an amide (Reaction 7)
- explain organic chemistry reactions using chemical equations and structural formulas
- understand conditions and catalysts necessary for certain reactions
- describe how molecules containing oxygen and nitrogen are part of organic chemistry reaction pathways.



In Module 9.2 you saw simple organic molecules, such as alkanes, converted by substitution and addition reactions to more complex molecules containing oxygen and nitrogen atoms. Important examples of these products are alcohols and amines. These molecules can undergo further chemical change, often increasing the complexity and chemical reactivity of their structures. Aldehydes, ketones, carboxylic acids, esters and amides, described in this module, are produced in this way. Eventually, after many reactions, much larger, biologically important molecules such as triglycerides and proteins are produced. The three key reactions explained in this module are oxidation, reduction and condensation. These reactions are introduced in Figure 9.3.1.

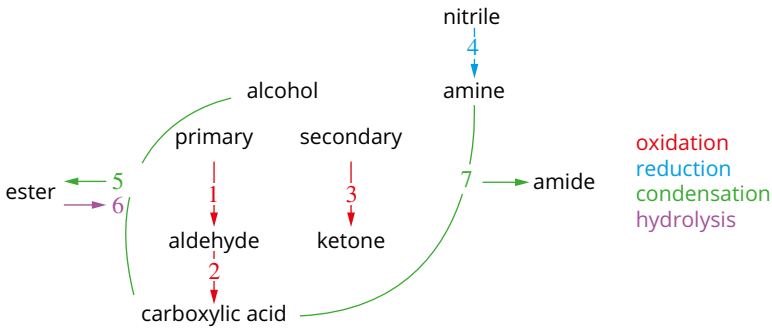


FIGURE 9.3.1 Overview of reaction pathways for compounds containing oxygen and nitrogen. Coloured numbers indicate the type of reaction—oxidation reactions are red, reduction reactions are blue, condensation reactions are green and hydrolysis reactions are purple.

Molecules containing oxygen and nitrogen are part of organic chemistry reaction pathways, as shown in Figure 9.3.2.

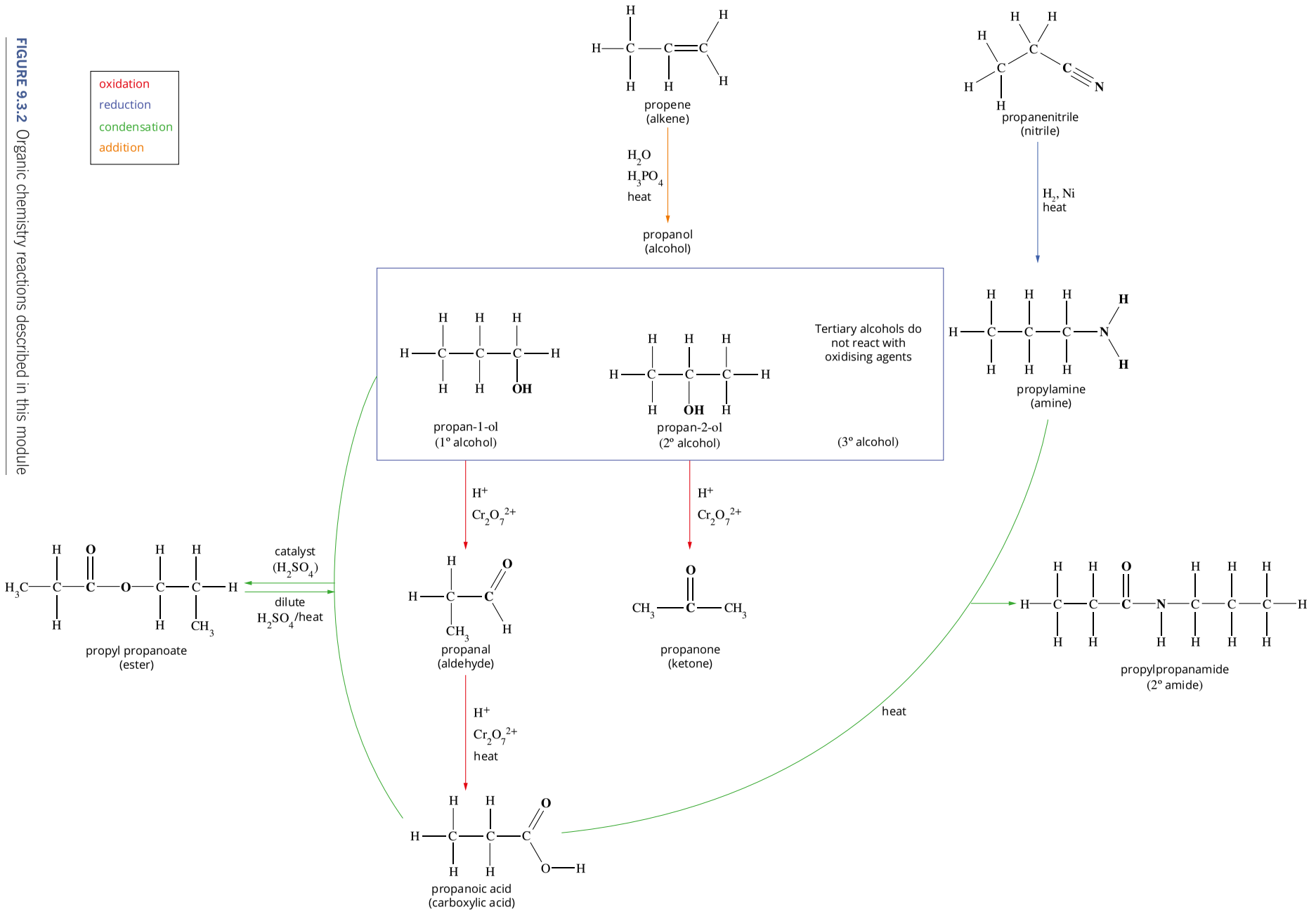


FIGURE 9.3.2 Organic chemistry reactions described in this module

OXIDATION AND REDUCTION REACTIONS OF ALCOHOLS AND NITRILES

In Module 9.2 you learnt that alcohols can be produced by addition reactions of alkenes, while nitriles are formed by substitution of a haloalkane using potassium cyanide. Alcohols and nitriles have functional groups which give their molecules very different properties from the alkene or haloalkane molecules from which they were made. These differences relate directly to the charge imbalances in the molecule generated by changes to its structure and polarity of its covalent bonds.

In this module you will examine the common oxidation reactions of alcohols and reduction reactions of nitriles. Oxidation and reduction were explained in Unit 3, and are defined by the loss or gain of electrons, respectively. However, when relating to organic reactions, we can restate the definitions as:

- oxidation is the gain of an oxygen atom(s) or the loss of a hydrogen atom(s)
- reduction is the gain of a hydrogen atom(s) or the loss of an oxygen atom(s).

By using these rules, you can identify oxidation and reduction in a range of organic chemistry reactions.

To understand reactions of alcohols you will need to remember the types of alcohols you learnt about in Module 8.4. Alcohols are classified into three types or isomers—primary, secondary and tertiary. The type depends on the position of the hydroxyl group within the molecule. The variation of the hydroxyl group makes the alcohols structural isomers of each other.

- Primary alcohols are alcohols in which the –OH group is bonded to a carbon that is attached to only one alkyl group. These alcohols first oxidise to form aldehydes and then further oxidise to form the corresponding carboxylic acids.
- Secondary alcohols are alcohols in which the –OH group is bonded to a carbon that is bonded to two alkyl groups. These alcohols oxidise to form ketones.
- Tertiary alcohols are alcohols in which the –OH group is bonded to a carbon that is bonded to three alkyl groups. These alcohols are resistant to oxidation by inorganic oxidising agents and will not normally react.

Figure 9.3.3 shows how the different isomers of butanol can be classified as primary, secondary or tertiary alcohols. Chemists often use the symbols 1°, 2° and 3° as a shorthand way of indicating whether an alcohol is primary, secondary or tertiary, respectively.

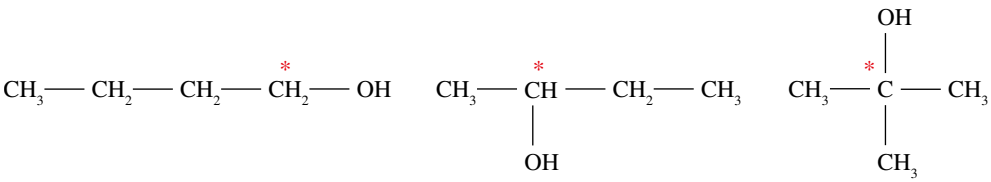


FIGURE 9.3.3 Structures of some primary (1°), secondary (2°) and tertiary (3°) alcohols. The asterisk identifies the carbon atom which determines the 1°, 2° or 3° nature of the alcohol.

Combustion of alcohols

Alcohols react with oxygen to produce carbon dioxide and water and significant amounts of energy. It is an **exothermic** oxidation–reduction reaction. If the supply of oxygen is plentiful, the products of combustion will be carbon dioxide and water. This is known as complete combustion. Combustion is an oxidation reaction because both the hydrogen and carbon atoms in the reactant become associated with oxygen as small molecules (CO_2 and H_2O) in the products. This agrees with our definition of oxidation as 'adding oxygen'. The chemical equation for combustion of ethanol is written as:

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



FIGURE 9.3.4 Burning brandy is sometimes poured over a Christmas pudding. Brandy can contain as much as 40% ethanol.

Ethanol (methylated spirits), which contains about 95% ethanol mixed with other chemicals, is used as a fuel for camping stoves. Some cooking techniques even make use of the burning of alcohol for drama. Figure 9.3.4 shows how the ethanol in the alcoholic drink brandy can also burn when it is added to enhance the flavour of a Christmas pudding.

Oxidation of alcohols

The second oxidation reaction type discussed here is mediated by strong inorganic oxidising agents such as acidic solutions of potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$). The products of these oxidation reactions depend on the type of alcohol involved.

Oxidation of primary alcohols

A primary alcohol can be oxidised to a carboxylic acid in two stages, as shown in Figure 9.3.5. The reaction requires an oxidising agent such as acidified potassium dichromate ($K_2Cr_2O_7$) or acidified potassium permanganate ($KMnO_4$). As we have seen, oxidation 'adds oxygen' or 'removes hydrogen', and during the oxidation of primary alcohols both reactions occur. In the first stage, the primary alcohol is oxidised to an aldehyde by the removal of two hydrogen atoms. In the second stage, further heating of the reaction mixture in the presence of the oxidising agent oxidises the aldehyde to a carboxylic acid by the addition of an oxygen atom.

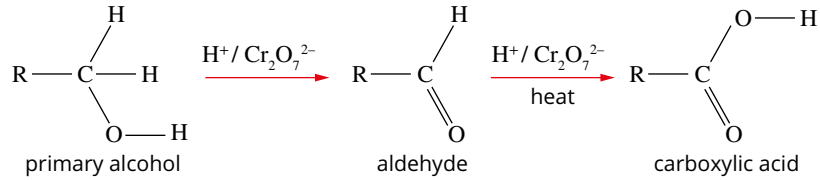


FIGURE 9.3.5 General equation for the two stages of the oxidation of a primary alcohol. The R groups in the structures represent alkyl groups.

Stage 1 in the oxidation of primary alcohols removes two hydrogen atoms from the alcohol structure and produces an aldehyde.

Stage 2 in the oxidation of primary alcohols adds an oxygen atom to the aldehyde structure and produces a carboxylic acid.

An example of oxidation of a primary alcohol is shown in Figure 9.3.6. It shows that propan-1-ol is first oxidised to propanal (an aldehyde) and then oxidised to propanoic acid (a carboxylic acid).

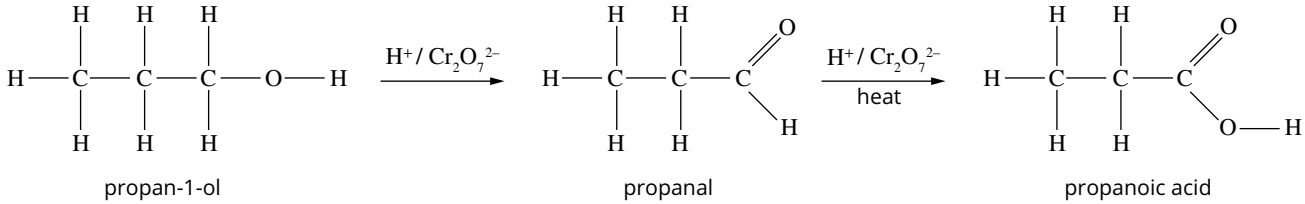


FIGURE 9.3.6 Equations for the oxidation of the primary alcohol propan-1-ol showing structural formulas. In the first oxidation, two hydrogen atoms are removed. In the second oxidation, an oxygen atom is gained.

Aldehydes are produced as an intermediate in the oxidation of a primary alcohol to a carboxylic acid. If an aldehyde is the desired product, milder temperature conditions must be used and the aldehyde product removed by distillation as it is formed.

If the desired product is an aldehyde rather than a carboxylic acid, milder conditions (lower temperatures and shorter reaction times) must be used, and the aldehyde can be distilled from the reaction mixture as it is formed so that it is not oxidised further. Higher temperatures and longer reaction times favour the formation of the carboxylic acid over the aldehyde.

Oxidation of secondary alcohols

When secondary alcohols are oxidised by strong oxidising agents, such as solutions of acidified potassium dichromate or acidified potassium permanganate, the corresponding ketones are produced. This agrees with our definition of oxidation as 'removing hydrogen' because the –OH group becomes a =O bond, and the carbon atom also loses a hydrogen atom. Figure 9.3.7 gives the general equation for the oxidation of secondary alcohols to ketones.

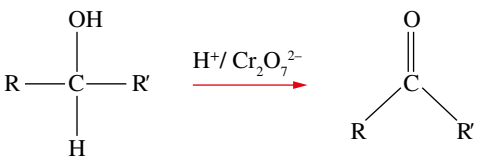


FIGURE 9.3.7 The general equation for the oxidation of a secondary alcohol

Oxidation of secondary alcohols to ketones removes two hydrogen atoms from the alcohol structure.

Figure 9.3.8 gives the equation for the production of the ketone propanone by the oxidation of the secondary alcohol propan-2-ol.

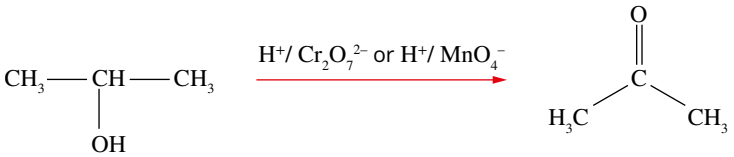
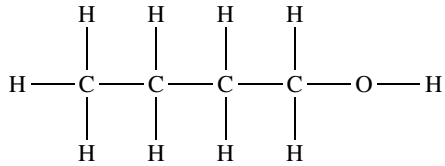
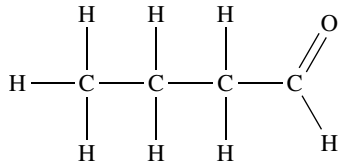
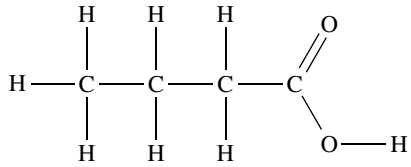


FIGURE 9.3.8 The secondary alcohol propan-2-ol can be oxidised to propanone

Worked example 9.3.1

IDENTIFYING AND DESCRIBING A REACTION OF AN ORGANIC ALCOHOL

Identify the name of the reaction and draw the product(s) formed when butan-1-ol is heated with acidified potassium dichromate.	
Thinking	**Working**
Recall that butanol has four carbon atoms and an OH functional group.	
Use the organic reaction pathways in Figure 9.3.2 on page 330 to recall that a primary alcohol will be first oxidised by acidified potassium dichromate to an aldehyde.	Butanol will be oxidised to butanal.
Butanal has a C=O functional group formed by the loss of two hydrogen atoms from butanol. Draw the structure of butanal.	
Use the organic reaction pathways in Figure 9.3.2 on page 330 to recall that aldehyde will be further oxidised, with heat and acidified oxidising agent to a carboxylic acid.	Butanal will be oxidised to butanoic acid.
The second oxidation adds an oxygen atom and so the CHO group becomes COOH. Draw the structure of butanoic acid.	

➤ Try yourself 9.3.1

IDENTIFYING AND DESCRIBING A REACTION OF AN ORGANIC ALCOHOL

Identify the name of the reaction and draw the product(s) formed when butan-2-ol is heated with acidified potassium dichromate.

Primary alcohols are oxidised to either aldehydes or acids.

Secondary alcohols are oxidised to ketones.

Tertiary alcohols cannot be oxidised.

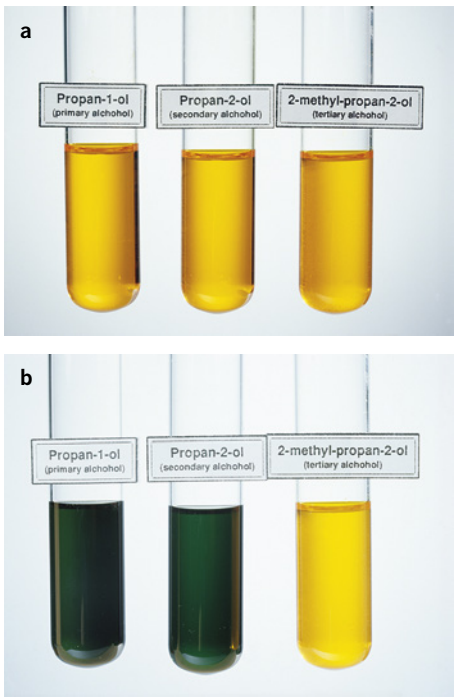


FIGURE 9.3.9 (a) Acidified potassium dichromate has an orange colour prior to reacting with alcohols. (b) Solutions of the primary alcohol propan-1-ol and secondary alcohol propan-2-ol with acidified potassium dichromate change from orange to green on heating. Tertiary alcohols such as 2-methylpropan-2-ol will not react under these conditions so no colour change is observed.

PA 4.1.2

Tertiary alcohols and oxidising agents

During the oxidation of alcohols, there is a C=O bond formed and a simultaneous decrease (at the same carbon atom) in the number of C–H bonds. However, tertiary alcohols are resistant to reaction with solutions of acidified potassium dichromate or potassium permanganate because the carbon attached to the hydroxyl group does not have a C–H bond to break so oxidation cannot occur at that carbon atom. As a result, tertiary alcohols cannot be normally oxidised by heating in the presence of a strong oxidant such as acidified dichromate or acidified permanganate. The primary and secondary alcohols have at least one hydrogen atom at the carbon being oxidised and so a C=O bond can form in this position.

Colour changes in oxidation reactions

In Module 9.1 you learnt that some organic compounds can be identified using colour change reactions. The strong oxidising agents potassium dichromate and potassium permanganate are both highly coloured due to the presence of the transition elements chromium (Cr) and manganese (Mn).

A solution of dichromate ions in water is orange in colour. When this acidified dichromate solution is used to oxidise a primary or secondary alcohol, the chromium (VI) in the dichromate is reduced to the Cr^{3+} ion which is green in colour. This colour change from orange to green can be used as a qualitative test to indicate that oxidation of an organic compound has taken place. The colour changes observed for the reaction of primary, secondary and tertiary alcohols with potassium dichromate are shown in Figure 9.3.9.

A solution of acidified potassium permanganate reagent is a deep purple colour. When this solution reacts with primary or secondary alcohols, the manganese (VII) in the permanganate ion (MnO_4^-) is reduced to Mn^{2+}, which is colourless. Tertiary alcohols do not react so there is no change in the colour of the solution, as shown in Figure 9.3.10.

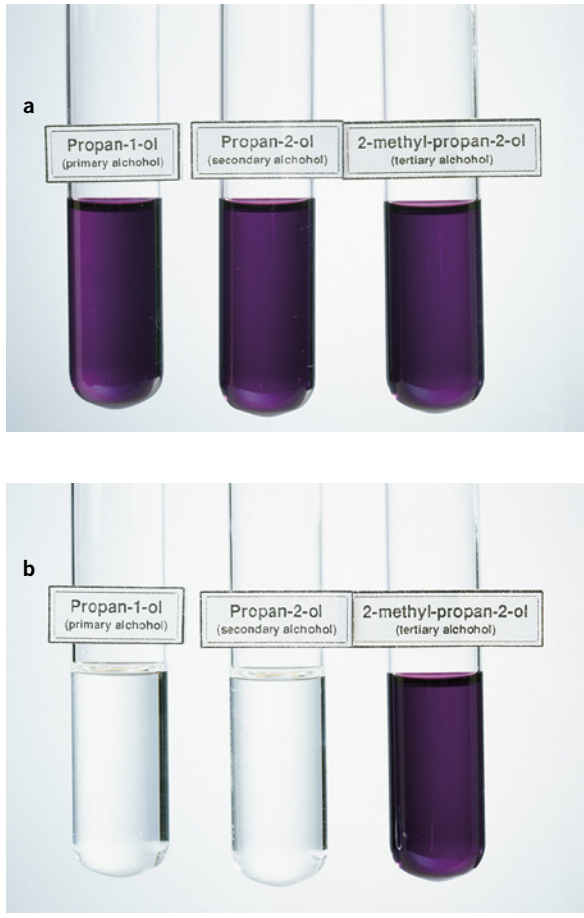


FIGURE 9.3.10 (a) The strong oxidising agent potassium permanganate is deep purple in colour. (b) On reaction with primary and secondary alcohols, the colour changes from purple to colourless. The tertiary alcohol is resistant to oxidation under these conditions and does not react, and so the solution does not change colour.

Table 9.3.1 summarises the reactions of primary, secondary and tertiary alcohols with an acidified solution containing dichromate or permanganate ions.

TABLE 9.3.1 Summary of the oxidation reactions of primary, secondary and tertiary alcohols with acidified dichromate solution or acidified permanganate solution

Type of alcohol	Products	Colour change of acidified potassium dichromate solution	Colour change of acidified potassium permanganate solution
primary (1°)	mild conditions produce aldehydes; higher temperatures and longer reaction times produce carboxylic acids	orange to green	purple to colourless
secondary (2°)	ketones	orange to green	purple to colourless
tertiary (3°)	no products because tertiary alcohols are resistant to oxidation by these oxidising agents	no change—solution stays orange	no change—solution stays purple

Reduction of nitriles

Nitriles are a class of compounds containing the cyano functional group (C≡N). In Module 9.2 you learnt that these molecules can be formed by substitution reaction of haloalkanes. The reduction of a nitrile involves addition of hydrogen atoms at the position of the triple bond, and agrees with our definition of reduction as 'adding hydrogen'. This results in a C–N single bond and a terminal amino group ($-NH_2$). The reaction requires increased temperature and a metal catalyst such as nickel or palladium and is shown in Figure 9.3.2 on page 330. The production of ethylamine from ethanenitrile is shown in Figure 9.3.11.

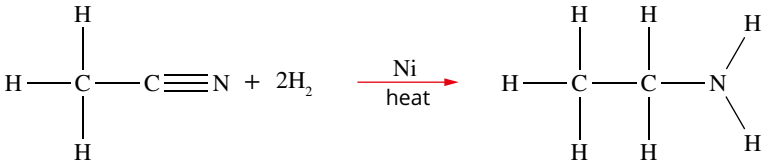


FIGURE 9.3.11 Reduction of ethanenitrile using hydrogen and a nickel catalyst producing ethylamine

CONDENSATION REACTIONS

Reactions that involve the combination of two reactants and the elimination of a small molecule, such as water, are called **condensation reactions**. These reactions show the important role that functional groups of organic compounds play in the formation of larger biomolecules. When the functional groups on two separate molecules react, the two molecules are covalently bonded. This creates a structure that has the combined size of the two reactants. When this process continues, many molecules (monomers) can be joined like beads on a string, forming polymers (see Module 13.1).

Ester formation and hydrolysis

Many biomolecules are composed of esters. In the natural world they give flowers and fruits their appealing aromas and tastes (Figure 9.3.12). For example, the ester 3-methylbutyl ethanoate gives bananas their aroma, and ethyl butanoate is found in pineapples.

Esters have the general structure shown in Figure 9.3.13.

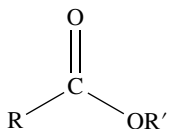


FIGURE 9.3.13 The general structure of esters

Reactions that involve the combination of two reactants and the elimination of a small molecule, such as water, are called condensation reactions.



FIGURE 9.3.12 The ripening of blackberries involves many chemical reactions, including the conversion of carboxylic acids to esters giving a fruity, ripe odour.

In this structure, we see a similarity to the carboxylic acids from which they are formed. The hydroxyl group (–OH) on the carboxylic acid has become a (–OR) group using the reaction described in Figure 9.3.14.

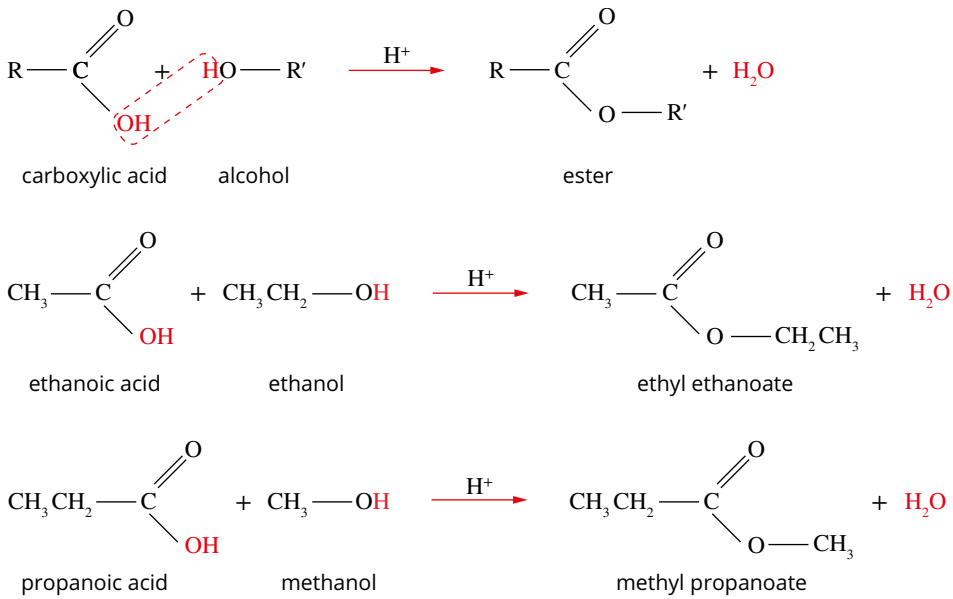


FIGURE 9.3.14 Esterification reactions occur when alcohols react with carboxylic acids and a small amount of sulfuric acid as a catalyst. The top reaction shows the general equation for esterification. Two specific examples are also shown: ethanoic acid with ethanol and propanoic acid with methanol.

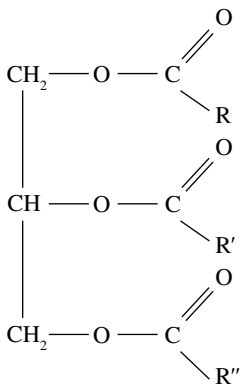


FIGURE 9.3.15 A triglyceride molecule showing its three long chains (R, R′, R″)

Ester polymers (**polyesters**) are synthesised to provide a range of fabrics and plastic products. Fats and oils are **triglycerides**—ester molecules made from a combination of a glycerol molecule and three molecules of long-chain carboxylic acids called **fatty acids**. This can be seen in Figure 9.3.15.

Esters are made by a condensation reaction between a carboxylic acid and an alcohol, also producing a water molecule. This is also known as an **esterification reaction**. For example, the ester ethyl ethanoate can be produced by reacting a mixture of ethanol and pure ethanoic acid with a trace amount of sulfuric acid. The sulfuric acid acts as a catalyst and the reaction will progress with little or no heating.

The general equation for the esterification reaction involving a carboxylic acid and an alcohol is shown in Figure 9.3.14. Two examples of esterification reactions are also shown.

In the esterification reaction, it is the hydrogen atom from the hydroxyl group of the alcohol and the –OH group from the carboxylic acid that combine to form water, which is the molecule eliminated in this condensation reaction. This means that the alcohol becomes the alkyl group bonded to the oxygen in the final ester. We see that, in the final ester, the part of the molecule derived from the carboxylic acid is identified by its C=O group, as shown in Figure 9.3.16.

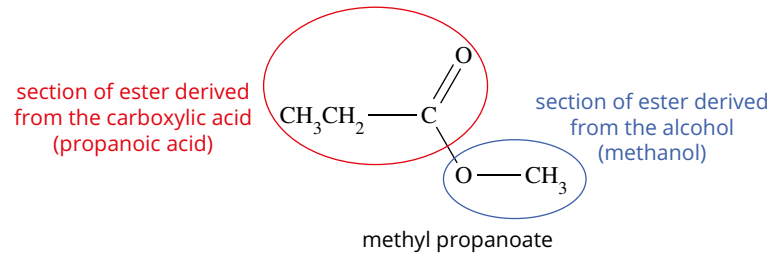


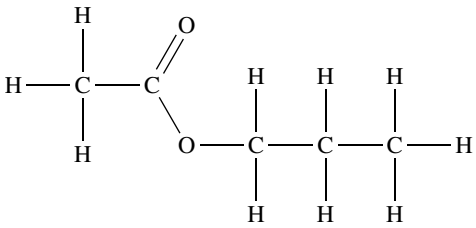
FIGURE 9.3.16 Identifying the acid and alcohol reacting to form an ester

As you learnt in Chapter 8, the first word of the name of an ester is derived from the name of the alcohol. The second word of the name is derived from the name of the carboxylic acid. Therefore, the name of the ester formed from methanol (alcohol) and propanoic acid (carboxylic acid) is methyl propanoate.

Worked example 9.3.2

DEDUCING THE PRODUCT OF AN ESTERIFICATION REACTION

Identify and draw the product(s) of the reaction of propanol and ethanoic acid in the presence of a sulfuric acid catalyst.

Thinking	Working
Use the organic reaction pathways in Figure 9.3.2 on page 330 to recall that a carboxylic acid and an alcohol will form an ester and water in the presence of an acid catalyst (condensation reaction).	An ester and a water molecule will be formed.
The first part of the name of the ester is derived from the name of the alcohol with '-yl' on the end.	propyl
The second part of the name is derived from the carboxylic acid with '-oate' on the end.	ethanoate
State the name using these two words.	propyl ethanoate
Recall that '-yl' refers to the part of the ester (R group) derived from the alcohol (propanol) and '-oate' refers to the part of the ester (R group) derived from the carboxylic acid (ethanoic acid). Draw an ester with both R groups with two carbons.	The ethanoate will have two carbons and the propyl will have three carbons. There will be COO in the centre (as for all esters). 

➤ Try yourself 9.3.2

DEDUCING THE PRODUCT OF AN ESTERIFICATION REACTION

Identify and draw the product(s) of the reaction of butanol and pentanoic acid in the presence of a sulfuric acid catalyst.

The condensation reaction between carboxylic acids and alcohols is a reversible reaction. You can see in Figure 9.3.17 that esters can react with water to form a carboxylic acid and an alcohol. Reactions of this type are described as hydrolytic reactions, or simply **hydrolysis**. This reaction is catalysed by an alkali or dilute acid and requires heat to proceed. This means that an esterification reaction can be reversed by the addition of heat and water to the ester.

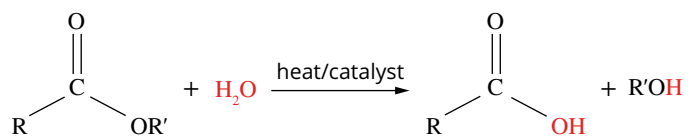


FIGURE 9.3.17 General equation for the hydrolysis of an ester

The products of a hydrolysis reaction can be deduced by identifying the R group derived from the carboxylic acid and the R' group derived from the alcohol. Figure 9.3.18 shows the equation for the hydrolysis of ethyl propanoate to form ethanol and propanoic acid using an acid catalyst. In the ester, the chain containing the C=O has three carbons and so we deduce that it was derived from propanoic acid. The chain on the other side of the oxygen atom has two carbons and so it must have been derived from ethanol. The products of hydrolysis of the ester, therefore, are propanoic acid and ethanol.

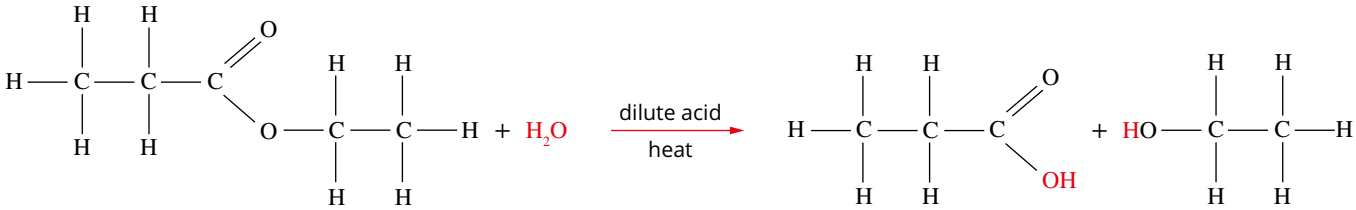
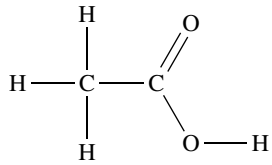
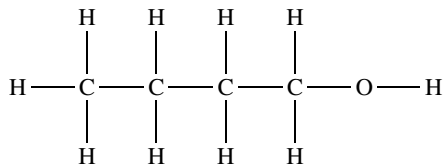


FIGURE 9.3.18 Equation for the acid-catalysed hydrolysis of ethyl propanoate to produce propanoic acid and ethanol

Worked example 9.3.3

DEDUCING THE PRODUCTS OF A HYDROLYSIS REACTION

Identify and draw the product(s) of the hydrolysis of the ester butyl ethanoate.	
Thinking	**Working**
Use the organic reaction pathways in Figure 9.3.2 on page 330 to recall that hydrolysis of an ester uses a water molecule and produces a carboxylic acid and an alcohol.	An acid molecule and an alcohol molecule will be formed.
Recall that in the name of the ester the '-yl' suffix indicates the R group derived from the alcohol (butyl). This indicates the alcohol formed.	Butanol is formed.
Recall that in the name of the ester the '-oate' suffix indicates the R group derived from the acid (ethanoic acid). This indicates the acid formed.	Ethanoic acid is formed.
OH is added to the two-carbon R group to form the acid. Draw the structure of ethanoic acid.	
H is added to the four-carbon R group to form the alcohol. Draw the structure of butanol.	

➤ Try yourself 9.3.3

DEDUCING THE PRODUCTS OF A HYDROLYSIS REACTION

Identify and draw the products of the hydrolysis of the ester propyl methanoate.

Amide formation

Another key condensation reaction of carboxylic acids is the preparation of amides by the reaction of a carboxylic acid with ammonia or an amine. Primary amides ($RCONH_2$) can be prepared by the reaction of a carboxylic acid with ammonia. In Figure 9.3.19 you can see the production of ethanamide from ethanoic acid and ammonia. The reaction is a condensation reaction similar to the one you saw between a carboxylic acid and an alcohol to form an ester. A water molecule is produced during the reaction.

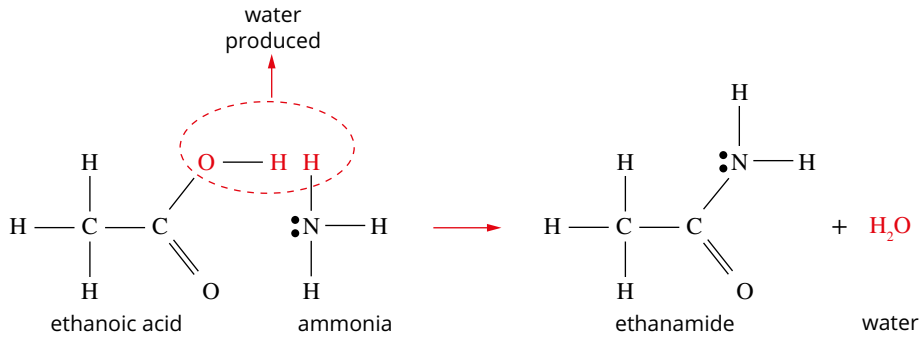


FIGURE 9.3.19 Reaction of ethanoic acid with ammonia to produce the primary amide ethanamide

Secondary amides have the general formula RCONHR′, where R and R′ represent alkyl groups. The condensation reaction between an acid and an amine forms a secondary amide and a water molecule (shown in Figure 9.3.20). An amide link is formed in this reaction.

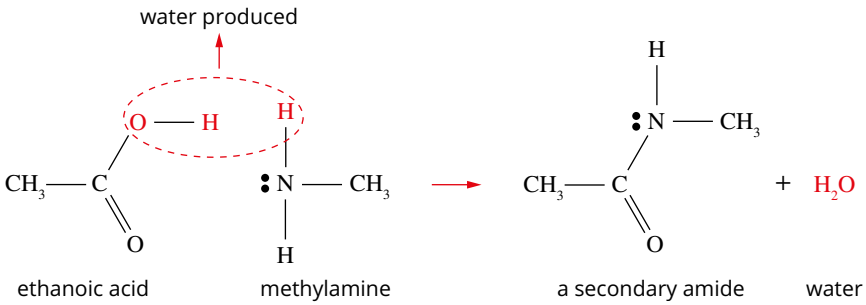


FIGURE 9.3.20 Formation of the secondary amide methylethanamide by a condensation reaction of ethanoic acid and methylamine

Carboxylic acids undergo condensation reactions with alcohols to form esters, and with ammonia or amines to form amides.

9.3 Review

SUMMARY

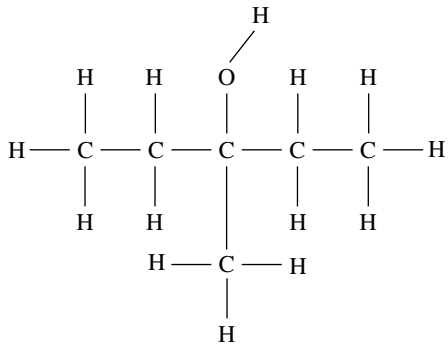
- Alcohols, aldehydes, ketones, carboxylic acids, esters, nitriles, amines and amides undergo reactions such as oxidation, reduction, condensation and hydrolysis.
- Alcohols undergo combustion when they react with oxygen to produce carbon dioxide, water and energy.
- Alcohols react with oxidising agents such as acidified solutions of dichromate ions and acidifed permanganate ions in different ways.
  - Primary alcohols are oxidised first to aldehydes, which may be oxidised further to carboxylic acids.
  - Secondary alcohols are oxidised to ketones.
  - Tertiary alcohols are resistant to oxidation by these oxidising agents.
- Nitriles can be reduced using metal catalysts such as nickel or palladium to produce amines.
- Carboxylic acids react with alcohols in a condensation reaction in the presence of an acid catalyst to produce esters.
- Esters can be hydrolysed by dilute acids to produce alcohols and carboxylic acids.
- Carboxylic acids react with amines in a condensation reaction to form amides.
- The reactions can be represented by chemical equations using chemical formulas or structural formulas, and showing reaction conditions above the arrow.

KEY QUESTIONS

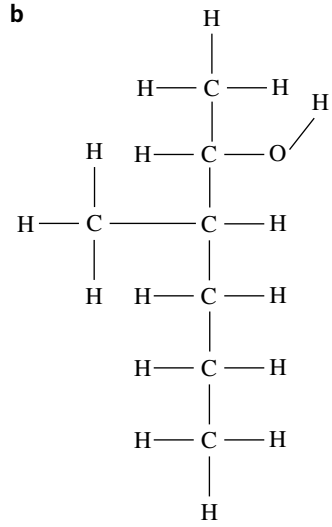
Retrieval

1 Identify each of the following alcohols as primary, secondary or tertiary.

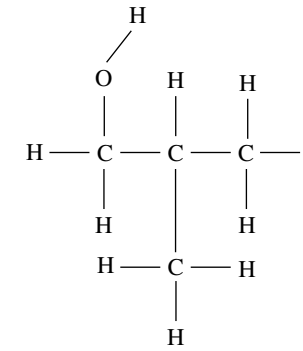
a



b



c



2 Pentan-3-ol, 2-methylbutan-2-ol and pentan-1-ol are all isomers of $C_5H_{12}O$.

a Construct an equation for the complete combustion of $C_5H_{12}O$.

b Identify each isomer as a primary, secondary or tertiary alcohol.

c For each isomer, show the equation (using structural formulas) for the reactions that would occur if the alcohol was heated with acidified potassium permanganate solution. Describe any colour changes that would be observed.

3 Identify the products of a reaction in the following table where compounds A to D are heated with an acidified oxidising agent for an extended period of time.

Compound	IUPAC name	Product
A	butan-1-ol	
B	pentan-2-ol	
C	2-methylpentan-2-ol	
D	propan-2-ol	

4 **a** State what reaction conditions are required for the hydrolysis of an ester.

b Name the products that would be formed from the acid hydrolysis of each of the following esters.

i $CH_3CH_2CH_2CH_2COOCH_3$

ii $CH_3COOCH_2CH_2CH_3$

iii $CH_3CH_2COOCH_2CH_2CH_2CH_2CH_2CH_3$

5 Recall the appropriate terms to complete the following sentences.

When a carboxylic acid reacts with an amine, the organic product is an _____. The other product in this reaction is _____. This is an example of a _____ reaction.

Comprehension

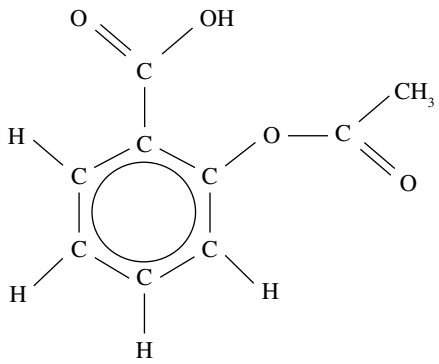
6 Draw and name the organic products of the reaction between:

a methyl butanoate and dilute acid solution and heat

b ethanol and propanoic acid, using concentrated sulfuric acid as a catalyst.

Analysis

7 The image below shows the chemical structure of aspirin (acetylsalicylic acid).



Identify the ester functional group in the structure of aspirin. Deduce the carboxylic acid that was used to prepare this ester.

9.4 Designing reaction pathways



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- recognise ways that organic chemistry reaction pathways are composed of individual reactions
- understand that reaction pathways may interconnect by having the same reactants and/or products
- distinguish reactions that require special conditions or catalysts to proceed
- deduce reaction pathways given a reactant and/or product
- understand conditions and catalysts necessary for certain reactions.

Organic chemists focus on developing compounds that have exactly the right properties needed for a particular purpose. These may be new pharmaceuticals, polymers or nanomaterials. Once the desired compound has been identified, chemists must devise a way to make it. This means devising an efficient method for converting readily available starting materials—often alkenes or alkanes—into the more complex product(s) required.

In this module, you will learn how to devise reaction pathways for the synthesis of some simple organic compounds by utilising the reactions you have learnt about in Modules 9.2 and 9.3.

While the syllabus states that conversions with more than two stages will not be assessed, this module will use short and longer synthetic pathways to demonstrate and test your understanding and knowledge of the reactions.

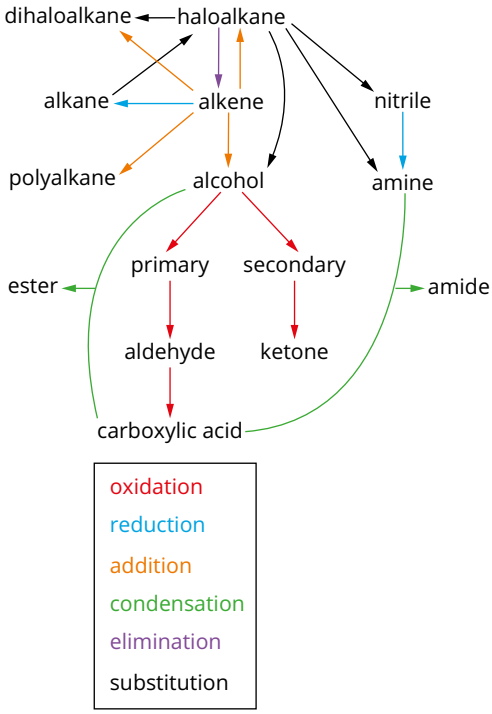


FIGURE 9.4.1 Common organic chemical pathways

REACTION PATHWAYS FOR ORGANIC COMPOUNDS

The in-depth discussions of organic chemistry reaction pathways provided in Modules 9.2 and 9.3 have focused on six key chemical reactions:

- oxidation
- reduction
- addition
- condensation
- elimination
- substitution.

These chemical reactions are summarised in Figure 9.4.1. You have learnt that simpler molecules such as alkanes, alkenes and alcohols may be used as starting materials to make other molecules such as carboxylic acids, esters and amides. This means that they are precursors of the final product, or target molecules. The individual reactions are a series of steps or stages that make up a reaction pathway that can be used to convert a reactant containing certain functional groups to a desired product with different functional groups.

For example, Figure 9.4.1 shows that an alcohol can be produced by starting with a haloalkane, enacting an elimination reaction to produce an alkene, or formed directly through a substitution reaction between the haloalkane and sodium hydroxide. The choice of reaction depends on the nature of the alcohol required. Both the haloalkane and the alkene are precursors of the alcohol. The elimination reaction removes a hydrogen halide, and the addition reaction adds a water molecule. Note also that if the haloalkane was not available for this pathway, it could be synthesised using a substitution reaction with an alkane.

You have also learnt that inorganic reactants are required for these reactions and that some of these reactions require special conditions to proceed (Figure 9.4.2).

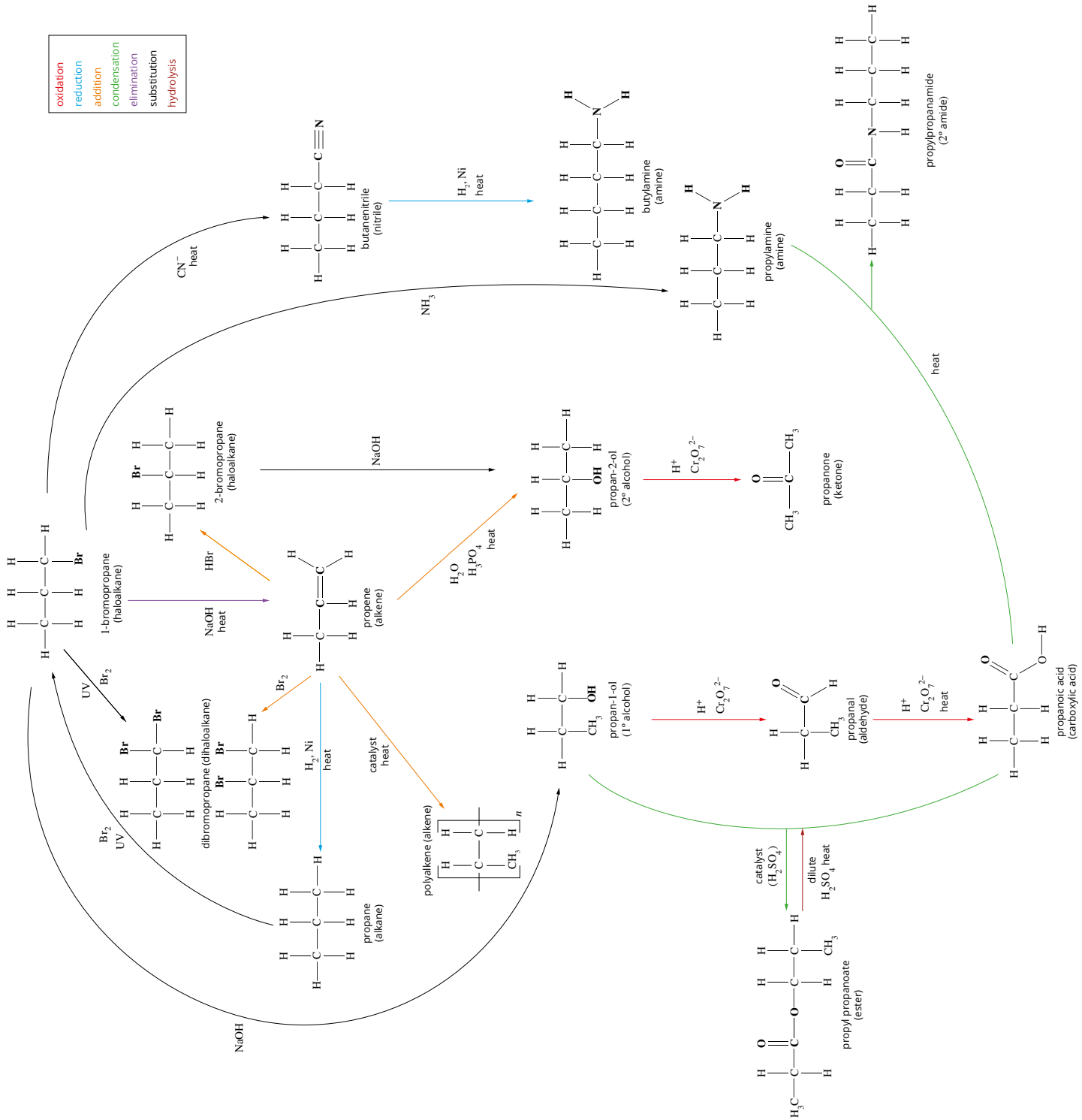


FIGURE 9.4.2 Reaction pathways described in this chapter showing chemical structures and reaction conditions such as catalysts (metal or acid), heat or oxidising agent (e.g. $H^+/Cr_2O_7^{2-}$). Functional groups are shown in bold. Note that addition reactions of alkenes must follow Markovnikov's rule and therefore the major product of halogen addition to an alkene is a secondary haloalkane not primary haloalkane.

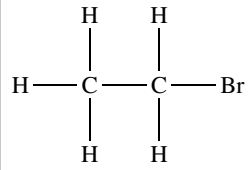
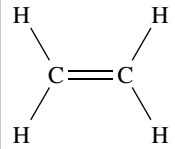
These conditions include catalysts (such as metal or acid), heat or an oxidising agent (e.g. $Cr_2O_7^{2-}$). You will notice that the structural formulas shown in Figure 9.4.2 give a better visual understanding of the chemical changes because functional groups (shown in bold) are clearly visible in each structure.

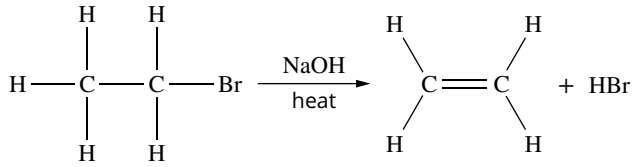
By understanding and recalling the reactions shown in Figure 9.4.2, you should be able to deduce the organic product from given starting molecules and reaction type. Conversely, the precursor can be deduced using information given about the product and process. For example, synthesis of ethylamine can occur in two ways. Firstly, a substitution reaction of chloroethane with NH_3 could be used. Alternatively, a substitution reaction of chloromethane using CN^- followed by a reduction reaction using hydrogen gas, nickel catalyst and heat. The following shows a simple and then a more complex deduction using the pathways in Figure 9.4.2.

Worked example 9.4.1

DEDUCING A SIMPLE REACTION PATHWAY

Use structural formulas to show the chemical reaction by which ethene is synthesised by an elimination reaction.

Thinking	Working
Use the reaction pathways in Figure 9.4.2 on page 343 to recall that alkenes are made from haloalkanes by an elimination reaction. The haloalkane required must have two carbon atoms.	
Recall that NaOH is required for this reaction to proceed and heat must be used because milder reaction conditions will favour substitution. NaOH is a catalyst not a reactant, and so is written above the arrow in the chemical equation.	NaOH, heat
The reaction eliminates HBr allowing a double bond to form between the two carbon atoms.	



➤ Try yourself 9.4.1

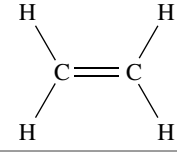
DEDUCING A SIMPLE REACTION PATHWAY

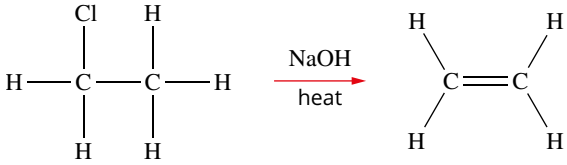
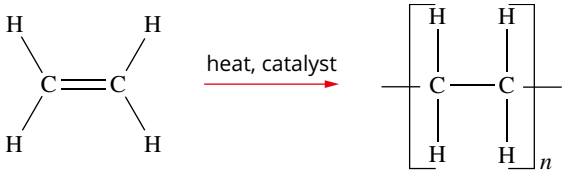
Use structural formulas to show the chemical reaction by which chloropropane is synthesised by a substitution reaction.

Worked example 9.4.2

DEDUCING A COMPLEX REACTION PATHWAY

Describe the reaction(s) required to synthesise polyethene from chloroethane. Draw all relevant structures.

Thinking	Working
Use the organic reaction pathways in Figure 9.4.2 on page 343 to recall that polyalkenes are synthesised from alkenes. The pathway required is: haloalkane → alkene → polyalkene	Synthesis of polyethene requires first making ethene. 

The reactant provided (chloroethane) must be converted to an ethene first. Sodium hydroxide (NaOH) and heat must be used for the elimination reaction. Milder conditions will favour the substitution reaction.	To make ethene, chloroethane undergoes an elimination reaction using NaOH and heat. 
A second reaction is required. This is the synthesis of polyethene from the ethene.	Then ethene is converted to polyethene using heat and a catalyst. 

➤ Try yourself 9.4.2

DEDUCING A COMPLEX REACTION PATHWAY

Describe the reaction(s) required to synthesise propanenitrile from ethane. Draw all relevant structures.

In Chapter 8 you learnt about reaction pathways using condensed structural formulas. The following chemical equation shows condensed structural formulas for the reaction shown in Worked example 9.4.1:

$$CH_3CH_2Br \xrightarrow{\text{UV light}} CH_2CH_2 + HBr$$

Condensed structural formulas are often a more efficient way to depict complex organic chemistry pathways than using structural formulas. Figure 9.4.3 shows a five-step reaction pathway, where an ester has been synthesised from an alkane (ethane). In this reaction pathway, we see that the target molecule, an ester, has five precursors and is the result of five chemical reactions. It is clear that condensed structural formulas provide an efficient notation in these situations.

$$CH_3CH_3 + Cl_2 \xrightarrow{\text{UV light}} CH_3CH_2Cl \xrightarrow{\text{NaOH}} CH_2CH_2 \xrightarrow[\text{heat}]{H_3PO_4} CH_3CH_2OH$$

$$\xrightarrow[\text{heat}]{H^+/Cr_2O_7^{2-}} CH_3COOH + ROH \xrightarrow{H_2SO_4} CH_3COOR + H_2O$$

FIGURE 9.4.3 Reaction pathway showing the synthesis of an ester from an alkane

Considerations in reaction pathways

To produce a target molecule, there must be sufficient quantities of all reactants. In addition, you have learnt that organic chemistry pathways often require catalysts and specific conditions for reactions to proceed. The role of these conditions and catalysts is to promote interactions between reacting molecules. They have the effect of enhancing charge interactions between molecules, as described in Module 9.1. The special conditions that we learnt about in our study of organic reactions are heat, metal catalysts, oxidising agents, strong acids or strong bases, as shown in Figure 9.4.2 on page 343. They are written above or below the arrow in a chemical equation because they catalyse the reaction but do not take part in it.

Often combinations of reaction conditions are used, and more than one reagent will achieve the result. For example, the oxidising agent acidified MnO_4^- can be substituted for acidified $Cr_2O_7^{2-}$. Metal catalysts can include Pt, Pd as well as Ni. Also, H_3PO_4 may be substituted for the acid catalyst H_2SO_4.

By writing some general rules these conditions can be more easily recalled. Table 9.4.1 summarises reaction type and conditions used. Most but not all reactions learnt in this chapter are represented here, and some of these reactions also require the application of heat.

TABLE 9.4.1 Some general rules for organic reaction conditions

Reaction type	Conditions used
oxidation	MnO_4^- or $Cr_2O_7^{2-}$ in acidic solution*
reduction	Ni, Pd or Pt (metal catalyst), heat
elimination	NaOH, heat

* to oxidise an aldehyde to a carboxylic acid heat must also be used

USING REACTION PATHWAYS

The complex understanding of interconversion of organic compounds that you have developed in this chapter means that you can devise laboratory procedures to produce a required compound. These procedures may have one or several reactions or steps comprising the overall reaction pathway. Reaction pathways can be compared to travelling in a car. Origin, destination and route must be considered. Using this analogy, we can compare Figures 9.4.1 and 9.4.2 to a map that indicates possible routes on which to travel to reach a destination. While you are expected to be familiar with the reactions described here, explanation of pathways with multiple steps (more than two) is not required.

Making ethyl ethanoate

Suppose you wanted to form ethyl ethanoate using only alkenes as starting materials. A close look at the structure of the compound shown in Figure 9.4.4 will show you that it is an ester produced by the condensation reaction between ethanoic acid and ethanol. We know this because the structure shows two different alkyl or R groups, with an ester functional group in the middle. The R group containing C=O is derived from the carboxylic acid, and the R group containing the –O is derived from the alcohol. This information is also obtained from the name of the ester. The 'yl' suffix indicates the alcohol (ethanol) that reacted to produce the ester, and the 'oate' suffix indicates the reacting carboxylic acid (ethanoic acid) that reacted to produce the ester.

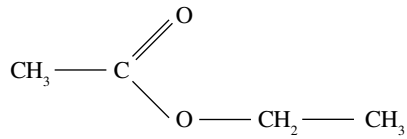


FIGURE 9.4.4 Structure of ethyl ethanoate

To form ethyl ethanoate, ethanol and ethanoic acid need to be synthesised first, before they can react to form the ester. As described, the designated reactants are alkenes. This means that the strategy to form ethyl ethanoate is to use an alkene to make ethanol and ethanoic acid, followed by a reaction of these two to form the ester.

Reagents and conditions for making ethanol

Ethanol can be synthesised from ethene by the addition reaction with water, as shown in Figure 9.4.5. You can see the conditions for the reaction require an acid catalyst (placed above the arrow) and a reactant (H_2O).

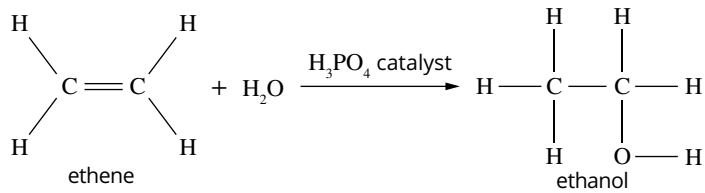


FIGURE 9.4.5 Synthesis of ethanol using ethene

Reagents and conditions for making ethanoic acid

Ethanoic acid is a carboxylic acid containing two carbon atoms. It can be prepared by the pathway shown in Figure 9.4.6. If you work backwards from ethanoic acid, you can see that it can be formed from the oxidation of the primary alcohol ethanol. This in turn can be formed by the reaction of ethene with phosphoric acid.

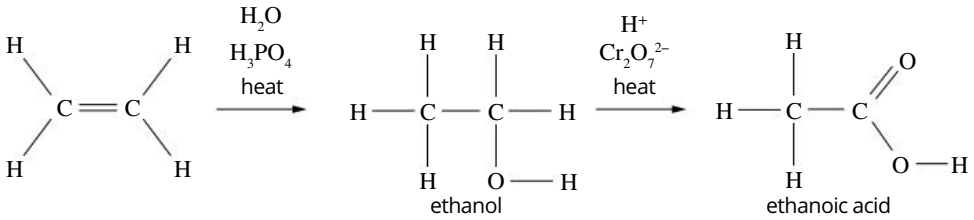


FIGURE 9.4.6 Synthesis of ethanoic acid from ethene

Having synthesised ethanol and ethanoic acid, you can now prepare the ester, ethyl ethanoate, using a condensation reaction as shown in Figure 9.4.7.

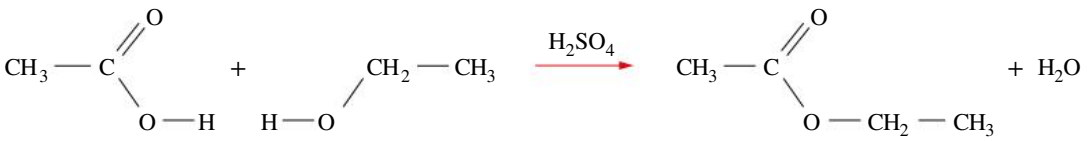


FIGURE 9.4.7 The formation of ethyl ethanoate from the condensation reaction of ethanol and ethanoic acid

The full reaction pathway for the preparation of ethyl ethanoate from ethene via ethanol and ethanoic acid is summarised in Figure 9.4.8.

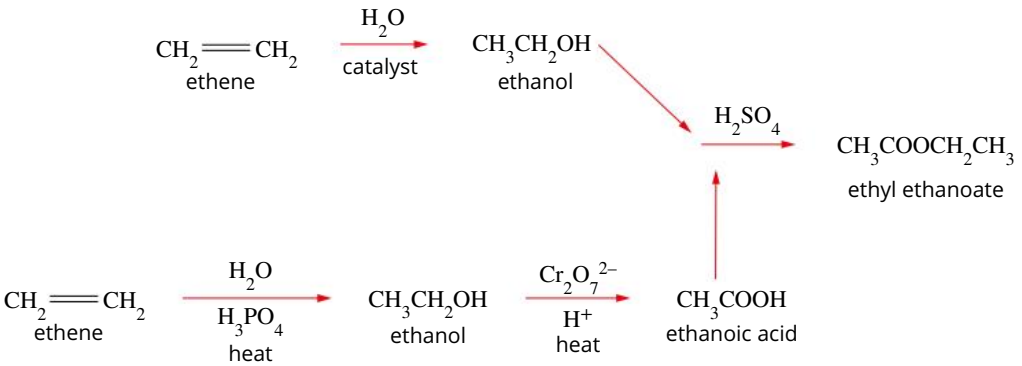


FIGURE 9.4.8 Reaction pathway for the preparation of ethyl ethoanate

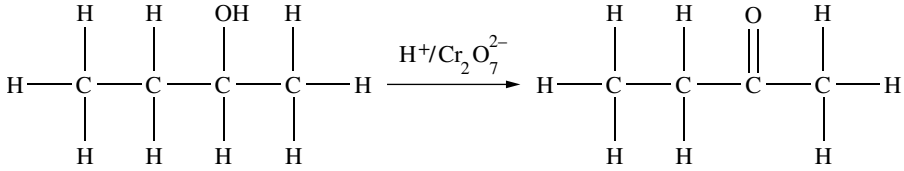
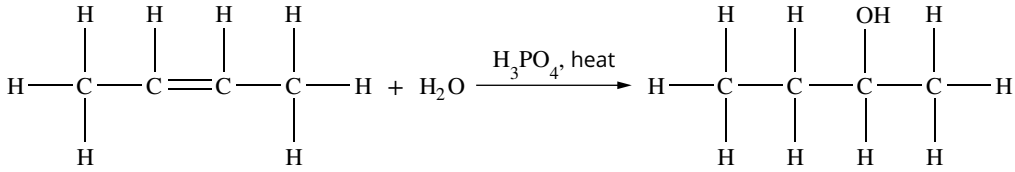
The desired ester product can be separated from the reaction mixture and purified by **fractional distillation**.

A reaction pathway summarises the reactions required to produce a product from simple starting materials.

WS 4.1.5

Worked example 9.4.3

DEDUCING A REACTION PATHWAY

Describe the reaction pathway for the synthesis of butanone from but-2-ene.	
Thinking	**Working**
Use the organic reaction pathways in Figure 9.4.2 on page 343 to work backwards and recall that butanone is synthesised from butanol by an oxidation reaction with hydrogen using dichromate ions in acid solution.	The second reaction of the pathway produces butanone by an oxidation reaction of butan-2-ol with dichromate ions in acid solution. 
Work backwards to but-2-ene from 2° butanol. The reaction that produces the alcohol from the alkene requires phosphoric acid and heat.	The first reaction of the pathway produces butan-2-ol by an addition reaction of but-2-ene with phosphoric acid. 
Show the reaction pathway in order of progression.	$CH_3CHCHCH_3 + H_2O \xrightarrow{H_3PO_4, heat} CH_3CH_2CHOHCH_3 \xrightarrow{H^+/Cr_2O_7^{2-}} CH_3CH_2COCH_3$

The addition of water to but-1-ene would also yield butan-2-ol, with Markovnikov's rule adding the H to carbon number 1 and the OH to carbon number 2. Therefore, it is important when designing reaction pathways to consider different options. This will be covered in Module 12.1 through a discussion of retrosynthetic pathways and atom economy (Module 12.8).

➤ Try yourself 9.4.3

DEDUCING A REACTION PATHWAY

Describe the reaction pathway for the synthesis of propylamine from propane.

The flow chart in Figure 9.4.9 shows some of the stages in the planning process for a synthesis scheme.

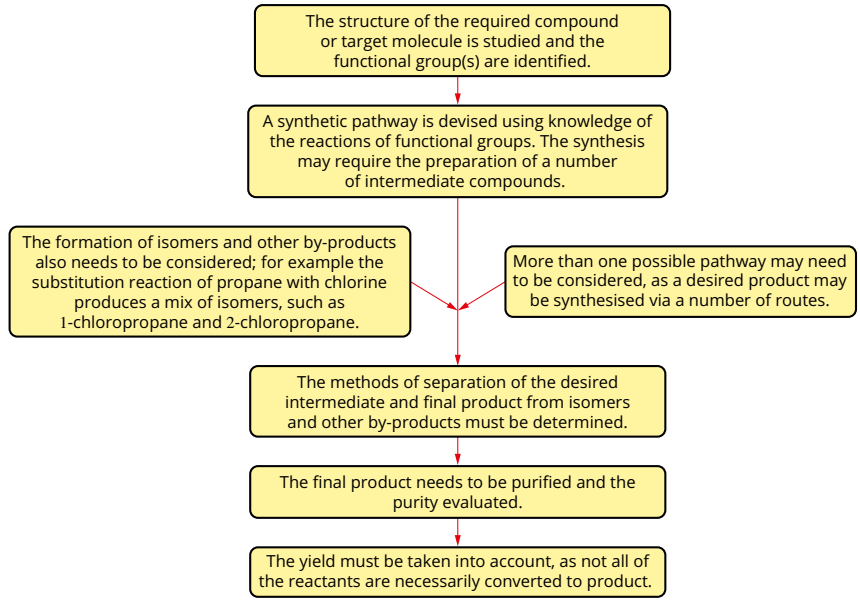


FIGURE 9.4.9 Steps in the design of a synthetic pathway of an organic compound

9.4 Review

SUMMARY

- A reaction pathway is a sequence of more than one reaction that is used to convert a reactant into a product.
- Reaction pathways can be constructed using the organic reactions studied in this chapter.
- Reaction pathways indicate the reaction conditions and reagents required for each step.

KEY QUESTIONS

Retrieval

1 Identify which of the following is involved in an addition reaction when an alcohol is formed from an alkene.

A a metal catalyst
B sodium hydroxide
C steam and an acid catalyst
D reaction with a halogen gas

2 N-ethylpropanamide can be made from propanol and ethanamine in the following reaction pathway.
1-propanol → compound A → compound B + ethanamine → N-ethylpropanamide

a Identify compound A.
b Name the chemical used to convert 1-propanol to compound A.
c Identify compound B.
d Name the chemicals and the reaction conditions used to convert compound A to compound B.
e State the name of the final reaction and the inorganic product.

Comprehension

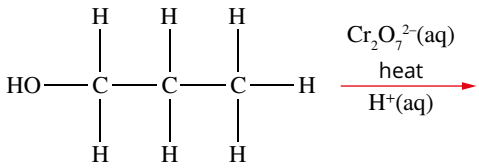
3 Show reaction pathways for the following reactions.

a ethylamine from chloroethane
b butan-1-ol from butane
c pentanoic acid from 1-chloropentane

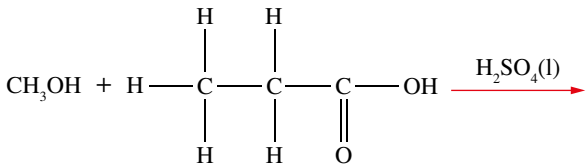
4 Describe a reaction pathway to synthesise butyl ethanoate from appropriate alkane or alkene starting materials.

5 Draw the structural formulas of the products of the following reactions.

a



b



Analysis

6 A student reacted a sample of bromopropane with ammonia, and then reacted the product with butanoic acid.

a Determine the names of the two reactions occurring.
b Deduce the class and the structural formula of the final product.

7 A sample was reacted with chlorine gas under UV light, then the substance was reacted with sodium hydroxide and heat. The final product was shown to change bromine water from brownish-red to colourless. Deduce which of the following correctly lists the likely changes to the contents of the test tube.

A alkene $\xrightarrow{\text{addition}}$ haloalkane $\xrightarrow{\text{elimination}}$ alkene
B alkane $\xrightarrow{\text{substitution}}$ haloalkane $\xrightarrow{\text{addition}}$ alkene
C alkene $\xrightarrow{\text{reduction}}$ alkane $\xrightarrow{\text{substitution}}$ haloalkane
D alkane $\xrightarrow{\text{substitution}}$ haloalkane $\xrightarrow{\text{elimination}}$ alkene

Chapter review

09

KEY TERMS

addition polymerisation
addition reaction
alkyl group
catalyst
combustion
complete combustion
condensation reaction
elimination reaction
esterification reaction
exothermic
fatty acid
fractional distillation
hydrolysis
Markovnikov's rule
monomer
oxidation–reduction reaction
polar bond
polyester
polymer
reaction pathway
substitution reaction
triglyceride

KEY QUESTIONS

Retrieval

1 When an ester is formed from a carboxylic acid and an alcohol, the condensation reaction that occurs involves:
- **A** two hydroxyl functional groups
- **B** a carboxyl functional group and an amino functional group
- **C** a hydroxyl functional group and a carboxyl functional group
- **D** a hydroxyl functional group and an amino functional group.

2 Substances that are required to make organic reaction pathways proceed but are not used up in the reaction are called:
- **A** catalysts
- **B** products
- **C** reactants
- **D** precursors.

Questions 3 to 6 refer to the following information.

The following list gives the formulas of a number of organic molecules.

I CH_3CH_2COOH
II $CH_3CH_2CH_2CH_2NH_2$
III CH_3OH
IV $CH_2CHBrCH_3$
V $CH_3CH_2CH_2CH_3$
VI $CH_3CHCHCH_3$

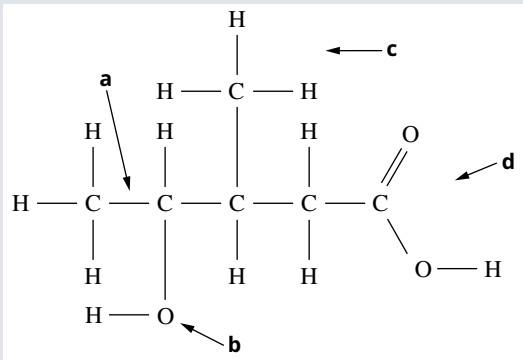
3 Identify two molecules that would react together to form an ester.
- **A** I and III
- **B** I and V
- **C** III and IV
- **D** IV and VI

4 Select two possible product sets that might be formed when an unsaturated molecule undergoes addition.
- **A** IV and V
- **B** I and III
- **C** V and VI
- **D** II and VI

5 Identify two molecules that are necessary for amide production.

6 Identify a product that might be formed when a haloalkane undergoes an elimination reaction.

7 Identify the structures or functional groups labelled a, b, c and d.



8 Identify which of the following best distinguishes the role of acidified potassium dichromate in organic reactions. It catalyses:
- **A** oxidation reactions by promoting the loss of H atoms
- **B** reduction reactions by promoting the gain of O atoms
- **C** oxidation reactions by promoting both the loss of H atoms and the gain of O atoms
- **D** reduction reactions by promoting both the loss of H atoms and the gain of O atoms.

9 Identify which of the following equations correctly represents the complete combustion of ethanol.

A $CH_3CH_2OH(l) + O_2(g) \rightarrow 2C(s) + 3H_2O(g)$

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

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

D $CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3COOH(l) + H_2O(g)$

Comprehension

10 Propene undergoes reaction 1 to form propanol and reaction 2 to form chloropropane. Determine which of the following statements correctly describes these two reactions.

A Both reactions are substitution reactions; reaction 1 requires water as a reactant and reaction 2 requires hydrogen chloride

B Both reactions require UV light; they are both substitution reactions

C Both reactions are addition reactions; reaction 1 requires water as a reactant and reaction 2 requires hydrogen chloride

D Reaction 1 is a substitution reaction and reaction 2 is an addition reaction; they both require an acid catalyst

11 Ethene molecules are able to undergo addition reactions because they possess a:

A C=C double bond

B large number of C–H bonds

C similar number of C and H atoms

D similar spatial arrangement of certain H atoms around each C atom.

12 Primary and secondary alcohols undergo oxidation but tertiary alcohols will not. This is because primary and secondary alcohols possess:

A a similar ratio of C:H:O atoms

B at least one C–C multiple bond

C a large number of hydroxyl groups

D the hydroxyl group attached to a carbon that has at least one H bonded to it.

13 Chloroethane (C_2H_5Cl) is a product in the reaction between ethane and chlorine. The equation for the reaction is:

$$C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$$

Recall the name of this reaction, explain this name and state the reaction conditions.

14 Construct a balanced chemical equation for each of the following reactions.

a gaseous ethene reacted with gaseous hydrogen chloride

b gaseous propene reacted with hydrogen gas in the presence of nickel and heat

15 Construct equations for the production of:

a propan-2-amine from 2-bromopropane

b chloropropane from propane

c butan-2-ol from butene.

16 Recall the name of the functional group that will be formed in reactions of the following types of alcohols with acidified potassium permanganate solution. (If there is more than one possible product, state both names.)

a primary alcohol

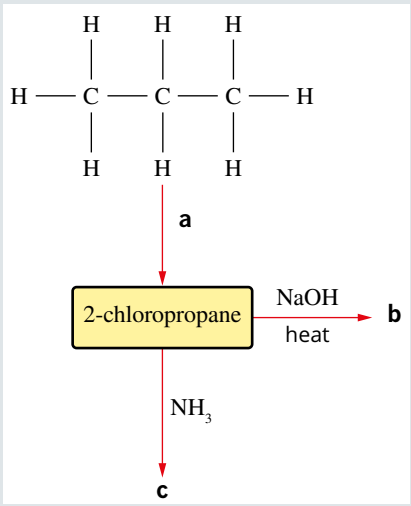
b secondary alcohol

c tertiary alcohol

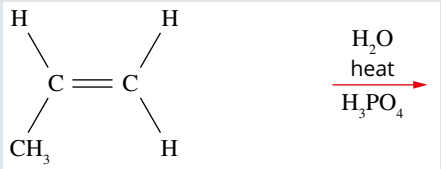
17 Identify the different reactions of alkenes by completing the following table.

Reactants	Type of reaction	Product(s)
alkene and hydrogen		
alkene and hydrogen bromide		
alkene and water (with a catalyst)		
alkene and bromine		

18 Indicate the correct reagents/products (**a**–**c**) by completing the following flow chart of organic reactions.



19 Show the structural formula for the product of this reaction and state the reaction type.



20 Construct chemical pathways in the form of flow diagrams to describe the preparation of:

a a haloalkane from an alkane

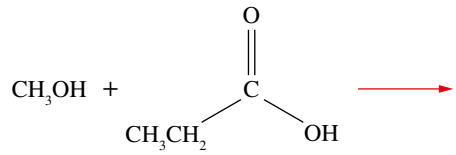
b a carboxylic acid from an alcohol.

Analysis

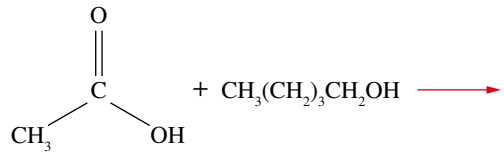
21 Construct chemical equations using condensed formulas for the reaction between:
- **a** butane and chlorine
- **b** ethane and oxygen.

22 Identify the product of the following reactions using condensed formulas.

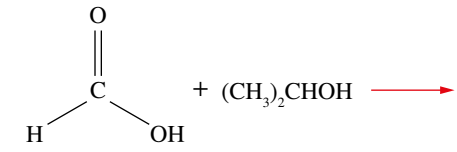
a



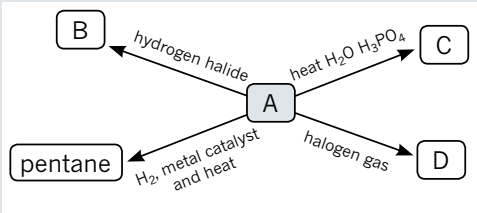
b



c



23 Deduce the identities of A, B, C and D.



24 Give the condensed formulas for the products of the hydrolysis of each of the following esters when an acid is used as a catalyst.
- **a** methyl ethanoate
- **b** propyl ethanoate
- **c** ethyl methanoate

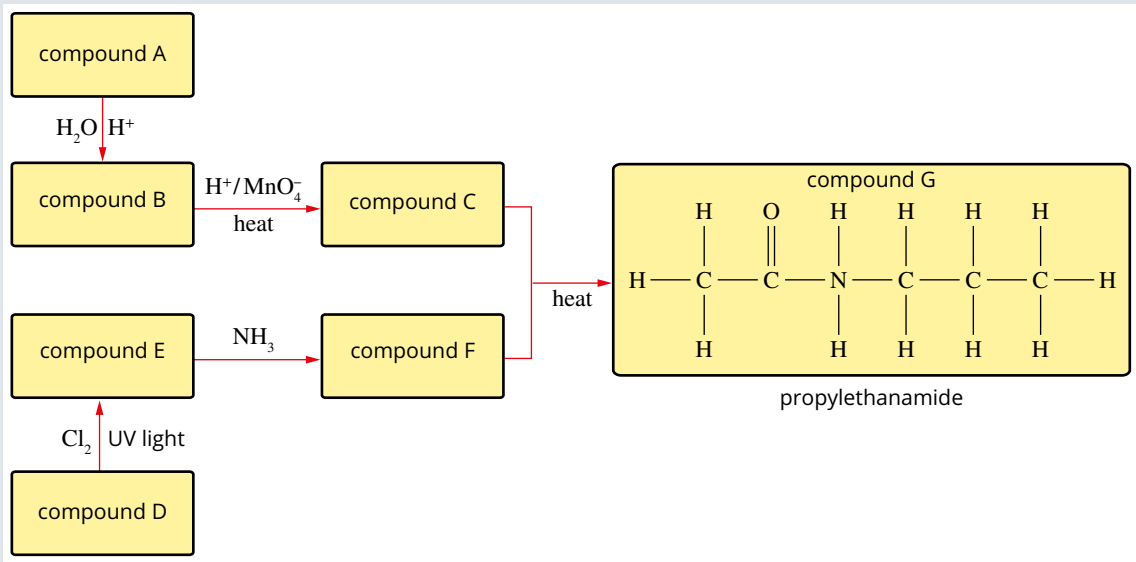
25 Draw the structural formula of the product that will be formed from the reaction of:
- **a** ethanoic acid and propylamine
- **b** methanamine and methanoic acid
- **c** pentan-3-ol heated with $H^+/Cr_2O_7^{2-}$
- **d** butan-1-ol with $H^+/Cr_2O_7^{2-}$, mild heat; the product is distilled off as it forms.

26 Construct a reaction pathway for the synthesis of ethyl ethanoate from an alkene.

27 Construct a balanced chemical equation and draw structures for the conversion of ethanitrile to ethylamine. Identify the type of reaction occurring.

28 Using the reaction described in question **27**, describe the changes to the carbon–nitrogen bond and suggest why this reaction requires both a metal catalyst and heat to proceed.

29 The reaction pathway shown below leads to the organic compound G (propylethanamide).
- **a** Identify the structural formulas of the appropriate compound for A–F and fill in the boxes to complete the pathway.
- **b** Describe a chemical test that could be carried out to distinguish between compounds A and D in the pathway.
- **c** Identify any substitution reactions.



Knowledge utilisation

30 Propose a reaction pathway that will synthesise:

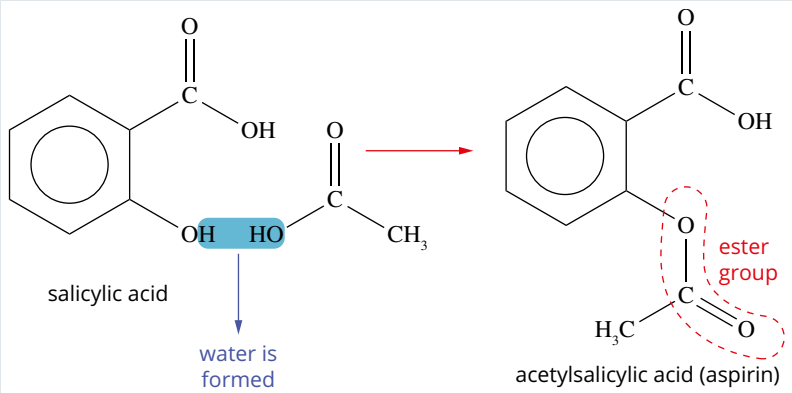
a butanone from butan-2-ol

b butanone from butan-1-ol

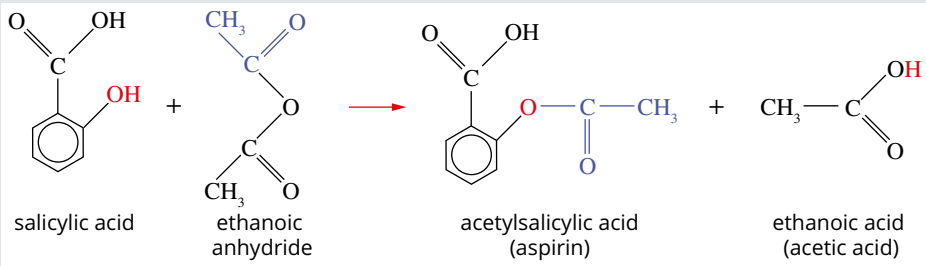
c ethanol from ethene

d propyl methanoate from methanol and propane.

31 Aspirin can be synthesised by an esterification reaction of salicylic acid and ethanoic acid. The process involves a reaction between hydroxyl and carboxyl functional groups to form an ester, according to the pathway shown below.



Although this reaction can be easily carried out in a laboratory, the yield is quite low. Another reaction (shown below) using salicylic acid and ethanoic anhydride is used to produce large quantities.



Research both of these processes on the internet and evaluate the similarities and differences between these two processes.



CHAPTER

10 Organic materials: structure and function

Food and the rituals associated with dining play a big part in everyday life in many countries. While eating can be a cultural experience, it is also a 'chemical' experience.

Most foods are complex mixtures of chemical substances. These substances have chemical structures and bonds like all the organic chemicals you studied previously. You eat to obtain the energy and raw materials your body needs to function and for growth and repair. Food contains the various organic compounds that provide the energy and raw materials your body needs.

Each food is different and contains common nutrients such as proteins, fats and carbohydrates. The labels on processed foods show how much they contain of these nutrients. In this chapter, you will study the structures, formation and function of these three major food groups.

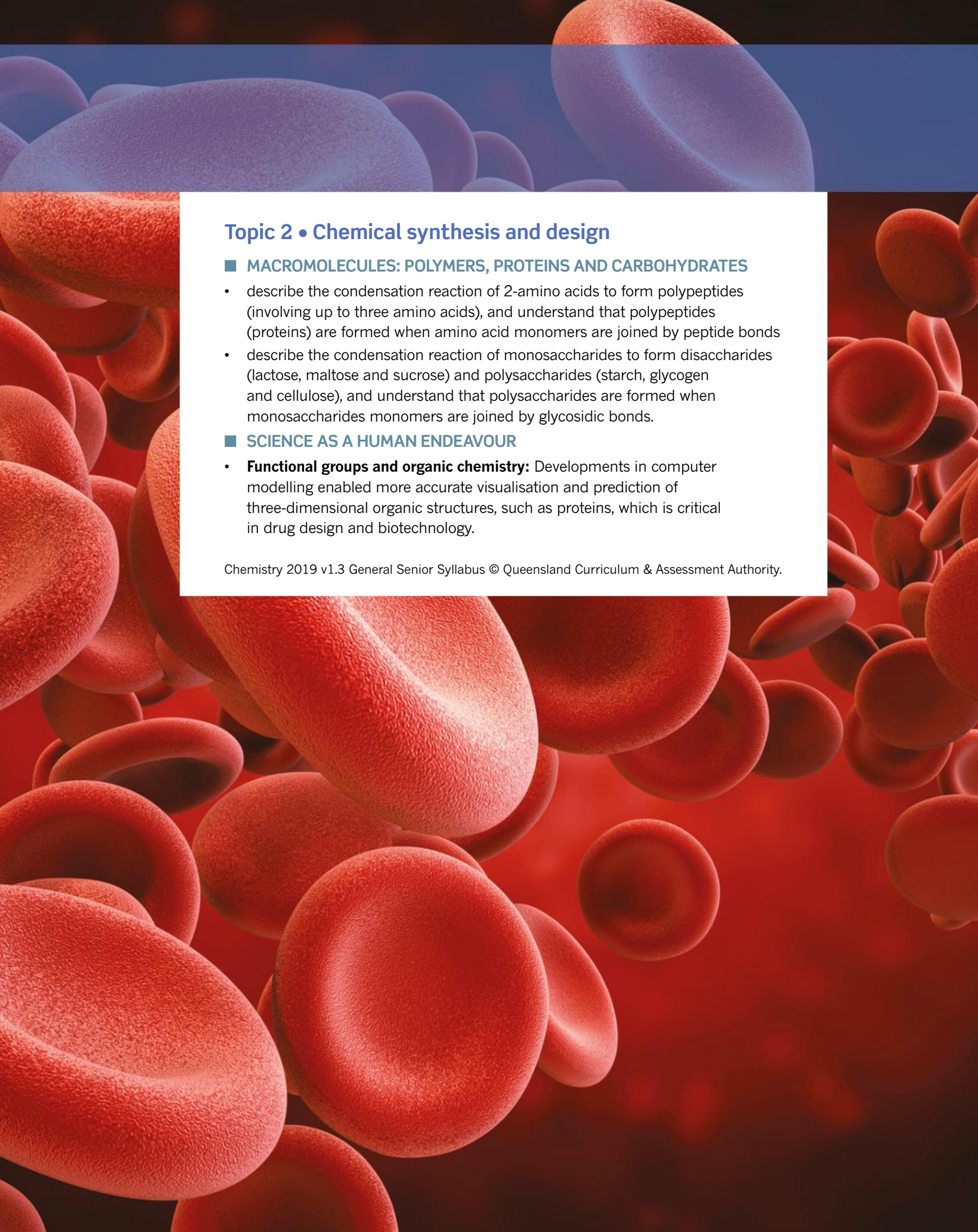
WS 4.2.1

Syllabus subject matter

Topic 1 • Properties and structure of organic materials

ORGANIC MATERIALS: STRUCTURE AND FUNCTION

- appreciate that organic materials including proteins, carbohydrates, lipids and synthetic polymers display properties including strength, density and biodegradability that can be explained by considering the primary, secondary and tertiary structures of the materials
- describe and explain the primary, secondary (α-helix and β-pleated sheets), tertiary and quaternary structure of proteins
- recognise that enzymes are proteins and describe the characteristics of biological catalysts (enzymes) including that activity depends on the structure and the specificity of the enzyme action
- recognise that monosaccharides contain either an aldehyde group (aldose) or a ketone group (ketose) and several –OH groups, and have the empirical formula CH_2O
- distinguish between α-glucose and β-glucose, and compare and explain the structural properties of starch (amylose and amylopectin) and cellulose
- recognise that triglycerides (lipids) are esters and describe the difference in structure between saturated and unsaturated fatty acids
- describe, using equations, the base hydrolysis (saponification) of fats (triglycerides) to produce glycerol and its long chain fatty acid salt (soap), and explain how their cleaning action and solubility in hard water is related to their chemical structure.



Topic 2 • Chemical synthesis and design

MACROMOLECULES: POLYMERS, PROTEINS AND CARBOHYDRATES

- describe the condensation reaction of 2-amino acids to form polypeptides (involving up to three amino acids), and understand that polypeptides (proteins) are formed when amino acid monomers are joined by peptide bonds
- describe the condensation reaction of monosaccharides to form disaccharides (lactose, maltose and sucrose) and polysaccharides (starch, glycogen and cellulose), and understand that polysaccharides are formed when monosaccharides monomers are joined by glycosidic bonds.

SCIENCE AS A HUMAN ENDEAVOUR

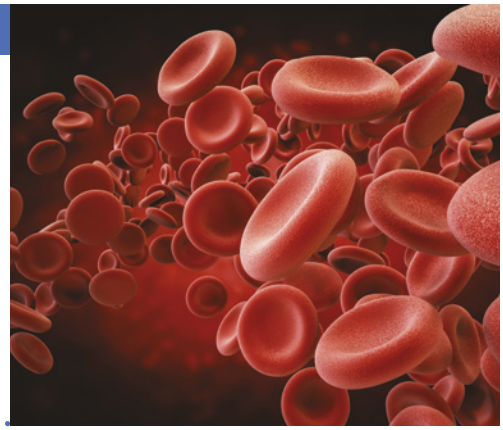
- **Functional groups and organic chemistry:** Developments in computer modelling enabled more accurate visualisation and prediction of three-dimensional organic structures, such as proteins, which is critical in drug design and biotechnology.

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10.1 Amino acids

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- recognise and draw the general structure for a 2-amino acid (α-amino acid)
- recognise a 2-amino acid from its structure
- understand that the side chain in a 2-amino acid can be polar or non-polar and recognise polar and non-polar side chains
- understand that the side chain in a 2-amino acid can be acidic or basic and recognise acidic and basic side chains
- recognise a zwitterion
- understand that the structure of an amino acid in solution depends upon the pH of the solution.



In this module, you will investigate the structure and properties of amino acids. Amino acids are the monomers that make the thousands of different **proteins** that are essential to life.

Proteins are organic biopolymers that have many important functions in living things. These include:

- enzymes that catalyse specific biochemical reactions
- hormones that control biological processes
- structural components in cell membranes, muscles, hair, feathers and spider silk (Figure 10.1.1)
- transport of substances across cell membranes or around the body; for example, haemoglobin is found in red blood cells (Figure 10.1.2) and binds to oxygen
- antibody molecules of the immune system.



FIGURE 10.1.1 A spider's web is formed from threads of spider silk, spun from a strong fibrous protein called fibroin.

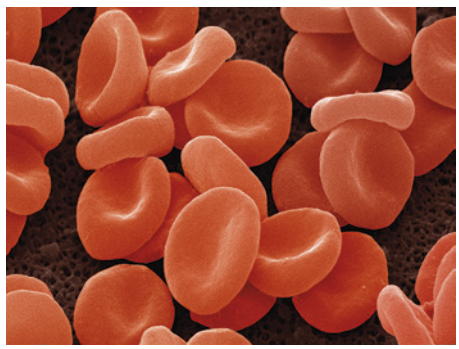


FIGURE 10.1.2 Red blood cells are biconcave disc-shaped cells that transport oxygen from the lungs to body cells. They contain the protein haemoglobin, which is able to bond reversibly to oxygen molecules.

The prefix 'mono-' means one, only or single. Therefore, the term 'monomer' means one unit. When monomers join other monomers, a polymer is formed (the prefix 'poly-' means many).

Plants can manufacture all the **amino acids** required to make proteins. They create amino acids from simple inorganic ingredients—such as carbon dioxide, water and nitrates—obtained from the atmosphere and soil. However, animals cannot do this. Animals obtain the amino acids they need to sustain their body functions from the plant and animal proteins in the food they eat.

STRUCTURE OF AMINO ACIDS

There are 20 different amino acids that make up all the proteins in the human body. Every amino acid has an amino functional group ($-NH_2$), a carboxyl functional group (–COOH), and a hydrogen atom attached to a central carbon called the α-carbon (alpha-carbon).

Two of the simplest amino acids are glycine and alanine. The structures of these two molecules are shown in Figure 10.1.3.

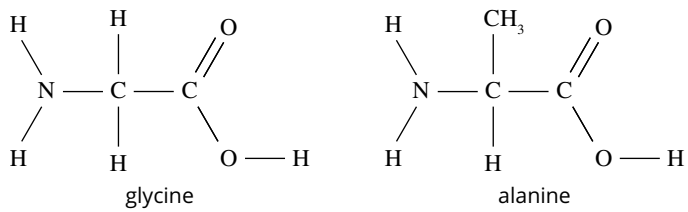


FIGURE 10.1.3 The structures of amino acids glycine and alanine

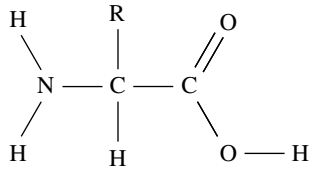


FIGURE 10.1.4 General structural formula of an amino acid. Different amino acids have different groups of atoms as the R group.

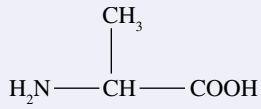
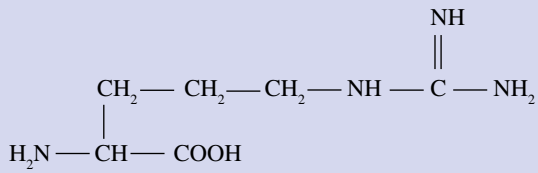
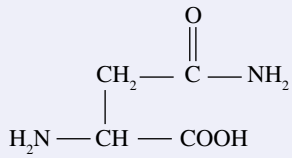
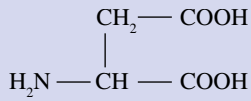
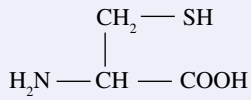
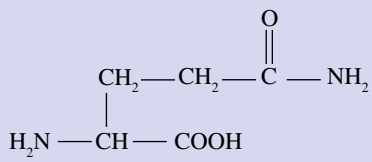
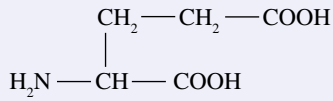
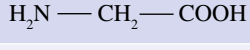
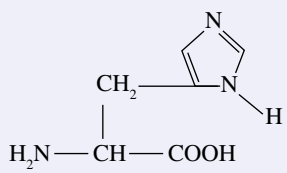
General formula of amino acids

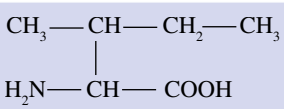
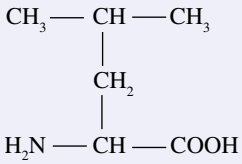
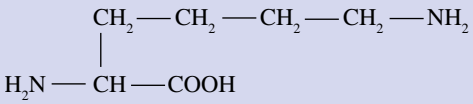
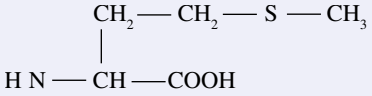
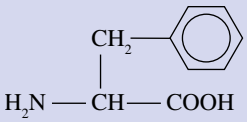
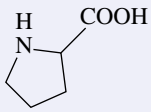
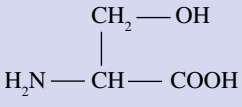
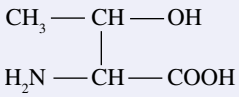
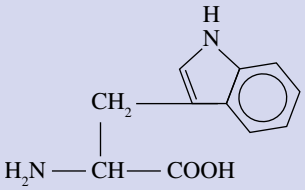
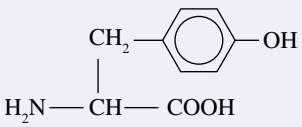
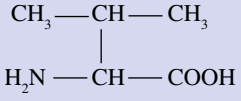
The amino acids used to produce the proteins in the human body have the general formula $H_2N–CH(R)–COOH$. The general structural formula of an amino acid is shown in Figure 10.1.4.

Amino acids, such as those shown in Figure 10.1.4, are known as **2-amino acids**. This is because the carbon atom of the carboxyl group is numbered as the first carbon in the chain (according to IUPAC rules) and the amino group is bonded to the carbon atom adjacent to it, numbered '2' in the chain. 2-amino acids are also called α-amino acids.

The 20 2-amino acids used to make human proteins are listed in Table 10.1.1, along with the three-letter abbreviations commonly used for them by biochemists.

TABLE 10.1.1 Amino acids found in the human body, with their three-letter abbreviations and R groups

Name	Symbol	Structure
alanine	Ala	
arginine	Arg	
asparagine	Asn	
aspartic acid	Asp	
cysteine	Cys	
glutamine	Gln	
glutamic acid	Glu	
glycine	Gly	
histidine	His	

isoleucine	Ile	
leucine	Leu	
lysine	Lys	
methionine	Met	
phenylalanine	Phe	
proline	Pro	
serine	Ser	
threonine	Thr	
tryptophan	Trp	
tyrosine	Tyr	
valine	Val	

Amino acids are commonly given three-letter abbreviations. For example, alanine is represented by Ala and glycine is represented by Gly.

Properties of R groups in amino acids

The major difference between one amino acid and another is the group of atoms that make up the **side chain**. This side chain is represented in the general structure as an **R group**. The side chain may be:

- non-polar (e.g. $-CH_3$ in alanine and $-CH(CH_3)_2$ in valine)
- polar (e.g. $-CH_2COOH$ in aspartic acid and $-CH_2OH$ in serine).

The side chain may also include functional groups that can behave as:

- proton donors (e.g. $-CH_2COOH$ in aspartic acid contains an acidic carboxyl group)
- proton acceptors (e.g. $-CH_2CH_2CH_2CH_2NH_2$ in lysine contains a basic amino group).

ESSENTIAL AND NON-ESSENTIAL AMINO ACIDS



FIGURE 10.1.5 This child is suffering from kwashiorkor, which is a form of malnutrition caused by a protein-deficient diet.

Within the cells in their bodies, humans can synthesise 11 of the 20 amino acids required to make proteins. These proteins sustain our bodily functions. However, the other nine amino acids (isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, valine and histidine, in the case of infants) must be provided directly through the proteins we eat. This is because human cells do not have the capacity to produce them.

These nine amino acids are known as **essential amino acids**. A healthy diet should include proteins that contain these essential amino acids. The human body does not store amino acids, so a balanced intake of protein is required each day. Lack of amino acids in the diet can cause serious diseases, such as kwashiorkor, which you can see in Figure 10.1.5. 'Kwashiorkor' means 'rejected one' in the Ga language of coastal Ghana where the disease is common. It reflects the incidence of the disease in children who have been weaned from breast milk to a diet that is high in carbohydrates and lacking in protein.

A balanced diet

Proteins from animal sources contain all the essential amino acids. As Table 10.1.2 shows, vegetable proteins are often deficient in one or more essential amino acids. For example, corn is too low in lysine and tryptophan to support normal growth in young children.

TABLE 10.1.2 Foods deficient in one or more of the nine essential amino acids

Food	Amino acid deficiency
legumes	methionine
soybeans	methionine
corn	lysine, tryptophan
nuts	methionine
wheat	lysine

For this reason, vegetarians must ensure that their diets contain **complementary proteins**. This means that instead of eating plant protein from a single source, vegetarians should eat a variety of plant foods. Deficiencies of amino acids in one plant can then be supplemented by the amino acids present in another. For example, rice and lentils contain complementary proteins. In Asia, rice and lentils have been part of the staple diet for thousands of years. In developed countries, people usually get all the amino acids they require by eating complementary proteins.

THE ACID–BASE PROPERTIES OF AMINO ACIDS

Amino acids are difunctional—they contain an amino group and a carboxylic acid group. The presence of these two groups in their structure means amino acids are amphoteric—they can react as either acids or as bases, depending on the circumstances. The nature of its side chain (R group) can also affect the acid–base properties of an amino acid.

Amino acids as zwitterions

Amino acids contain polar amino and carboxyl functional groups. Therefore, amino acids can form hydrogen bonds with water molecules and are soluble in water. In solution, the:

- $–NH_2$ group can act as a base, accepting a proton to become a $–NH_3^+$ group
- –COOH group can act as an acid, donating a proton to become a $–COO^–$ group.

As a result, an amino acid molecule in an aqueous solution may be in the form $^+H_3N–CH(R)–COO^–$. Such a molecule is shown in Figure 10.1.6 and is called a **zwitterion** or **dipolar ion**.

The crystalline nature and relatively high melting points of amino acids in the solid state is evidence that in the solid state the zwitterion is present and that in the solid state amino acids exist as ionic crystals.

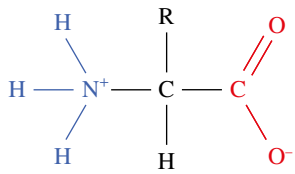


FIGURE 10.1.6 Structure of a zwitterion of an amino acid molecule. A zwitterion is a molecule that contains positive and negative charges but has no charge overall.

Acid–base properties

The dual acidic and basic nature of amino acids means that different chemical forms of an amino acid can be in equilibrium in a solution. The predominant form depends on the pH of the solution and the particular amino acid concerned.

- At intermediate pH (typically pH 5–7), the zwitterion $^+H_3N–CH(R)–COO^–$ is most abundant.
- At low pH, the cation $^+H_3N–CH(R)–COOH$ is most abundant. The H_3O^+ ions in solution can react with the amino acid according to the equation:

  $$^+H_3N–CH(R)–COO^–(aq) + H_3O^+(aq) \rightleftharpoons {}^+H_3N–CH(R)–COOH(aq) + H_2O(l)$$

  If the concentration of $H_3O^+(aq)$ is very high (as it is in a solution of low pH), the position of this equilibrium lies well to the right.
- At high pH, the anion $H_2N–CH(R)–COO^–$ is most abundant. The $OH^–$ ions in solution can react with the amino acid according to the equation:

  $$^+H_3N–CH(R)–COO^–(aq) + OH^–(aq) \rightleftharpoons H_2N–CH(R)–COO^–(aq) + H_2O(l)$$

  If the concentration of $OH^–(aq)$ is very high (as it is in a solution of high pH), the position of this equilibrium lies well to the right.

As you can see in Table 10.1.3, the charge on the predominant form of the amino acid depends on the pH of the solution.

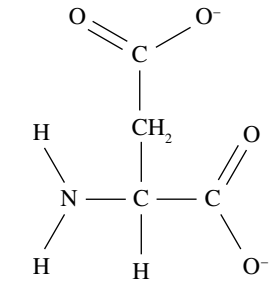
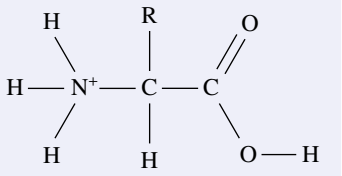
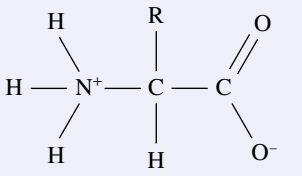
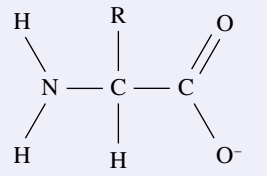


FIGURE 10.1.7 The structure of aspartic acid at pH 12 showing that it has a charge of 2–

TABLE 10.1.3 Formation of cations, anions and zwitterions when amino acids are in solutions of various pH

Low pH	Intermediate pH	High pH
		

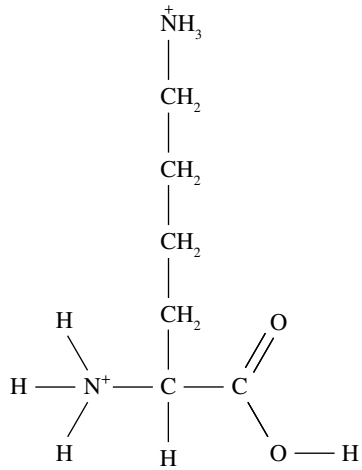


FIGURE 10.1.8 The structure of lysine at pH 2 showing that it has a charge of 2+

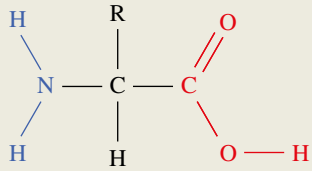
Effect of the R group on the acid–base properties of amino acids

If the R group contains a functional group with acid–base properties, it is possible for other charged structures of the amino acid to form. For example, at a pH of 12, the predominant form of aspartic acid is an ion with a charge of 2– (Figure 10.1.7). On the other hand, at a pH of 2, lysine exists predominantly as an ion with a charge of 2+ (Figure 10.1.8).

10.1 Review

SUMMARY

- 2-amino acids have the structure shown in the following figure.



- Amino acids contain a carboxyl group (highlighted in red), an amino group (highlighted in blue), a hydrogen atom and a side chain called the R group, all bonded to the same carbon atom.
- There are 20 different amino acids found in human proteins.
- The nine essential amino acids must be provided directly through the proteins in the diet, as human cells cannot produce them.
- Non-essential amino acids can be manufactured in the body from other dietary components.
- Three-letter abbreviations are commonly used to represent an amino acid.
- The R group, also known as the side chain, may be a non-polar group of atoms or a group of atoms that includes a polar functional group. The R group may also exhibit acid–base properties.
- Zwitterions are present in crystalline salts of amino acids and also in amino acid solutions of intermediate pH.
- An amino acid is present in cationic form in solutions of low pH and in anionic form in solutions of high pH.

KEY QUESTIONS

Retrieval

1 Use Table 10.1.1 on page 358 to find the names of the amino acids with the following three-letter abbreviations.
- **a** Asn
- **b** Tyr
- **c** Asp
- **d** Met

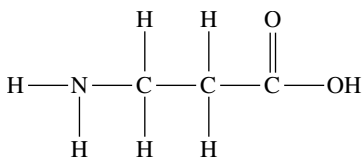
2 Recall why essential amino acids should be included in a healthy diet.

3 State the reason why vegetarians must ensure that their diet contains complementary proteins.

4 **a** Identify the pH at which 2-amino acids exist as anions.
- **b** Give the general structure for a 2-amino acid in its anionic form.

Comprehension

5 Explain why the structure below is not classified as a 2-amino acid.



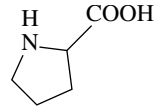
6 Use your understanding of bond polarity and the acid–base properties of functional groups to complete the following table that categorises properties of an amino acid's R group.

Structure of R group	Is the R group polar or non-polar?	Is the R group acidic, basic or neutral?
$-CH(CH_3)_2$		
$-CH_2COOH$		
$-CH_2C_6H_5$		
$-(CH_2)_4NH_2$		

7 Show an equation for the amino acid cysteine forming a cation. Explain the conditions needed for it to form the cation. The zwitterion formula for cysteine is: $^{+}H_3N–CH(CH_2SH)–COO^{-}$.

Analysis

8 Identify the carboxylic acid group, amino group and R group in proline by circling and labelling the relevant parts of the structure. Classify the R group as polar or non-polar.

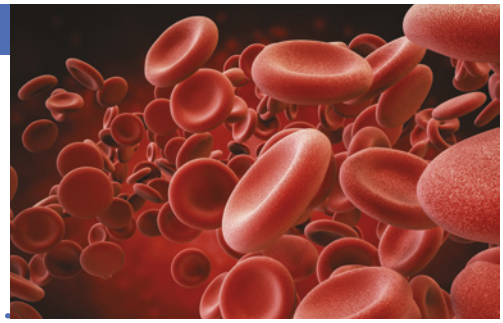


9 Mixtures of amino acids can be separated by a technique called ion-exchange chromatography. In this technique, the mixture flows through a column containing an inert resin that has charged side chains. If a mixture of lysine and glutamic acid in a solution with pH 6 is passed through a column that has resin with negatively charged side chains, the glutamic acid will travel down the column faster and can be collected at the bottom of the column. The lysine will be attracted to the resin. Use Table 10.1.1 on page 358 to compare the structures of lysine and glutamic acid and explain why they can be separated in this way.

10.2 Formation of proteins

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- describe the condensation reaction of 2-amino acids to form polypeptides
- recognise and draw peptide bonds
- recognise and draw the structure of dipeptides and tripeptides
- recognise the 2-amino acids in a polypeptide
- understand that polypeptides (proteins) are formed when amino acid monomers are joined by peptide bonds.



In this module, you will learn about the chemical reactions of amino acids that produce larger molecules called polypeptides and proteins. These reactions are examples of condensation polymerisation reactions.

The monomers in condensation polymerisation reactions have a pair of functional groups that can react together. When they react, a new functional group is produced that links the monomers. At the same time, a small molecule, such as water, is also produced. In fact, the word 'condensation' to describe this type of polymerisation originally indicated water is a product, although other types of condensation reactions are now recognised that release other small molecules.

Many biologically important molecules are produced by condensation polymerisation. These molecules include proteins, DNA, cellulose and **starch**. Insulin, as shown in Figure 10.2.1, is a small protein made from 51 amino acids. It allows your body to use **glucose** from carbohydrates in your food, either for energy or for storing glucose for future use.



FIGURE 10.2.1 This young girl is injecting herself with insulin to control diabetes. Insulin is one of the many proteins that is formed by the polymerisation of amino acids. Diabetes is a group of diseases associated with abnormally high levels of sugar in the blood.

DIPEPTIDES

As you learnt in Chapter 9, a condensation reaction can occur between a molecule that contains a carboxyl group (–COOH) and a molecule that contains an amino group ($–NH_2$). An amide functional group (–CONH–) is formed that links the two molecules. A molecule of water is also produced, as shown in Figure 10.2.2.

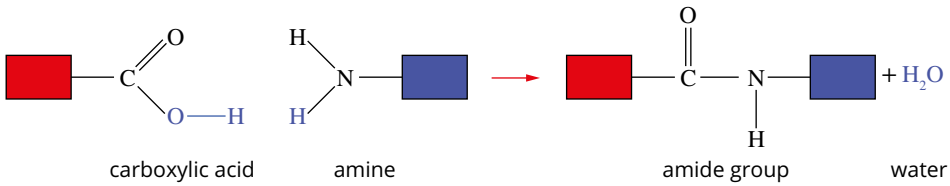


FIGURE 10.2.2 An amide group forms when a carboxyl group reacts with an amino group. A water molecule is also produced. The red and blue boxes represent the remaining atoms in the amino acids involved in this reaction.

Because 2-amino acids contain both an amino functional group and a carboxyl functional group, they can undergo condensation reactions with each other. When two amino acids react, an amide group, called a **peptide link** (also called a peptide group or peptide bond), is formed that links the molecules together.

Molecules made from amino acids are often called peptides. When two amino acid molecules react together as shown in Figure 10.2.3, the product is referred to as a **dipeptide**.

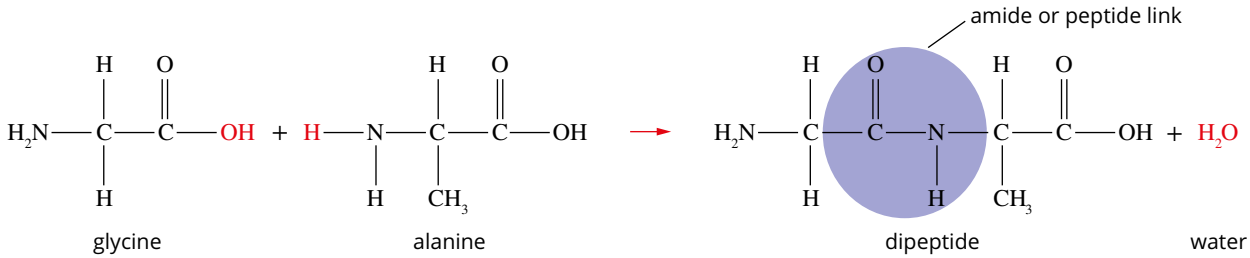


FIGURE 10.2.3 A condensation reaction between two amino acids, glycine and alanine. Note how the carboxyl and amino groups react to form the dipeptide and water.

Each time a pair of different amino acids react in this way, there are two possible product molecules, depending on which ends of each molecule react together (Figure 10.2.4).

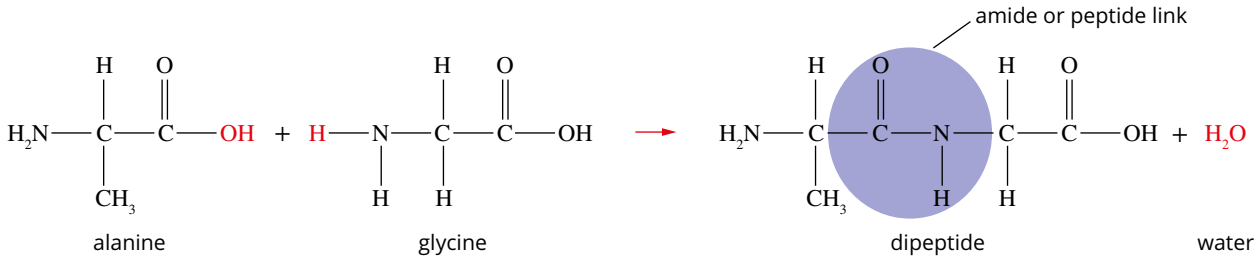


FIGURE 10.2.4 Another dipeptide molecule formed from the reaction between glycine and alanine

POLYPEPTIDES

Polypeptides are polymers formed by condensation polymerisation of amino acids. During these reactions, the amino acids can form long chains. When three amino acid molecules react together, a **tripeptide** is formed. A polymer made from many amino acids is known as a **polypeptide**.

Naming polypeptides

A shorthand notation is often used to describe the amino acid sequence in a polypeptide, using the three-letter abbreviations of 2-amino acid structures listed in Table 10.1.1 on page 358. By convention, the structure is drawn so the free amino group is on the left and the free carboxyl group is on the right. A reaction between six amino acids to form part of a polypeptide is shown in Figure 10.2.5. The polypeptide would be named Ala–Glu–Gly–Cys–Val–Lys.

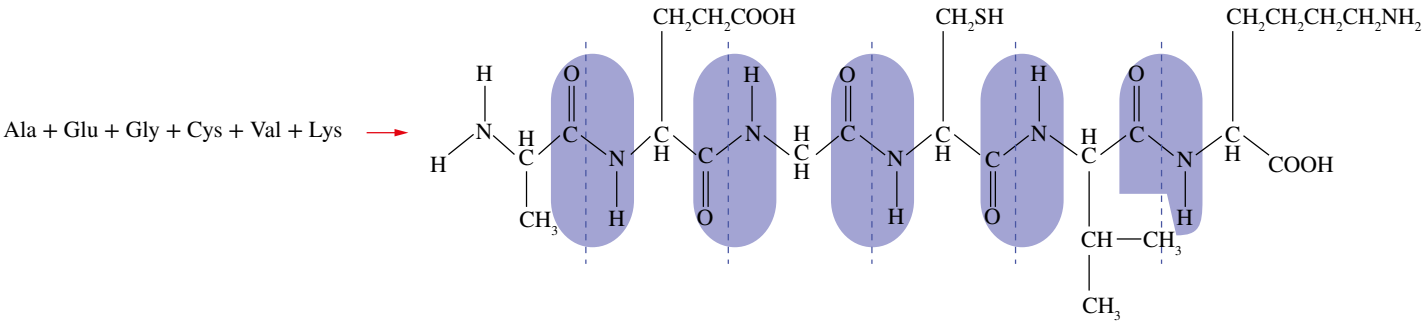


FIGURE 10.2.5 A condensation reaction between many amino acids produces a polypeptide. Peptide links are shaded in blue.

A polypeptide constructed from more than 50 amino acids is usually called a protein. The hormone insulin is a protein that regulates the metabolism of sugars and fats in the human body. Insulin is one of the smallest proteins in the human body. It is made up of two linked chains, with a total of 51 amino acid residues. The sequence of amino acids in the two chains is shown in Figure 10.2.6. You can also see that the chains are linked by covalent bonds between sulfur atoms from the R group of cysteine residues. At the start of the longer chain (Chain B) is a free amino group on the phenylalanine (Phe). This is known as the **N-terminal** amino acid of that chain. At the end of the longer chain is threonine (Thr), which has a free carboxyl group and is therefore called the **C-terminal** amino acid.

You have seen that when polypeptides are formed, water is produced as a by-product. When proteins are broken down in the body (through digestion), water molecules are required to break the peptide bonds. This type of reaction is known as hydrolysis and, in this case, hydrolysis can be regarded as the reverse reaction to the condensation reactions that formed the protein.

When amino acids react with each other, peptide bonds form. Small molecules, such as water, are also released in this process, making this a condensation polymerisation reaction.

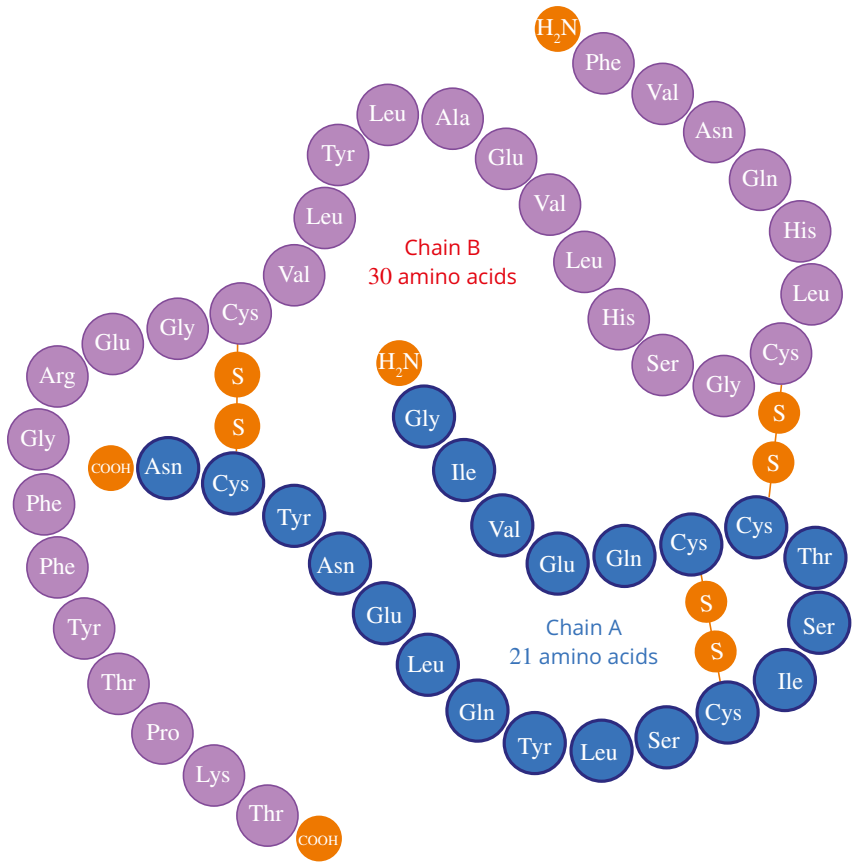


FIGURE 10.2.6 The amino acid sequence in the human insulin molecule. The polymer contains 51 amino acid units.

10.2 Review

SUMMARY

- The carboxyl group and amino group of 2-amino acids can take part in a condensation reaction that links them through a peptide group.
- Water is also produced as a by-product, making this reaction an example of a condensation polymerisation reaction.
- In a similar manner, several amino acids combine to produce a polypeptide.
- Proteins are large polypeptide chains containing approximately 50 or more amino acids.

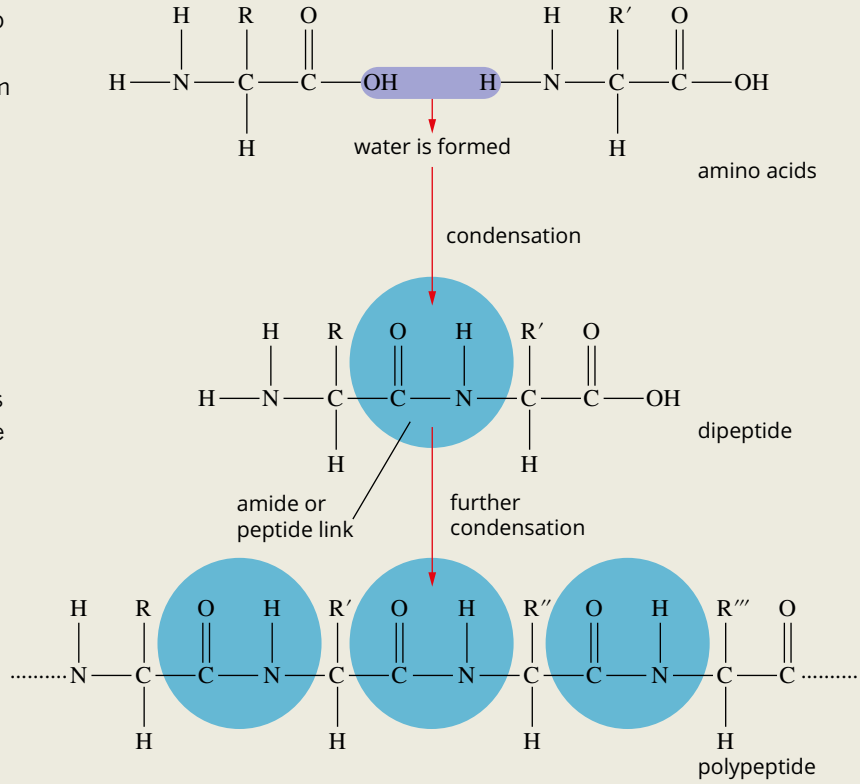


FIGURE 10.2.7 An example of a condensation polymerisation reaction

KEY QUESTIONS

Retrieval

1 Match the terms on the left with their description on the right.

tripeptide	by-product of the reaction that produces polypeptides
R group	three amino acids joined by peptide links in a polypeptide chain
polypeptide	variable part of an amino acid
amino group	several amino acids that are joined by peptide links
water	functional group present in all amino acids

2 **a** Name the type of reaction that causes the breakdown of proteins when they are digested in the body.

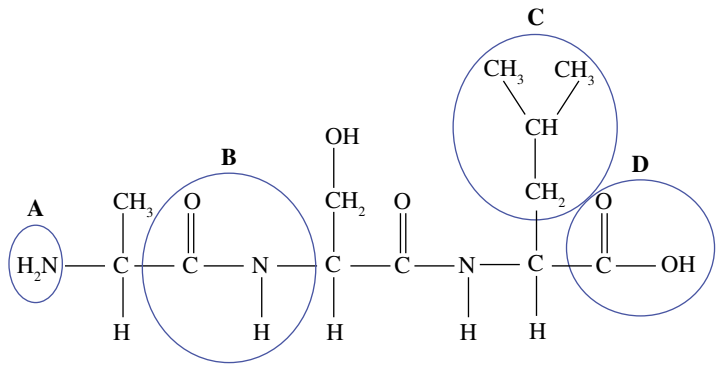
b Complete the equation below for the digestion of the dipeptide Ala-Val.

$H_2NCH(CH_3)CONHCH(CH(CH_3)_2)COOH + A \rightarrow B + C$

3 The following figure shows a tripeptide molecule.

a Identify the parts labelled A–D.

b Referring to Table 10.1.1 on page 358, name the three amino acids in the tripeptide molecule.



Comprehension

4 Explain why 2-amino acids have the capacity to form polymers.

5 **a** Draw structural formulas of serine ($H_2NCH(CH_2OH)COOH$) and cysteine ($H_2NCH(CH_2SH)COOH$).

b Write condensed formulas for the two possible dipeptides that could be formed from these amino acids.

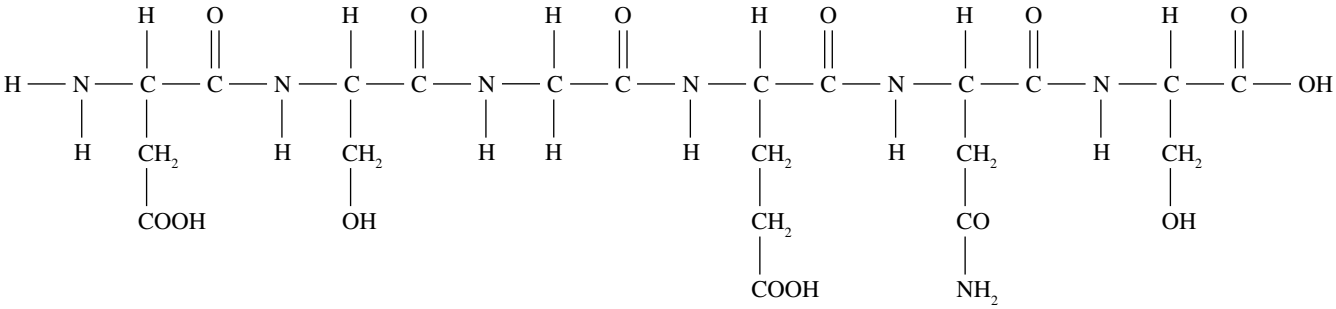
c Show the formation of one of these two dipeptides by writing an equation for this. Name the type of reaction used to make the dipeptide.

Analysis

6 Analyse the structure of the polypeptide, as shown in the figure below, to identify the:

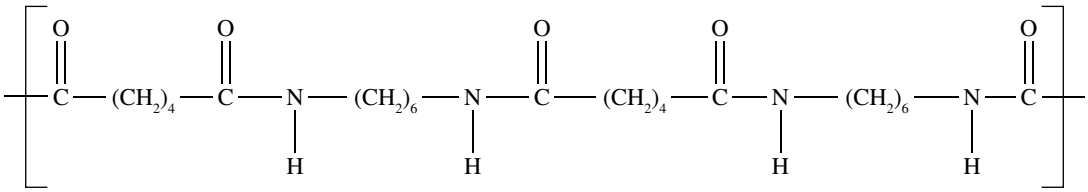
a number of amino acids used to make this polypeptide

b number of water molecules produced in the reaction to make this polypeptide.

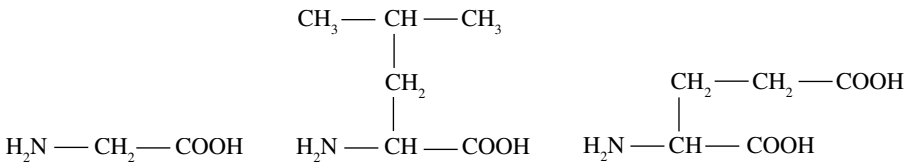


7 **a** Compare the structure of the polypeptide shown in question **6** to the structure of a section of the synthetic polymer nylon-6,6, as shown in the figure below. Identify and name the structural group common to both polymers.

b Like the amino acid monomers that link to form a polypeptide, the monomers used to make nylon-6,6 have two functional groups. Examine the nylon-6,6 structure to identify and draw structures for the two monomers that are used to synthesise nylon-6,6.

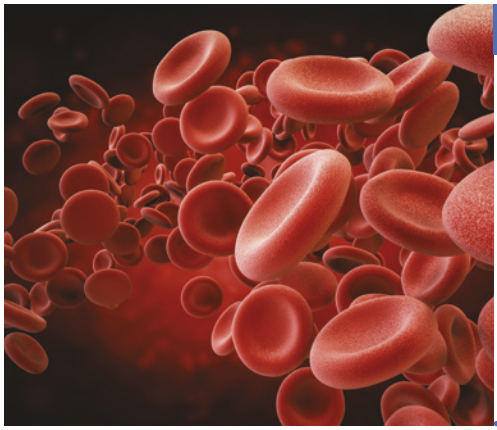


8 The three figures below show the structures for the amino acids glycine, leucine and glutamic acid. Determine why when glycine and leucine react they can form two possible dipeptides, while when glycine and glutamic acid react they can form three possible dipeptides.



glycine leucine glutamic acid

10.3 Structures of proteins



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- describe and explain what is meant by the primary structure of a protein
- identify the amino acids in a protein from its primary structure when given structures for amino acids
- describe and explain what is meant by the secondary structure of a protein
- describe and explain what is meant by the tertiary structure of a protein
- describe and explain what is meant by the quaternary structure of a protein
- describe the types of interactions that are important in forming the secondary, tertiary and quaternary structures of proteins.

Proteins differ from one another in the number, type and sequence of their constituent amino acids. Each protein has a precise chemical composition and amino acid sequence, which leads to it having a unique three-dimensional shape. There may be more than 500 amino acid units in a large protein. Determining the structure of these complex materials has proved challenging for chemists. Myoglobin, as shown in Figure 10.3.1, was one of the first proteins to have its amino acid structure determined. It is made up of 153 amino acids.

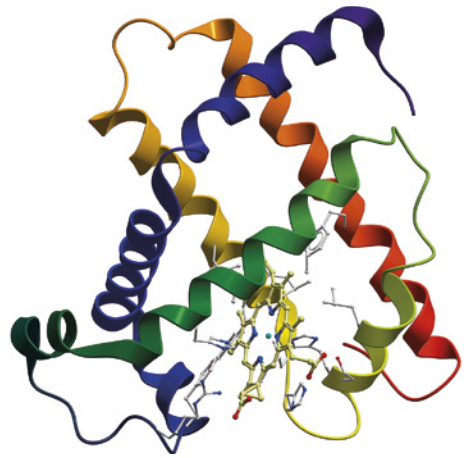


FIGURE 10.3.1 A representation of myoglobin. Myoglobin is a protein consisting of 153 amino acids in one polypeptide chain. This protein is found in muscle tissue where it binds to oxygen.

The role of any protein in an organism depends on the protein's shape. The structure of a protein is usually considered at several levels of organisation within the molecule. All proteins are regarded as being made up of a primary, secondary and tertiary structure, while some of them also display a quaternary level of organisation.

In this module, you will investigate the primary, secondary, tertiary and quaternary structures of proteins.

PRIMARY STRUCTURE OF PROTEINS

The number, type and sequence of the amino acid units in a protein are known as the protein's **primary structure**. As you can see in Figure 10.3.2, the primary structure may be represented by the three-letter abbreviations for the amino acids or by a structural formula of the protein. By convention, the sequence is written from left to right, starting from the N-terminal amino acid and ending with the C-terminal amino acid.

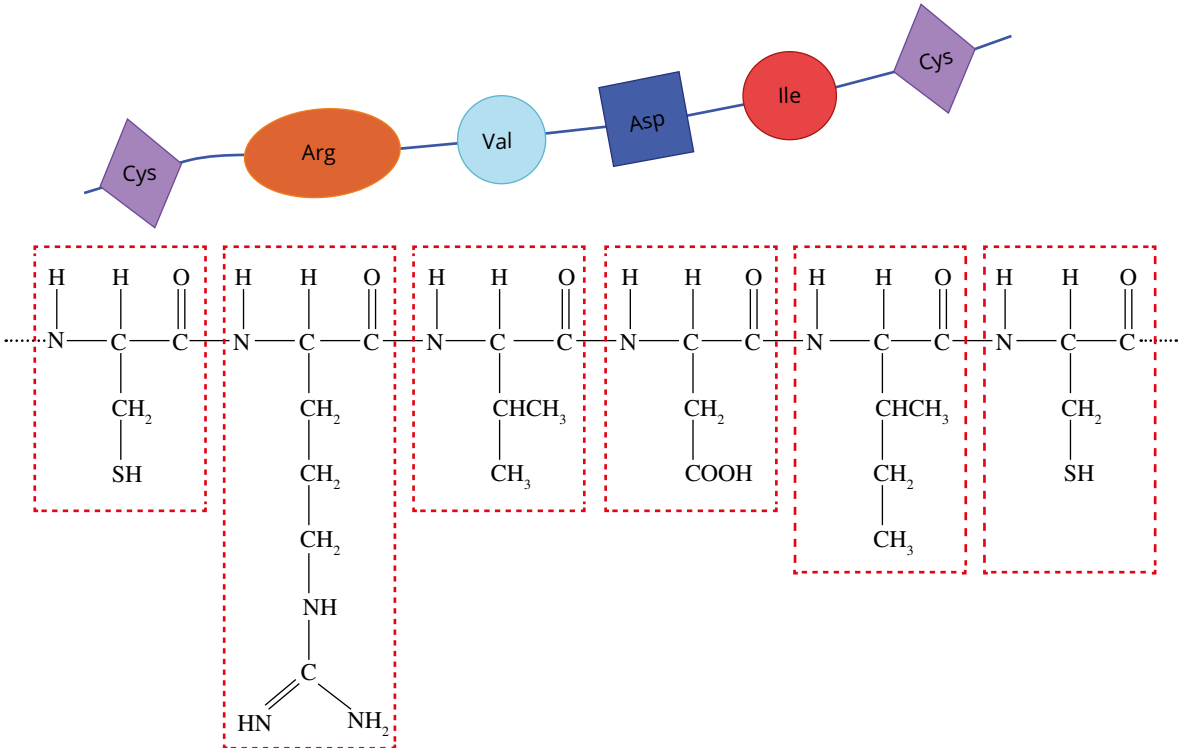


FIGURE 10.3.2 A small section of a protein molecule showing the primary structure represented by three-letter abbreviations and its structural formula. Each amino acid in the structural formula is shown in a rectangle.

The entire shape of a protein is determined by the precise order in which its amino acids are joined together. One of the smallest proteins in the human body, insulin, has a specific sequence of 51 amino acids. Many proteins contain hundreds of amino acids in a specific sequence.

> The function of a protein is a consequence of its shape. Therefore, the order of amino acids is extremely important in determining the function of a protein.

Protein sequencing

Determining the primary structure or sequence of amino acids in a protein can be a very useful piece of information. It can help in understanding a protein's function and enables the polypeptide chains in a protein to be synthesised in the laboratory. The primary structure of a protein is found experimentally by the process of **protein sequencing**, as shown in Figure 10.3.3.



FIGURE 10.3.3 This scientist is preparing to use an automated microsequencer machine to analyse the amino acid sequence of samples of protein.

The identity of the amino acids in a polypeptide can be determined by heating it in a 6.0 mol L^{-1} solution of hydrochloric acid (HCl). The polypeptide undergoes hydrolysis, forming the individual amino acid monomers. The amino acid mixture is separated by column chromatography, and then each amino acid is identified by its retention time. However, this technique does not give any indication of the sequence of amino acid units in a polypeptide.

One method of determining the sequence of a polypeptide begins with using different enzymes to hydrolyse specific peptide links within the molecule. For example, trypsin is an enzyme that hydrolyses the peptide link at the carboxyl side of arginine and lysine. This process is repeated with different enzymes to produce shorter peptides of varying lengths. These peptides can then be sequenced through a process called Edman degradation or by mass spectrometry. Careful analysis of how the sequences of the peptides overlap allows the overall sequence of the polypeptide to be determined.

One of the first people to work on protein sequencing was Dr Fred Sanger (Figure 10.3.4), who determined the order of different amino acids in the two chains of the insulin protein.



FIGURE 10.3.4 Fred Sanger (1918–2013)

Sanger identified the amino acid sequence of (bovine) insulin extracted from cattle, as shown in Figure 10.3.5. Sanger was the first person to determine a protein sequence and was awarded the first of his two Nobel Prizes in Chemistry in 1958 in recognition of his important discovery.

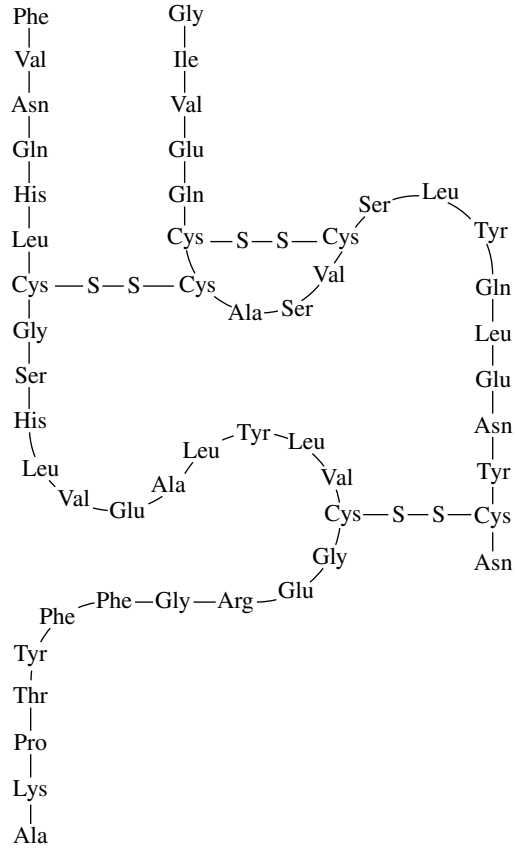


FIGURE 10.3.5 The amino acid sequence of bovine insulin. Its sequence of amino acids differs from human insulin by just three amino acids.

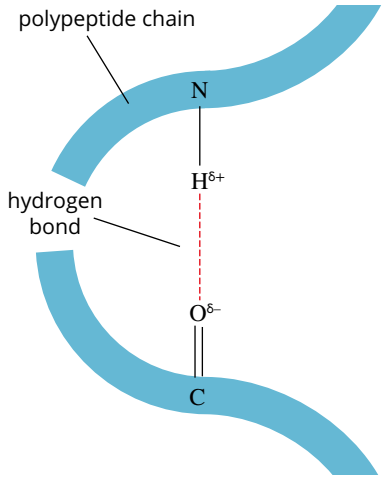


FIGURE 10.3.6 Hydrogen bonds can form between the polar –NH group in one peptide link and the polar –C=O group in another peptide link further along the polypeptide chain.

SECONDARY STRUCTURE OF PROTEINS

Folding of sections of a protein molecule produce a secondary level of structure in a protein. Hydrogen bonds between the polar –NH group in one peptide link and the polar –C=O group in another peptide link can form at regular intervals (Figure 10.3.6).

This folding creates regions in which the molecule coils into a spiral shape called an **α-helix**, or where sections line up parallel to each other, forming a **β-pleated sheet**.

Such highly ordered segments, stabilised by hydrogen bonds, are referred to as the **secondary structure** of the protein.

α-helices

Keratin is a protein found in the fibres of hair and wool. The helical structure of keratin results from extensive hydrogen bonding between peptide links within the polypeptide chain. In this case, the hydrogen bonds result from the attraction between the partial positive charge on the H of an –NH group in a peptide link with the partial negative charge on the O of a –C=O group of a peptide link four amino acid units along the chain.

The hydrogen bonds make the molecule coil into the shape of an α-helix, the same shape as a spring, as shown in Figure 10.3.7.

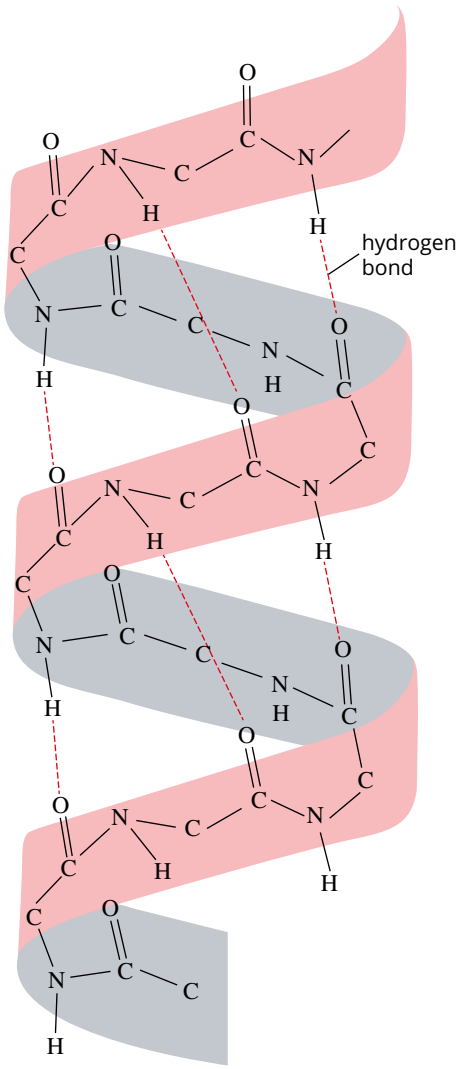


FIGURE 10.3.7 A polypeptide chain coils in an α-helix due to hydrogen bonds. The R groups (side chains) and hydrogen atoms on the α-carbons have been omitted for clarity.

β-pleated sheets

Hydrogen bonds can also form between peptide links on neighbouring polypeptide chains to produce regions where two or more parts of the polypeptide chains line up parallel to each other. The repeating structure of the backbone of the protein chain (–N–C–C–N–C–C–N–C–C–) allows these hydrogen bonds to form at regular intervals. This stabilises the protein structure. This type of secondary structure in the protein is called a β-pleated sheet, as shown in Figure 10.3.8. Note how the CO–NH part of the polypeptide chain is in the 'flat' part of the β-pleated sheet and the 'bend' in the sheet coincides with the C atom that is bonded to the R group.

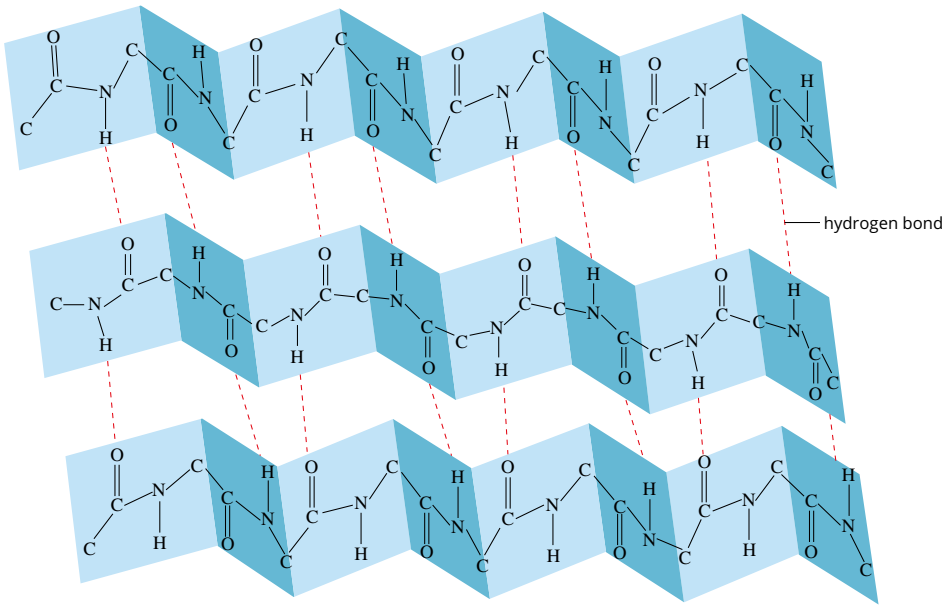


FIGURE 10.3.8 β-pleated sheet. Hydrogen bonds between the sheet are shown as dashed lines. The R groups (side chains) and hydrogen atoms on the α-carbons have been omitted for clarity.

Silk is a protein with a β-pleated sheet structure. The polypeptide chains mainly contain the amino acids glycine, alanine and serine, as shown in Figure 10.3.9. Notice that every second R group is H.

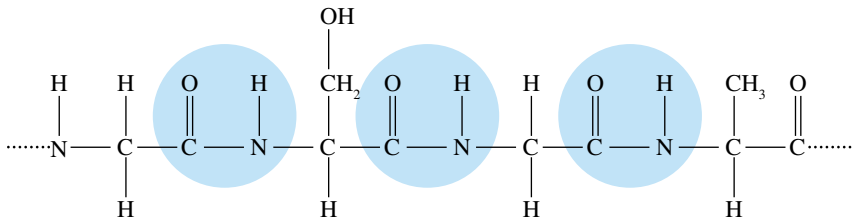


FIGURE 10.3.9 The amino acid sequence that is found in large parts of the polypeptide of silk. Peptide bonds are shaded blue.

With only these small side groups, sections of the protein molecule in silk can line up closely, enabling hydrogen bonds to form between these adjacent sections and producing β-pleated sheets.

The secondary structure of a protein results from hydrogen bonding within different regions of the amino acid sequence. This leads to the formation of α-helices or β-pleated sheets.

TERTIARY AND QUATERNARY STRUCTURES OF PROTEINS

You have learnt that the sequence and order of amino acid units in a protein chain is called the primary structure of the protein, and that as a consequence of hydrogen bonding between –C=O and –N–H groups along the chain, the protein chain can be twisted and folded into arrangements such as α-helices and β-pleated sheets, which are described as the secondary structure of the protein.

The overall three-dimensional shapes of proteins are due to forces between the different functional groups in the R group or side chain of amino acid units. The types of forces and bonds between the R groups cause proteins to adopt their different shapes.

Overall shape of a protein

The overall three-dimensional shape adopted by a protein molecule is called its **tertiary structure**. A tertiary structure is produced by the three-dimensional folding of its secondary structures (α-helices and β-pleated sheets). Proteins in solution fold spontaneously to increase their stability. The protein can twist back over itself to create a unique shape, which is responsible for the protein's function (Figure 10.3.10).

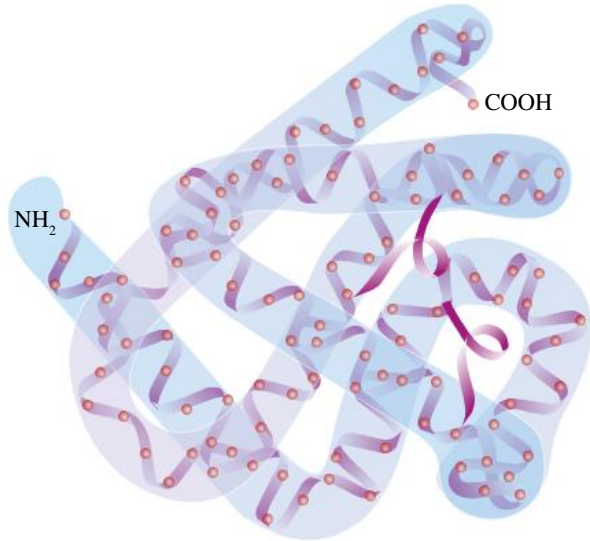


FIGURE 10.3.10 A model representing the tertiary structure of the protein myoglobin

R groups of amino acids influence the properties of the amino acid. There are four main groups of amino acids, which can be classified as polar, non-polar, acidic or basic. These were discussed in Module 10.1.

The side chains (R groups) of the amino acid units making up the polypeptide chain influence the overall three-dimensional shape of the molecule. Not only are some side chains relatively large (such as in phenylalanine), but others also contain polar functional groups, or can become charged depending on the pH of their surroundings. In addition, some amino acids have hydrophobic (non-polar) chains, which tend to fold towards the interior of protein molecules, away from contact with water molecules.

Bonding in the tertiary structure of proteins

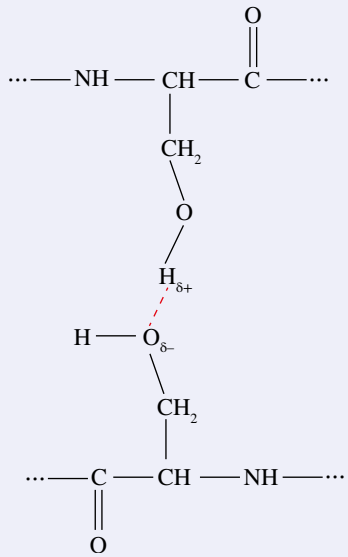
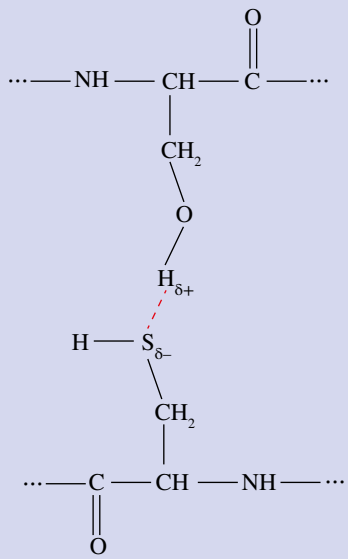
Five types of attractions that are important in chain folding are summarised in Table 10.3.1, which also identifies the features of the side chains that are involved.

Acidic and basic amino acids have the potential to become charged and so can form an ionic bond with each other. For example, at pH values around 7.4, which is the usual pH for body fluids, the $–NH_2$ group in the side chain of lysine (see Table 10.1.1 on page 358 for structure) will be protonated to form $–NH_3^+$, while the –COOH group in the side chain of glutamic acid (see Table 10.1.1 on page 358 for structure) will be deprotonated to form $–COO^–$. Proteins with amino acids that have acidic or basic side chains, such as aspartic acid and lysine, also tend to fold in a way that results in any acidic and basic side chain being on the exterior of the protein.

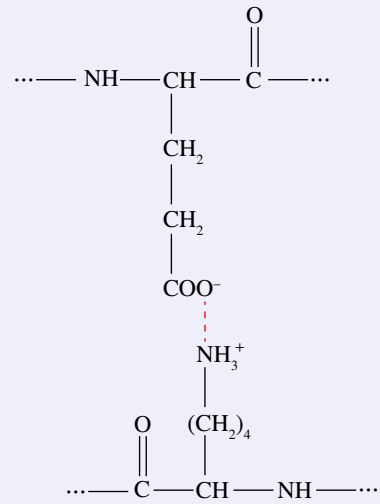
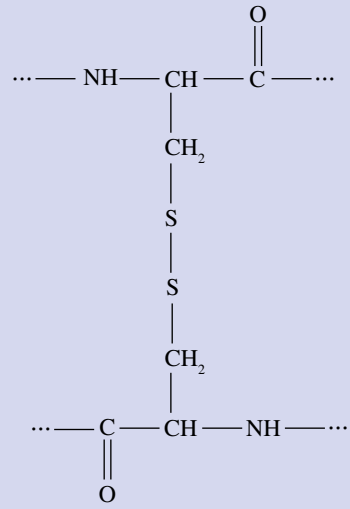
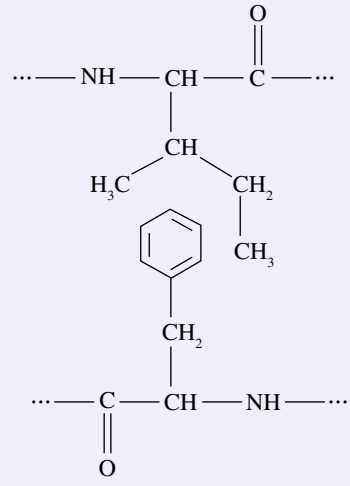
Here they interact with water molecules while amino acids with non-polar side chains, such as leucine and isoleucine, are usually on the inside to minimise interaction with water.

When two cysteine side chains are near to each other their –SH groups can react to form a bond between the S atoms to create a **disulfide bridge**. This covalent bond can strongly hold parts of a polypeptide chain together. Although not as strong as disulfide bridges or ionic bonds, hydrogen bonding and dipole–dipole attractions also have an important role in determining the overall shape of a protein. Dispersion forces between non-polar hydrocarbon side chains are the weakest of the interactions but they too contribute to the three-dimensional shape of a protein.

TABLE 10.3.1 Types of bonds formed from interactions of specific R groups in different regions of the protein

Bond type	Required components in R group	Visual representation
hydrogen bonds	contains –O–H, –N–H or –C=O	 a hydrogen bond linking two parts of a polypeptide chain
dipole–dipole interactions	any polar group such as those containing –S–H, –O–H or –N–H	 a dipole–dipole interaction linking two parts of a polypeptide chain

continued over page

Bond type	Required components in R group	Visual representation
ionic interactions	contains $-NH_3^+$ and another group that contains $-COO^-$	 an ionic interaction linking two parts of a polypeptide chain
covalent cross-links	cysteine side groups react to form a disulfide bridge (–S–S–)	 a disulfide bridge linking two parts of a polypeptide chain
dispersion forces	any non-polar group	 dispersion forces can link two parts of a polypeptide chain

As a consequence of the different types of bonds that can fold a polypeptide into a three-dimensional shape, an enormous variety of protein shapes exist. Some proteins resemble flat sheets, others are long and helical, and others are compact and globular.

Quaternary structure

Some proteins are composed of two or more polypeptide chains, and may even interact with non-protein molecules to produce a larger, more complex functional unit, known as the **quaternary structure**. Haemoglobin is an example of a protein with a quaternary structure.

Haemoglobin—the oxygen-transporting protein

Red blood cells are manufactured by the bone marrow at a rate of about 2 million per second. Red blood cells are functional for about three months in the human body. Each red blood cell contains approximately 250 million molecules of haemoglobin.

Figure 10.3.11 is a diagrammatic representation of haemoglobin. The four distinct subunits that make up its quaternary structure are highlighted in colour. Each subunit contains a polypeptide chain (collectively called globin) that is coiled into α-helices and then folded into a tertiary structure. Within each subunit, there is also an oxygen binding site, or haem group (light blue). Each haem group contains one atom of iron (green). Haemoglobin transports oxygen around the body by binding one oxygen molecule to each haem group.

The iron of the haem group can bond to one oxygen molecule, so each haemoglobin molecule is able to carry four oxygen molecules. In this form, the molecule causes the characteristic bright red colour of oxygenated blood and it is called oxyhaemoglobin.

Proteins that function in water, such as haemoglobin, tend to fold so that their hydrophobic non-polar R groups are least exposed to water molecules. The polar R groups are hydrophilic and are therefore located near the outer surface.

Two or more separate polypeptide chains can assemble together so that hydrophobic sections in the chains are in contact with each other, which minimises the contact of these sections of the chains with water. Haemoglobin has four chains that join together in this way. Dispersion forces are the major force of attraction holding the separate polypeptide chains together. However, hydrogen bonding, dipole–dipole attractions and ionic interactions may also be present between the chains.

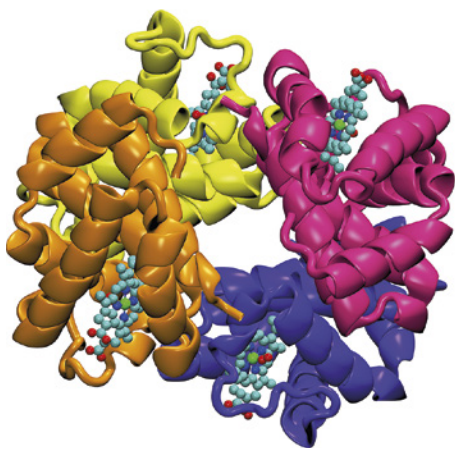


FIGURE 10.3.11 A representation of the structure of haemoglobin. Within each subunit is a haem group (light blue). Each group contains one atom of iron (green). In this model, the haem groups are oxygenated and the oxygen molecules are shown as paired red spheres.

SCIENCE AS A HUMAN ENDEAVOUR

Modelling protein structure

The function of a protein is determined by its three-dimensional structure. If the structure of a protein is known it may be possible to make a synthetic protein to carry out similar functions to our benefit, or other molecules that can interact with a protein to control its activity. For example, when a protein is involved in causing a disease, knowing its three-dimensional structure can be very important in the design of a pharmaceutical drug that can inhibit its action.

While the three-dimensional structure of a protein can be determined experimentally, the experimental techniques needed to resolve a protein's overall shape are time-consuming and expensive. Also, there are vastly greater numbers of proteins that have been discovered than have had their overall shape determined. Thus, prediction of a protein's shape by computer modelling can facilitate understanding of a protein's function and contribute to the development of drugs.

The prediction of a protein's three-dimensional structure (which is a function of its secondary, tertiary and quaternary structures) is based on its primary structure. Three main methods are used to predict a protein's shape using computer modelling—template-based modelling, threading and *ab initio* prediction.

Template-based modelling (also called homology modelling) is done by comparing a protein of unknown shape to one with a similar primary structure whose shape has been experimentally determined. This method also recognises that proteins in the same family often adopt similar three-dimensional shapes. This is the most reliable of the methods.

Threading, or fold recognition, involves comparing sequences in a protein of unknown shape to folds for sequences in a database of known folds. Each amino acid in the sequence of the unknown protein is aligned to a position in a sequence with a known fold. This comparison process is done until the closest match for the new sequence is found and a fold predicted based on the level of similarity to the fold for the known sequence. The overall shape is made up by combining the folds for these sequences.

When a similarity cannot be found in a protein database, or threading for similar sequences cannot be used, the shape must be predicted from first principles. This is called *ab initio* prediction and involves making predictions based on the properties of the amino acids that make up the protein. These include their ionisation properties, including those of their side chains, their interactions with water and the polarity of side chains.

A computer model of a protein is shown in Figure 10.3.12. In computer models of protein structure, a segment twisted into an α-helix is often represented as a twisted ribbon and sections of β-pleated sheets are represented by a set of wide parallel ribbons with arrows. There are wide variations in the relative amounts of α-helix and β-pleated sheet structures in individual proteins, with many proteins containing several regions of both.

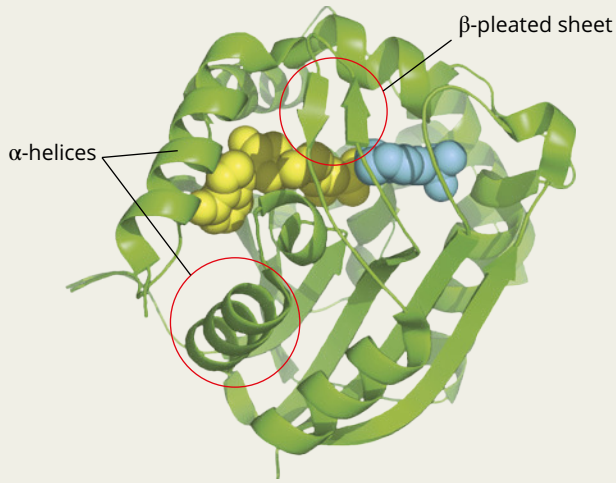


FIGURE 10.3.12 Computer model of a protein (green and yellow) in which several regions of α-helices and β-pleated sheets are seen. The blue part shows drug-like molecules interacting with the protein.

Review

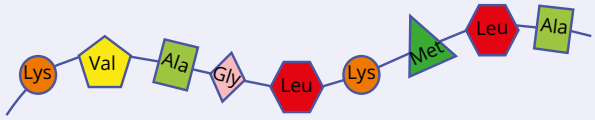
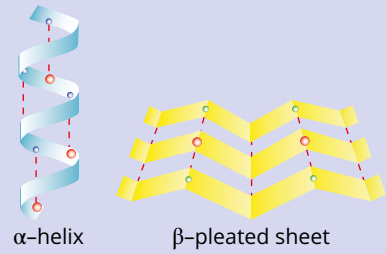
1. Identify the reasons the shape of a newly discovered protein may be predicted using computer modelling rather than being determined by experimental techniques.
2. Explain the circumstances under which threading would be used to predict the shape of a new protein rather than template-base modelling. Describe how threading gives a prediction for the shape of a new protein.

10.3 Review

SUMMARY

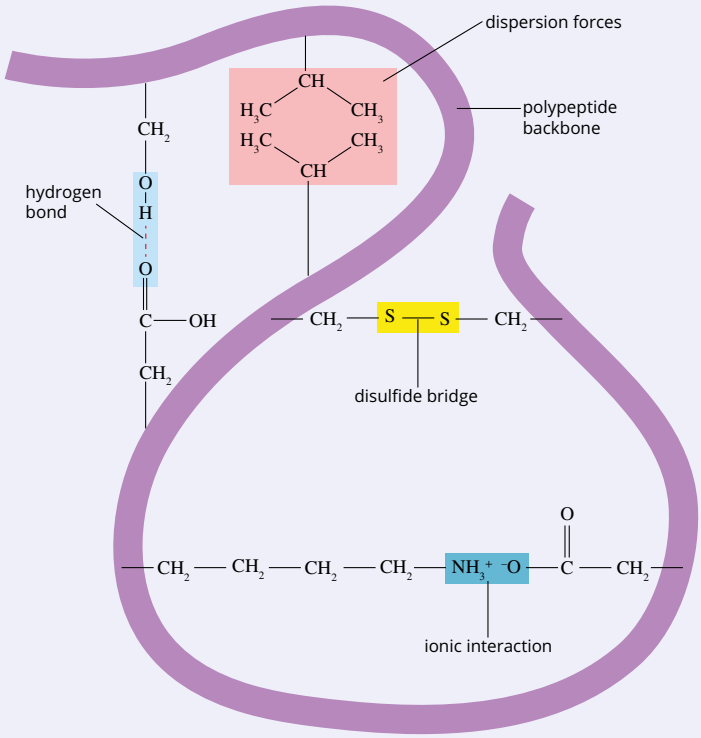
- There are 20 different 2-amino acids from which tens of thousands of different protein molecules are synthesised by cells. Each protein has a unique structure and function in the organism.
- The complex structure of these large molecules is often considered in distinct levels. The primary and secondary levels are summarised in the following table.

TABLE 10.3.2 Summary of the primary and secondary structural levels of proteins

Structural level	Description	Bonds involved
primary	the sequence of amino acids in the polypeptide chain 	Only covalent bonds are responsible for joining the monomer units together in the polymer. Monomers are linked by –CONH⁻ groups, known as peptide links in proteins.
secondary	the shape of the polypeptide as it is either twisted into an α-helix or bent back on itself to produce regions of β-pleated sheets 	Hydrogen bonding between –NH and –C=O bonds in peptide links introduces a secondary structure to protein molecules, producing regions of α-helices or β-pleated sheets.

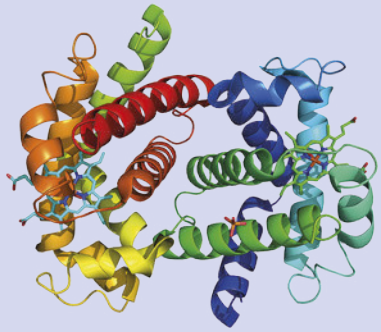
- The tertiary and quaternary levels of proteins are summarised in the following table.

TABLE 10.3.3 Summary of the tertiary and quaternary structural levels of proteins

Structural level	Description	Bonds involved
tertiary	The overall three-dimensional shape adopted by a protein molecule is called its tertiary structure. 	Hydrogen bonding can occur between polar functional groups in side chains, such as –OH and –C=O. Only dispersion forces are present between two non-polar R groups, such as $–CH(CH_3)_2$. Cysteine's R groups are able to form a covalent link, known as a disulfide bridge. Charged R groups are attracted by ionic interactions.

continued over page

10.3 Review *continued*

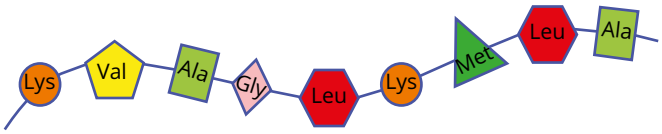
Structural level	Description	Bonds involved
quaternary	Some proteins consist of several associated polypeptide chains. 	Dispersion forces between non-polar R groups are the major reason for the attraction between adjacent parts of the chains. Dipole–dipole attractions, hydrogen bonds, ionic interactions and disulfide bonds involving R groups may also occur.

- Many bond types produce the three-dimensional shape of proteins, including:
  - dispersion forces
  - dipole–dipole attractions
  - hydrogen bonds
  - covalent bonds in disulfide bridges
  - ionic interactions.

KEY QUESTIONS

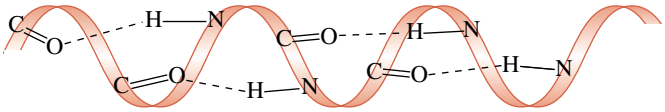
Retrieval

1 The figure below represents a section of a polypeptide molecule. Recall the missing words to complete the paragraph. You may need to refer to Table 10.1.1 on page 358 to answer this question.



The image shows a section of the primary structure of part of a polypeptide. It consists of _____ amino acid units that are linked together by _____ groups. It was produced by a _____ _____ reaction. In this polypeptide there are two units of leucine, two units of _____, two units of _____ and one unit each of _____, _____ and _____.

2 The figure below shows a section of a protein.



a Identify the secondary structure represented by the diagram.

b Describe how this type of secondary structure forms. Refer to particular atoms and functional groups associated with the bonding that forms this structure.

3 List the five main bond interactions that form when R groups in different regions of a polypeptide chain interact with each other. Give examples of the required components in R groups involved in such interactions, and an example of an amino acid that has an R group of this type.

Comprehension

4 Explain why it is important to be able to determine the specific sequence of amino acids in a protein.

5 Explain why more stable β-pleated sheets are usually those with amino acids that have small R groups.

Analysis

6 Contrast α-helices and β-pleated sheets.

7 Globular proteins are those where the polypeptide chains are mainly folded to give the protein a spherical tertiary structure. This type of protein is typically soluble in water. Explain, with reference to amino acids in the polypeptide chains, why these proteins are water soluble.

8 When the tertiary structure of a protein is destroyed, the protein is described as denatured. Most protein tertiary structures are stable in a limited pH range. Placing the protein in a solution with a pH above or below the range will cause the protein's tertiary structure to be destroyed. One cause of this is the disruption of ionic attractions between amino acid side chains. Determine why changing the pH will disrupt ionic attractions between side chains.

10.4 Action of enzymes

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- recognise that enzymes are proteins
- understand that enzymes are biological catalysts
- describe the characteristics of biological catalysts (enzymes)
- recognise that enzyme activity depends on the structure and the specificity of the enzyme action.



Thousands of chemical reactions are involved in sustaining life. These reactions occur in a highly organised, sequential fashion. The biological catalysts that accelerate the rate of chemical reactions in cells are a particular type of protein called enzymes.

In this module, you will learn about several models that biochemists use to describe enzyme catalysis. Enzymes are highly efficient catalysts that can increase reaction rates by as much as a factor of 10^{10}. This is like taking one second to complete a task that would normally take 300 years!

ROLE OF ENZYMES

You have already learnt about inorganic catalysts in Unit 2. Just like inorganic catalysts, enzymes:

- are only needed in relatively small amounts
- are not used up or changed at the end of the reaction
- do not alter a reaction's equilibrium position
- provide an alternative reaction pathway that lowers the activation energy for a reaction (Figure 10.4.1).

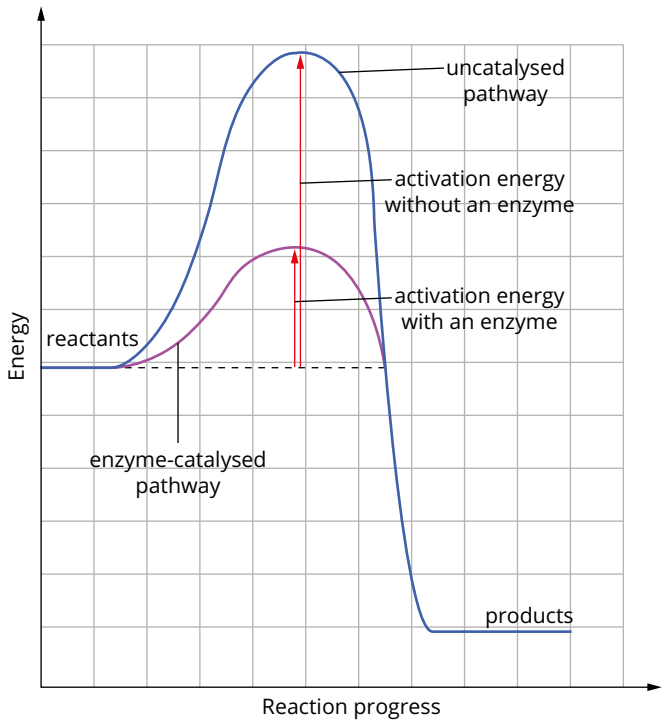


FIGURE 10.4.1 Both inorganic catalysts and enzymes lower the activation energy of a reaction by providing an alternative pathway by which the reaction can occur.

WS 4.1.7

The catalytic action of enzymes is specific for a single reaction or type of reaction.

However, there is a significant difference between the behaviour of enzymes and inorganic catalysts. An inorganic catalyst, such as metallic platinum, can be used to catalyse many different reactions often using a variety of reactants. Enzymes generally only catalyse one specific reaction or a reaction that involves a particular chemical bond or functional group. This characteristic is often referred to as the 'specificity of enzymes'. For example, the hydrolysis of the peptide bond on the C-side of the amino acid arginine in a polypeptide and hydrolysis of the peptide bond on the C-side of phenylalanine are catalysed by different enzymes (Figure 10.4.2). The models of enzyme action developed by scientists must account for this key difference.

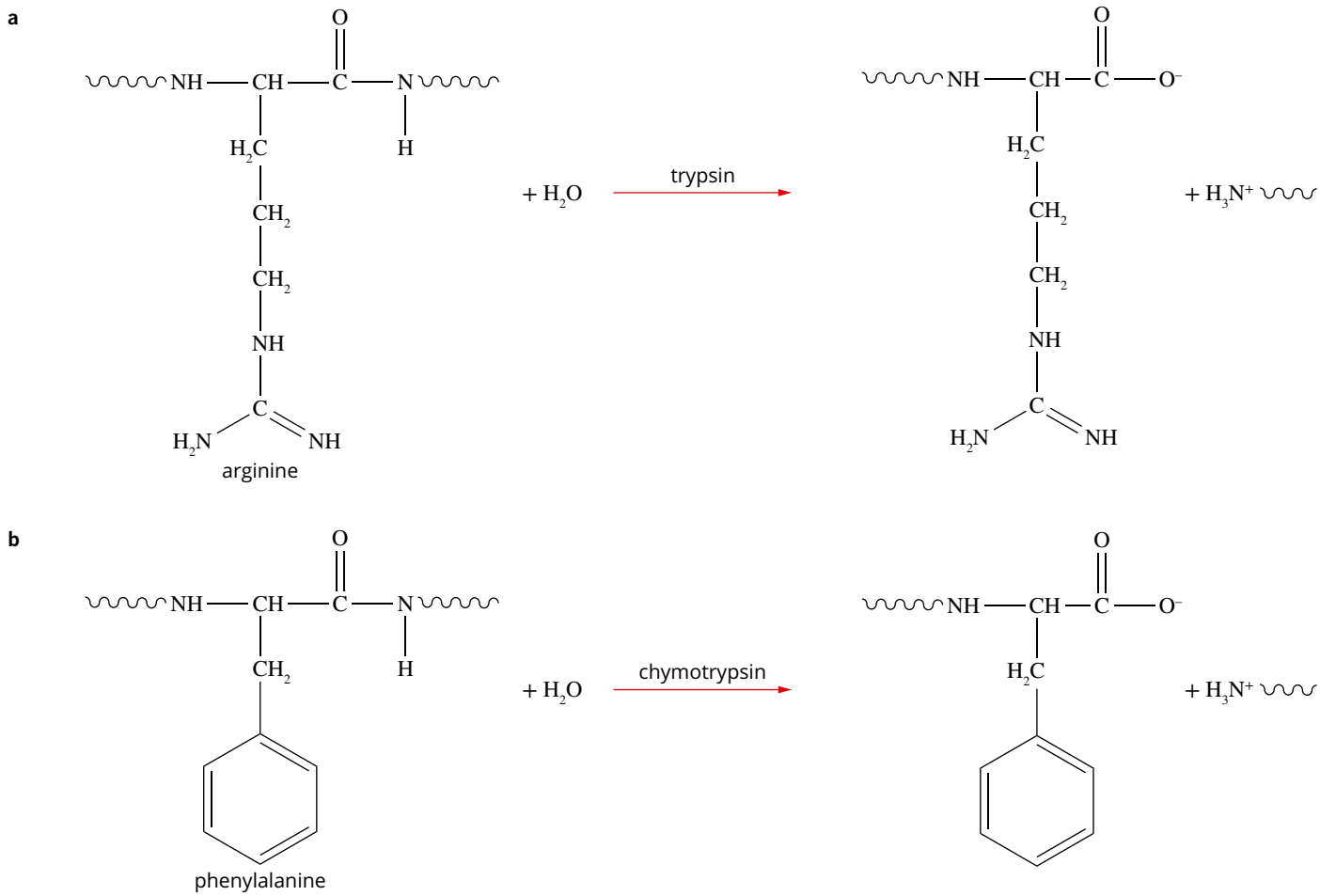


FIGURE 10.4.2 The hydrolysis of peptide chains by different enzymes. (a) Arginine as part of a polypeptide chain is cleaved to two smaller polypeptides on the C-side of the peptide bond by the enzyme trypsin. (b) Phenylalanine as part of a polypeptide chain is cleaved to two smaller polypeptides on the C-side of the peptide bond by the enzyme chymotrypsin.

Enzymes are sensitive to changes in environment, such as temperature and pH.

Enzymes are also more sensitive than inorganic catalysts to changes in reaction conditions. Enzymes lose their catalytic activity outside a relatively narrow pH range and temperature range. This is because the shape of an enzyme is critical in determining its function, and as enzymes are proteins, their three-dimensional shape is affected by pH and temperature. A change in pH and/or temperature will disrupt the attractions (see Table 10.3.1 on page 373) in the protein (enzyme) that determine its tertiary shape.

Living organisms are very complex systems. With so many reactions required to sustain each living organism, thousands of different enzymes are needed. It is important that chemists understand the role of enzymes and their action when they develop new medications. It is also important to investigate the potential of these complex catalysts for use in greener industrial processes.

LOCK-AND-KEY MODEL OF ENZYME ACTION

The catalytic activity of an enzyme is highly specific and depends on its overall three-dimensional structure. Because enzymes are proteins, their overall three-dimensional structure is dictated by their tertiary and quaternary structure. The specific part of the enzyme molecule with which a reactant can interact is known as its **active site**. The active site is usually a uniquely shaped flexible hollow or cavity within the protein where the reaction occurs. The reactant molecule that binds with the active site is referred to as the **substrate**. The types of intermolecular bonds formed between an enzyme and a substrate are the same as those that dictate the tertiary structure of proteins. The intermolecular forces are determined by the side chains of the amino acids in the peptide sequence and can include hydrogen bonds, ionic interactions, dipole–dipole attractions and dispersion forces.

One early model for the catalytic action of an enzyme is the 'lock-and-key' model. This model provides an explanation for the critical importance of the three-dimensional shape of the enzyme. In the lock-and-key model, the substrate molecule fits into the enzyme like a key in a lock, forming an **enzyme–substrate complex**, allowing the enzyme to break the bonds in the substrate. Figure 10.4.3 shows the steps involved in an enzyme-catalysed reaction according to the lock-and-key model. The enzyme is specific for a particular substrate, so binding of a different molecule will not result in a reaction.

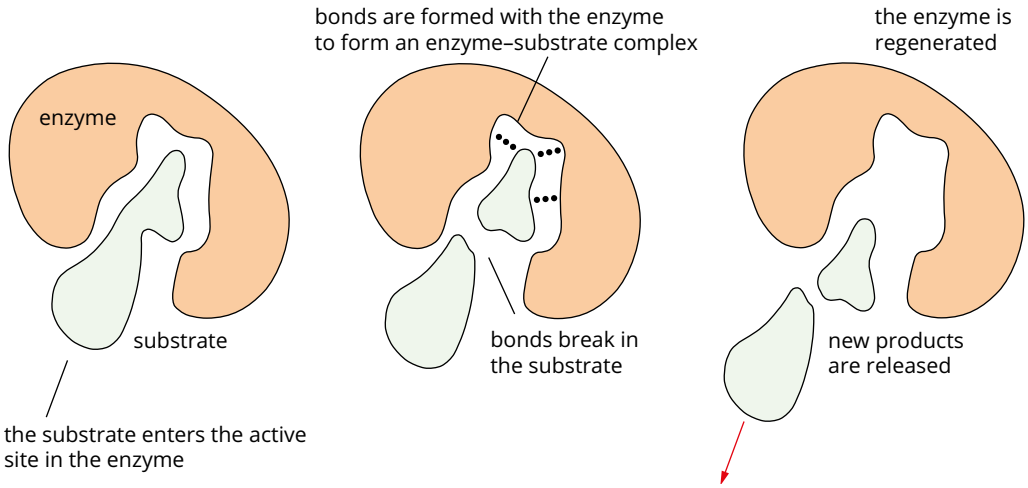


FIGURE 10.4.3 Steps in the action of an enzyme, according to the lock-and-key model

The shape of the substrate molecule must match the shape of the active site. Only reactant molecules that have a suitable 'key' shape can enter and form the necessary intermolecular interactions with the active site ('lock') of the enzyme.

Mirror-image isomers and enzymes

In Chapter 8 you learnt about geometric (*cis* and *trans*) isomers in alkenes. You learnt that stereoisomers are compounds with the same structural formula but with a different arrangement of atoms in space. Another type of stereoisomerism occurs in organic molecules containing a carbon atom bonded to four different substituents. This type of molecule can have mirror-image forms called **enantiomers**. These mirror images (or enantiomers) cannot be superimposed on each other because the four groups attached to the central carbon atom, called a **chiral carbon**, have a different spatial arrangement in each mirror image.

This is like our left and right hands. When the palms of our hands are held against each other we can see they are mirror images. When we place our hands on top of each other with both palms facing upward (or downward) we cannot match the thumbs and fingers with each other. Our hands are non-superimposable mirror images.

PA 4.1.3

The diagrams in Figure 10.4.4 illustrate this property in alanine, one of the simplest biomolecules. All of the amino acids in your body, except glycine, have this type of stereoisomerism. This means that all enzymes also have this type of stereoisomerism.

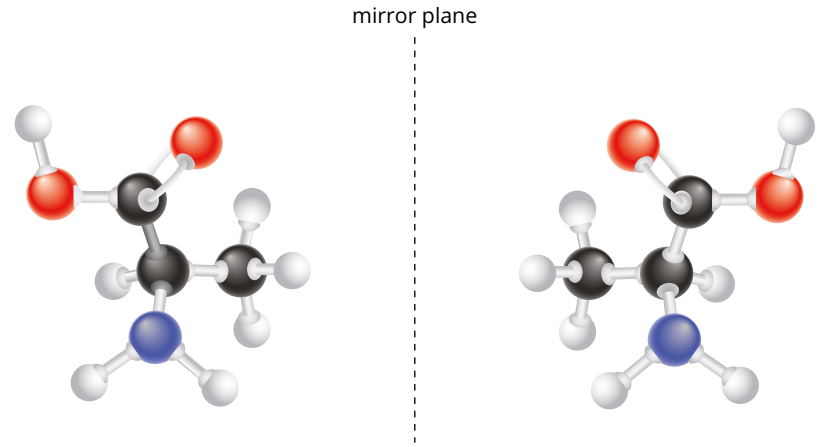


FIGURE 10.4.4 Two mirror-image isomers (enantiomers) of the amino acid alanine. These two molecules cannot be superimposed.

A good example of the different properties of enantiomers is the amino acid phenylalanine. In the chiral environment of the taste buds of the tongue, one enantiomer (Figure 10.4.5) tastes sweet but the other enantiomer is tasteless.

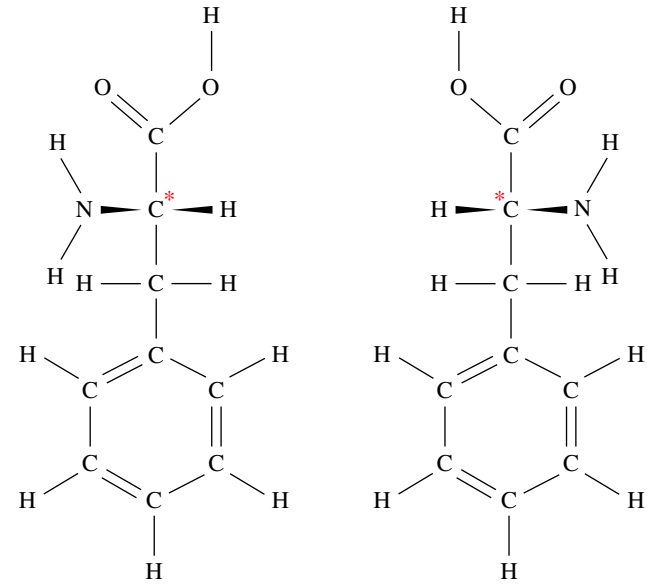


FIGURE 10.4.5 The two enantiomers of phenylalanine interact differently with taste receptors in your body. The enantiomer on the left tastes sweet, while the enantiomer on the right is tasteless. The chiral carbon is highlighted with an asterisk and the wedges represent bonds to atoms above the plane of the page.

Enzymes can distinguish between enantiomers of a chiral substrate. Typically only one enantiomer is biologically active.

Many substrate molecules have more than one chiral centre. Therefore, the way they interact with the chiral enzymes is specific. Enzymes can distinguish between the enantiomers of a chiral substrate. Because enantiomers have different three-dimensional shapes, they may interact with an active site differently. Only one enantiomer might fit the active site and participate in the reaction, so that enantiomer is the only one that is biologically active.

Example—catalysis of polypeptide hydrolysis

Figure 10.4.6 shows how a section of a larger polypeptide molecule might enter the active site of an enzyme that catalyses its hydrolysis. Intermolecular bonds are formed with groups on the enzyme surface, which weaken the peptide bond and make it easier to break. As a result, the activation energy barrier for the hydrolytic reaction is lowered.

The same enzyme–substrate interactions are impossible for enantiomers of this substrate molecule because their shape and the active site will not match up. The hydrolysis of the other isomers could not be catalysed by the same enzyme.

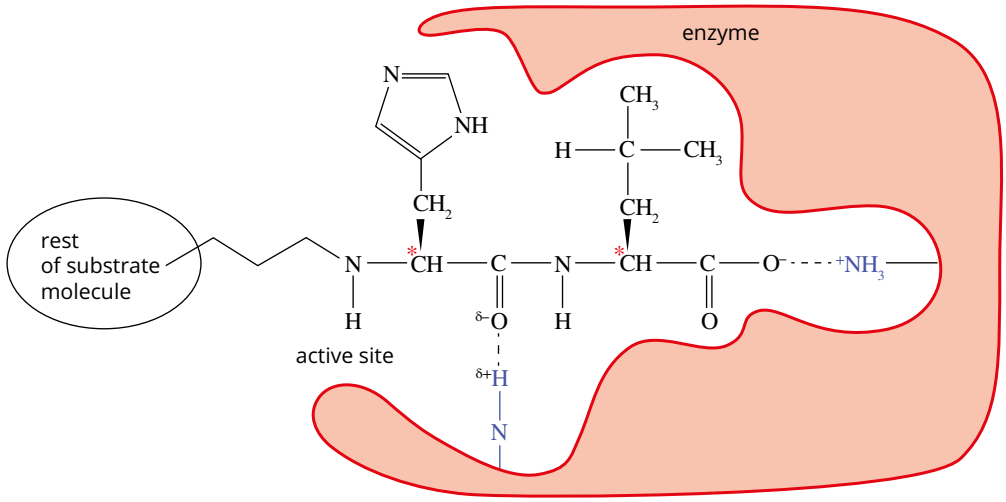


FIGURE 10.4.6 The active site of a protease enzyme, with a polypeptide molecule held by hydrogen bonds, ionic interactions and dispersion forces. The asterisks indicate chiral carbon atoms.

INDUCED FIT MODEL OF ENZYME ACTION

Since the lock-and-key model for enzyme action was proposed, chemists have realised that enzymes have flexible structures. The shape of an enzyme's active site can be modified markedly by the binding of a substrate. This discovery led to a modification of the lock-and-key model and the development of the 'induced fit' model. The induced fit model for enzymes can be applied to a large number of chemical reactions.

As Figure 10.4.7 shows, the flexible active site can mould itself to achieve a better fit for substrate molecules. After the reaction, the products are released from the active site and the active site returns to its initial shape.

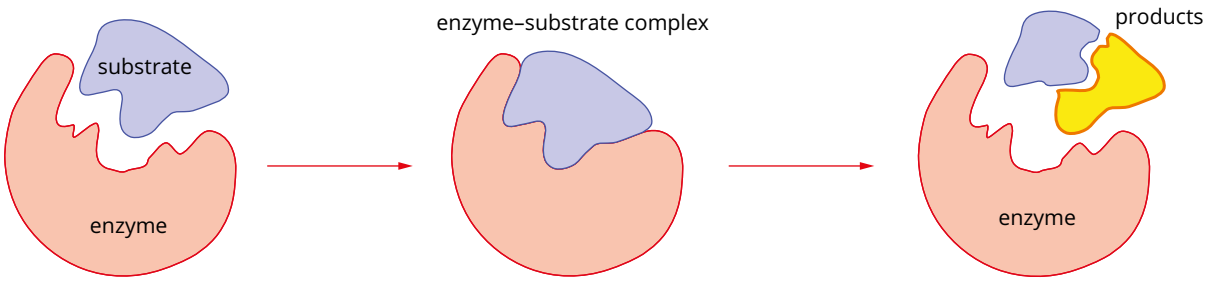


FIGURE 10.4.7 Steps in the action of an enzyme, according to the induced fit model

10.4 Review

SUMMARY

- Enzymes are proteins that catalyse biochemical reactions by providing an alternative reaction pathway with a lower activation energy.
- Enzymes are not changed as a result of the process of catalysis.
- Enzymes are highly specific; enzymes generally only catalyse one specific reaction or a reaction with a particular chemical bond or functional group.
- There are hundreds of enzymes in the human body to catalyse different biochemical reactions.
- Enzyme molecules have uniquely shaped active sites that interact with specific reactant molecules (substrates), weakening or breaking the bonds in the reactant molecules.
- Because of the difference in the three-dimensional shape of the two enantiomers of a mirror-image substrate, only one enantiomer may be able to interact with an enzyme's active site. As a consequence, only a reaction with that enantiomer may be catalysed.
- The earliest model to account for enzyme action was the lock-and-key model; its features are summarised in Figure 10.4.3 on page 381.
- A newer model for enzyme action is the induced fit model, summarised in Figure 10.4.7 on page 383. This model accounts for the flexibility of many enzymes' active sites.

KEY QUESTIONS

Retrieval

1 Identify the type of catalyst (inorganic, enzyme or both) that displays each of the following properties.
- **a** lowers the activation energy
- **b** is highly specific
- **c** is made of proteins
- **d** is not changed by the reaction
- **e** increases reaction rate

2 State the role of the active site of an enzyme.

3 State whether each of the following assertions about the induced fit model of enzyme catalysis is true or false.
- **a** This model explains why enzymes do not catalyse a wide range of reactions.
- **b** The enzyme molecule has an active site.
- **c** The active site does not change shape as the substrate enters.
- **d** An enzyme–substrate complex forms.
- **e** The active site is able to form relatively strong intermolecular bonds with both enantiomers of a substrate.

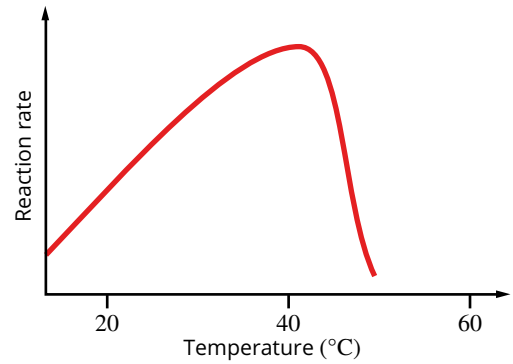
Comprehension

4 Explain why the effectiveness of an enzyme is usually over only a narrow pH and temperature range.

5 **a** The steps in the action of an enzyme involve an active site and a substrate. Draw a diagram to describe the action of an enzyme according to the lock-and-key model of enzyme action.
- **b** The forces of attraction that enable a substrate to bind to an active site can vary. Identify four such forces.

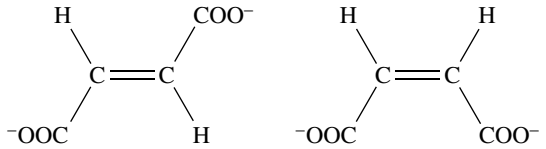
6 Explain why the induced fit model of enzyme action is considered a more accurate model of how enzymes act as catalysts than the lock-and-key model.

7 The following graph shows the typical dependence of human enzyme activity on temperature. Explain the shape of the graph.

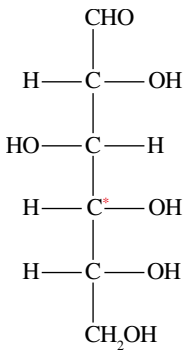


Analysis

8 The citric acid cycle is an important series of reactions in the human body. Consider the following figure. In one step of this cycle, the compound fumarate is converted to malate by the enzyme fumarase. If the stereoisomer of fumarate, maleate, is mixed with the enzyme fumarase no reaction will occur. Determine why no reaction occurs for the maleate.



9 Sugars are chiral molecules. One of the chiral centres in the form of glucose shown below is indicated by the asterisk. Determine the total number of chiral centres in this form of glucose.



10 Compare and contrast the lock-and-key model and the induced fit model of enzyme action.

11 Collagens are a group of fibrous proteins with an elongated shape. Collagens are typically strong but flexible and have structural functions in an animal's body including tendons, cartilage and walls of blood vessels. Their strength is a result of their secondary structure. They have straight, tightly coiled α-helices with limited branching. This secondary structure is possible because the primary structure of collagens is about one-third glycine with a repeating pattern of three amino acids, Gly-X-Y. X and Y can be any amino acid but Y is often proline. Apply your knowledge of amino acids and proteins to explain why this high percentage of glycine contributes to the formation of tightly coiled and straight α-helices.

10.5 Fats and oils



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- recognise that triglycerides (lipids) are esters
- describe the condensation reaction to form triglycerides
- describe the difference in structure between saturated and unsaturated fatty acids
- understand how the structure of lipids relates to their melting point.



FIGURE 10.5.1 Fields of canola crops growing in South East Queensland near Greenmount

Fats and oils are present in meat, fish, dairy products, eggs, all fried foods and vegetable oil. Canola, as shown in Figure 10.5.1, is one of the sources of oils used in food production. It is an excellent source of the unsaturated fatty acids used in margarine, cooking and salad oils. It is also the source of a by-product used as a livestock feed. There has been an increased demand for canola oil in recent years, which has led to many Australian farmers planting this crop.

Fats and oils are a major energy source in your diet. Fats are used by animals to store chemical energy. In this module, you will learn about the reactions that produce fats and oils. You will see the differences in the structure of fats and oils of animal and vegetable origin, and the way this affects their melting points. You will also learn about the place of fats and oils in a healthy, balanced diet.

TRIGLYCERIDES

Fat is a name used to describe a large number of organic compounds belonging to an even larger class of biological molecules called **lipids**. Fats and oils are the best known types of lipids. Compounds such as waxes and steroids (which include cholesterol) are also members of the lipid family.

Fats and oils contain large non-polar molecules known as triglycerides. Fats and oils have very similar chemical structures and are distinguished simply on the basis of their physical state at room temperature. At room temperature:

- fats are solids
- oils are liquids.

Being non-polar, triglycerides are unable to form hydrogen bonds with water, so fats are insoluble in water and oils are immiscible (cannot mix) with water. On the other hand, non-polar organic compounds such as vitamins A, D, E and K can dissolve in triglycerides.

Fats and oils belong to the class of biological molecules called lipids. Fats are solids at room temperature and oils are liquids at room temperature.

General structure of a fatty acid and glycerol

Triglycerides are made by condensation reactions between a glycerol molecule and three fatty acid molecules. Glycerol (propane-1,2,3-triol) is a relatively small molecule with three hydroxyl functional groups (Figure 10.5.2). Fatty acids have a carboxyl functional group attached to a long unbranched hydrocarbon chain, or 'tail'. This tail makes up the bulk of the molecule. Most have an even number of carbon atoms, usually between eight and 20.

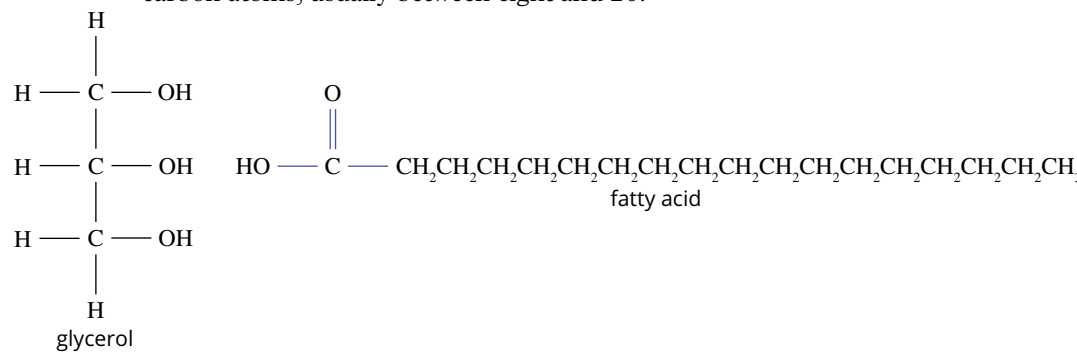


FIGURE 10.5.2 A glycerol molecule and a fatty acid molecule

Condensation reactions to form triglycerides

As you learnt in Chapter 9, a condensation reaction can occur between a molecule that contains a carboxyl group (–COOH) and a molecule that contains a hydroxyl group (–OH). An ester functional group (–COO–) is formed, linking the two molecules. A molecule of water is also produced.

A triglyceride is produced by a condensation reaction that involves the carboxyl group of a fatty acid and a hydroxyl group of glycerol, forming an **ester link**. During a condensation reaction involving one glycerol molecule and three fatty acids, three ester links form and three molecules of water are released. This process is shown in Figure 10.5.3.

When a small molecule, such as water, is produced in a reaction as a by-product, the reaction is said to be a condensation reaction.

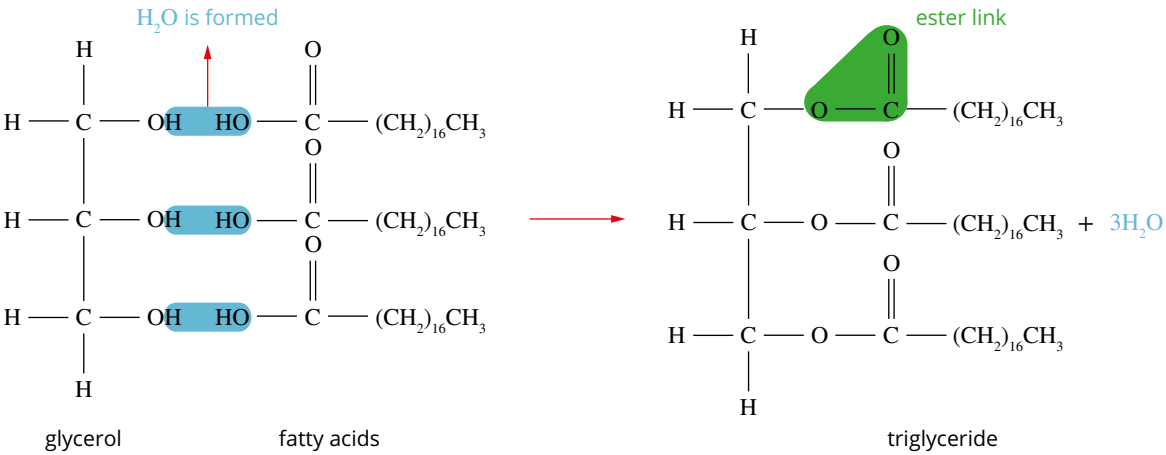


FIGURE 10.5.3 Equation showing a reaction between glycerol and fatty acids to produce a triglyceride and water

Most triglycerides have two or three different fatty acid hydrocarbon chains. The hydrocarbon chains may differ in length. Some hydrocarbon chains may also contain one or more carbon–carbon double bonds.

SATURATED AND UNSATURATED FATTY ACIDS

Fats are classified on the basis of the structural features of the hydrocarbon chains of their fatty acid components.

- Saturated fatty acids have hydrocarbon chains that contain only single carbon–carbon bonds. Stearic acid, which occurs widely in meats, has a condensed structural formula of $CH_3(CH_2)_{16}COOH$ and a molecular formula of $C_{17}H_{35}COOH$. Saturated fatty acids have the general formula $C_nH_{2n+1}COOH$.
- Monounsaturated fatty acids contain one carbon–carbon double bond in their hydrocarbon chain. The main dietary example is oleic acid, which is found in a number of vegetable oils. Its condensed structural formula is $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ and its molecular formula is $C_{17}H_{33}COOH$. Monounsaturated fatty acids have the general formula $C_nH_{2n-1}COOH$.
- Polyunsaturated fatty acids contain more than one carbon–carbon double bond in their hydrocarbon chain. Fish and vegetable oils are the main dietary source of polyunsaturated fatty acids. For example, sunflower oil is a good source of linoleic acid. Linoleic acid has the condensed structural formula $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ and its molecular formula is $C_{17}H_{31}COOH$.

The structure and general formulas of stearic acid, oleic acid and linoleic acid are shown in Figure 10.5.4.

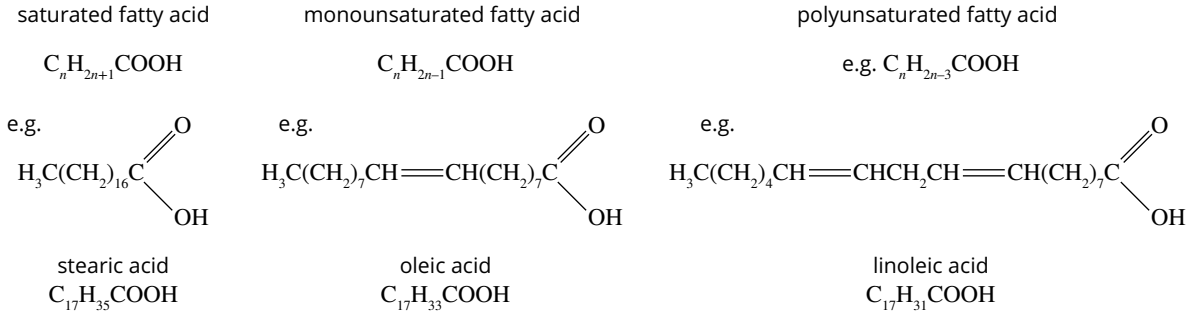


FIGURE 10.5.4 The general formula and condensed structural formula of a representative saturated fatty acid, monounsaturated fatty acid and polyunsaturated fatty acid

Table 10.5.1 lists further examples of saturated and unsaturated fatty acids as well as some dietary sources of these fatty acids.

TABLE 10.5.1 Examples of fatty acids and their sources

	Name	Condensed structural formula	Molecular formula	Food sources
Saturated fatty acids	lauric acid	$CH_3(CH_2)_{10}COOH$	$C_{11}H_{23}COOH$	laurel oil, coconut oil, dairy products
	myristic acid	$CH_3(CH_2)_{12}COOH$	$C_{13}H_{27}COOH$	butter, coconut oil, nutmeg
	palmitic acid	$CH_3(CH_2)_{14}COOH$	$C_{15}H_{31}COOH$	dairy products, beef, palm oil
	stearic acid	$CH_3(CH_2)_{16}COOH$	$C_{17}H_{35}COOH$	beef, dairy products
Unsaturated fatty acids	palmitoleic acid (monounsaturated)	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	$C_{15}H_{29}COOH$	cheese, macadamia nuts
	pleic acid (monounsaturated)	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	$C_{17}H_{33}COOH$	olive oil, canola oil, peanuts
	linoleic acid	$CH_3(CH_2)_4(CH=CHCH_2)_2(CH_2)_6COOH$	$C_{17}H_{31}COOH$	corn, peanuts, soybean oil
	linolenic acid	$CH_3CH_2(CH=CHCH_2)_3(CH_2)_6COOH$	$C_{17}H_{29}COOH$	walnuts, linseed oil, legumes
	arachidonic acid	$CH_3(CH_2)_4(CH=CHCH_2)_4(CH_2)_2COOH$	$C_{19}H_{31}COOH$	peanut oil
	eicosapentaenoic acid (EPA)	$CH_3(CH_2CH=CH)_5(CH_2)_3COOH$	$C_{19}H_{29}COOH$	salmon, tuna, seaweed



FIGURE 10.5.5 These foods are all sources of saturated fatty acids.

Saturated fats

Saturated fats are made from saturated fatty acids only. They are generally unreactive and exist as waxy solids at room temperature. Saturated fats occur in higher proportions in animal fats, such as those shown in Figure 10.5.5.

Unsaturated fats: omega-3 fatty acids and omega-6 fatty acids

Unsaturated fatty acids are classified according to the position of the first double bond from the end of the hydrocarbon chain. As shown in Figure 10.5.6, the **omega carbon** of an unsaturated fatty acid is the carbon in the methyl group at the end of the hydrocarbon chain. An **omega-3 fatty acid** has a carbon–carbon double bond on the third carbon from the omega carbon. For example, linolenic acid, which is obtained from linseed oil, walnut oil and peanut oil, is an omega-3 (ω-3) fatty acid.

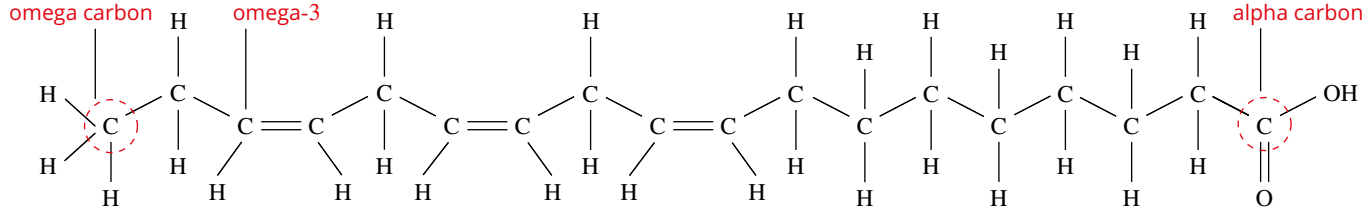


FIGURE 10.5.6 Molecular structure of linolenic acid, an omega-3 (ω-3) fatty acid

Similarly, the **omega-6 fatty acids** have a carbon–carbon double bond on the sixth carbon from the omega carbon (Figure 10.5.7). Sunflower oil, soya bean oils and corn are sources of omega-6 fatty acids.

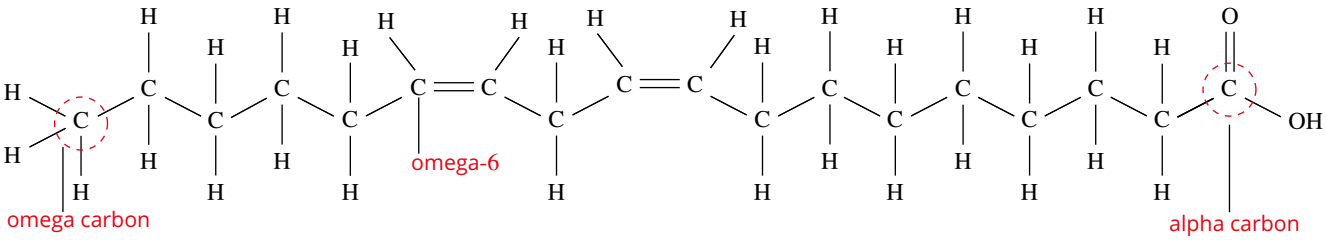


FIGURE 10.5.7 Molecular structure of linoleic acid, an omega-6 (ω-6) fatty acid

Algae produce oils containing omega-3 fatty acids such as eicosapentaenoic acid (EPA). The algae are consumed by prawns and fish such as salmon (Figure 10.5.8). Eating these foods provides you with an excellent supply of omega-3 fatty acids.

Numerous claims have been made about the health benefits of omega-3 fatty acids, such as reduced incidence of heart disease, inflammation of the skin and arthritis. However, much of the supporting evidence has not been based on scientifically rigorous data. The optimum ratio of omega-3 fatty acids to omega-6 fatty acids in a healthy diet is also an area of contention. It may be that the actual ratio of omega-3 to omega-6 fatty acids is a far more significant factor than the intake of either.

MELTING POINTS OF FATS AND OILS

Fats, which are solids at room temperature and occur widely in foods of animal origin, have higher melting points than oils. Oils are liquids that often originate from vegetable sources.

The melting points of triglycerides are often an important factor to consider when preparing or processing foods. For example, cocoa butter, which melts at close to body temperature, is ideal for making chocolate (Figure 10.5.9). It is extracted from cocoa beans and contains a higher proportion of saturated fatty acids (stearic and palmitic) than most other vegetable oils.

The different melting points of triglycerides can be explained in terms of the length and degree of saturation of their fatty acid hydrocarbon chains.

Table 10.5.2 shows that as the hydrocarbon chain increases in length, the melting point of the fatty acid increases. This is due to the increasing strength of dispersion forces between fatty acid molecules as molecular mass increases. The fatty acid tails can pack more closely and so these intermolecular forces become stronger.

TABLE 10.5.2 Effect of hydrocarbon chain length on the melting points of fatty acids

Fatty acid	Number of carbon atoms	Number of C=C bonds	Melting point (°C)	Source
lauric acid	12	0	44	coconut oil
palmitic acid	16	0	63	cocoa beans
stearic acid	18	0	70	beef tallow

Furthermore, as Table 10.5.3 shows, when the number of carbon–carbon double bonds increases, the melting point of the fatty acid decreases. Most naturally occurring unsaturated fatty acids have a ***cis*-arrangement** of the alkyl groups around the double bond. This produces a permanent bend or 'kink' in the hydrocarbon chain, as shown in Figure 10.5.10 on page 390. As a result, the fatty acid tails are unable to line up and pack closely. The intermolecular dispersion forces are much weaker than those formed between saturated fatty acid tails.

In fatty acids, the carboxylic acid end is regarded as the start of the fatty acid chain (the α-carbon). The methyl end is considered the ω-carbon.



FIGURE 10.5.8 Foods that are rich in omega-3 fatty acids include salmon, prawns, nuts and broccoli.



FIGURE 10.5.9 Chocolate makers take advantage of the melting point of cocoa butter to produce intricate structures, such as this gorilla.

TABLE 10.5.3 Effect of number of double bonds on the melting point of unsaturated fatty acids

Fatty acid	Number of carbon atoms	Number of C=C bonds	Melting point (°C)	Source
stearic acid	18	0	70	beef tallow
pleic acid	18	1	13	olive oil
pinoleic acid	18	2	–5	safflower oil
linolenic acid	18	3	–11	fish oil

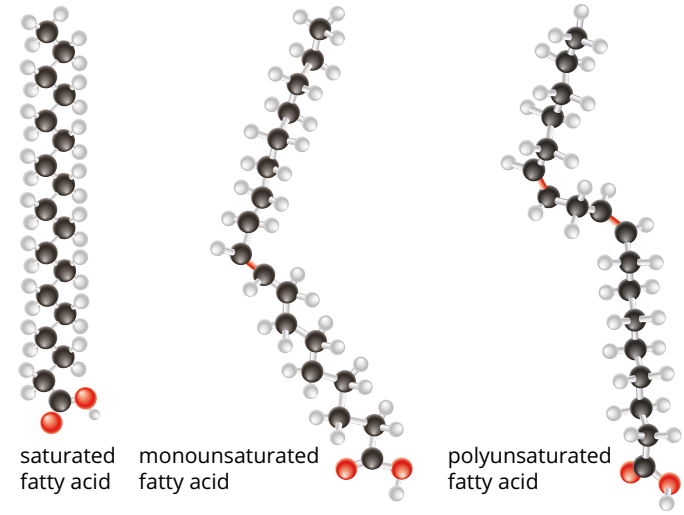


FIGURE 10.5.10 The different shapes of the hydrocarbon chains of these three fatty acids are produced by the double bonds in unsaturated fatty acids. Notice also the *cis* arrangement across the double bonds (highlighted in red).

A *cis* arrangement occurs when the longest hydrocarbon chains attached to the carbons of a double bond are on the same side of the double bond.

Margarine

Unlike butter, which is made from saturated animal fats, margarine is usually made from vegetable oils that contain more polyunsaturated fats (Figure 10.5.11). Vegetable oils from plants such as sunflower, palm, soya and coconut are blended together to make margarine. In order to convert the unsaturated oils to solid form, they are partially saturated by an addition reaction with hydrogen in the presence of a nickel catalyst.

Antioxidants and stabilisers are added to margarine because the carbon–carbon double bonds in polyunsaturated fats are reactive. These additives prevent the polyunsaturated fats from reacting with oxygen in the air and producing substances with unpleasant odours, whose presence leads to a condition known as rancidity.



FIGURE 10.5.11 Margarine contains additives that slow the oxidation of the double bonds present in its molecular structure.

ESSENTIAL AND NON-ESSENTIAL FATTY ACIDS

Most Western diets include more than enough fat to provide the fatty acids needed for the human body. In addition, fats can be converted into other fatty acids. Therefore, most fats are classified as containing non-essential fatty acids. For example, stearic acid can be converted into oleic acid if oleic acid is in short supply from dietary sources.

Several fatty acids are classified as essential fatty acids because humans are unable to produce them. These are all polyunsaturated fatty acids:

- linolenic acid, an omega-3 fatty acid
- linoleic acid, an omega-6 fatty acid
- arachidonic acid, an omega-6 fatty acid.

These fatty acids are required in small amounts to produce a number of compounds with a wide range of functions. These compounds include a group of hormones called prostaglandins and thromboxane, which is needed for blood clotting and also to form cell membranes.

Essential fatty acids are in high concentrations in fish oil and soybean oil, but a balanced diet that includes plenty of fruit and vegetables provides them in adequate amounts. Sunflower oil, which is used to produce margarine, is particularly rich in linoleic acid. It can be found in the sunflower seeds used in muesli, health bars and animal feedstocks.

Trans fatty acids

You may have noticed the amount of *trans* fats listed on a food label, such as the popcorn label in Figure 10.5.12.

Nutrition Facts	
Serving Size: 1 Tbsp (14 g)	
Servings Per Container: about 32	
Amount Per Serving	
Calories 100	Calories from Fat 100
	% **Daily Value**
Total Fat 11 g	**17%**
Saturated Fat 2.5 g	**12%**
Trans Fat 2.5 g	
Cholesterol 0 mg	**0%**
Sodium 105 mg	**4%**
Total Carbohydrate 0 g	**0%**
Dietary Fibre 0 g	**0%**
Sugars 0 g	**0%**
INGREDIENTS: WHOLEGRAIN POPCORN, PARTIALLY HYDROGENATED SOYBEAN OIL, SALT, NATURAL AND ARTIFICIAL FLAVOUR (MILK), COLOUR ADDED, FRESHNESS PRESERVED BY PROPYL GALLATE.	

FIGURE 10.5.12 Nutrition data shown on a pack of popcorn

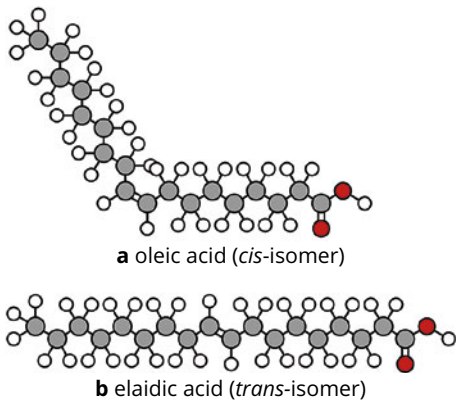
As you learnt in Chapter 8, unsaturated molecules can have geometric isomers described as *cis*-isomers and ***trans*-isomers**. Most unsaturated fats occurring naturally have the *cis* orientation of hydrocarbon chains. *Trans* fats are unsaturated fats with a *trans* orientation of hydrocarbon chains across the double bond.

You can see this difference in orientation in Figure 10.5.13. These models also illustrate another significant structural difference between the isomers. Notice that only the *cis* isomer has a noticeable 'kink' in the hydrocarbon chain.

Partial reaction of the polyunsaturated fats in vegetable oils with hydrogen reduces the number of double bonds present. Hydrogenation is used commercially to increase the melting point of products such as chocolate, to improve shelf life and to make cooking fats for commercial deep-frying. However, it can also lead to double bond isomerism reactions producing *trans* fats.

In recent years, there has been considerable evidence to show that consumption of *trans* fats leads to increased risk of heart disease due to higher low-density lipoprotein or LDL cholesterol levels. Many countries have moved to ban or minimise their intake, or at least to require amounts of *trans* fats to be stated on food packaging.

According to the World Health Organization, 'industrial *trans* fats (found in fast foods, snack foods, fried foods and frozen foods) are not part of a healthy diet' and should be reduced 'to less than 1% of total energy intake'.



a oleic acid (*cis*-isomer)

b elaidic acid (*trans*-isomer)

FIGURE 10.5.13 Two isomers of the fatty acid *cis*-oleic; (a) acid and its (b) *trans*-isomer

10.5 Review

SUMMARY

- Fats and oils are composed of molecules called triglycerides.
- Triglycerides have a number of important roles in the human body, including energy storage and insulation, and as a source of fatty acids from which other important compounds are produced.
- Triglycerides are formed in a condensation reaction between glycerol and fatty acids.
- Three ester links are formed in the condensation reaction between a glycerol molecule and three fatty acids to form a triglyceride molecule.
- Fatty acids are carboxylic acids with a long hydrocarbon chain.
- Saturated fatty acids have only carbon–carbon single bonds.
- Unsaturated fatty acids have one or more carbon–carbon double bonds.
- Unsaturated fatty acids with a double bond on the third last carbon atom in the hydrocarbon chain are classified as omega-3 fatty acids; unsaturated fatty acids with a double bond on the sixth last carbon atom are classified as omega-6 fatty acids.
- The most significant intermolecular forces between triglyceride molecules or fatty acid molecules are dispersion forces.
- Saturated fatty acids pack together more closely and can form stronger intermolecular bonds than unsaturated fatty acids. Saturated fatty acids, therefore, have higher melting points and are more likely to be solids at room temperature.
- In a similar way, unsaturated triglycerides, which are common in vegetable oils, have lower melting points than the saturated triglycerides common in animal fats.
- The essential fatty acids, linoleic acid, linolenic acid and arachidonic acid, must be included in the diet as they cannot be manufactured by humans from other organic compounds via biochemical pathways.

KEY QUESTIONS

Retrieval

1 Name the two functional groups that are directly involved in the formation of a triglyceride.

2 Identify the three classes of fatty acids. Briefly describe the distinguishing feature of each class of fatty acid.

3 Name the major type of intermolecular bond that is responsible for the melting point of triglycerides.

4 State why the fatty acid linolenic acid is classified as an essential fatty acid.

Comprehension

5 **a** Represent with an equation the formation of the triglyceride glyceryl trioleate from the reaction of glycerol ($HOCH_2CH(OH)CH_2OH$) and oleic acid ($CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$).

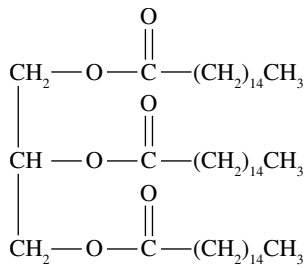
b Draw the structure of glyceryl trioleate, showing the ester bonds.

6 Explain why increasing the proportion of saturated fats in a vegetable oil will cause it to become solid.

7 Elaidic acid is a fatty acid with the condensed formula $CH_3(CH_2)_7CHCH(CH_2)_7CO_2H$. It is the *trans*-isomer of the *cis* fatty acid oleic acid. Elaidic acid can be found in some margarines and fried foods. Draw a structure of elaidic acid to show its *trans* nature.

Analysis

8 A fat present in a vegetable oil has the structure shown below.



a Identify an ester functional group.

b Determine if this triglyceride is saturated or unsaturated. Explain your answer.

9 Classify the following fatty acids obtained from various food sources as being saturated, monounsaturated or polyunsaturated by referring to Table 10.5.1 on page 388.

a stearic acid

b $CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$

c $C_{13}H_{27}COOH$

d arachidonic acid

e $C_{17}H_{31}COOH$

f $CH_3(CH_2)_{14}COOH$

g $C_{11}H_{23}COOH$

h $C_{17}H_{33}COOH$

10 Sort the structures of the fatty acids A–F from lowest to highest melting point. Explain the basis on which you made your ranking.

A $CH_3(CH_2)_{18}COOH$

B $CH_3(CH_2)_{10}COOH$

C $CH_3(CH_2)_5CHCH(CH_2)_7COOH$

D $CH_3(CH_2)_7CHCH(CH_2)_9COOH$

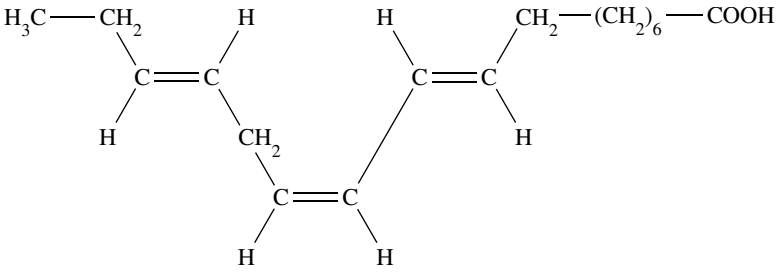
E $CH_3(CH_2)_4(CHCHCH_2)_4(CH_2)_2COOH$

F $CH_3CH_2CHCHCH_2CHCHCH_2CHCH(CH_2)_7COOH$

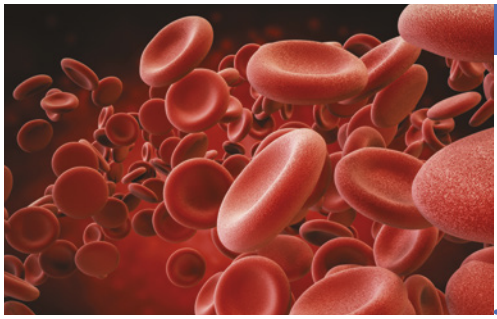
11 Fish oils are generally high in omega-3 fatty acids such as linolenic acid. Cold-water fish are particularly high in omega-3 fatty acids. Determine why this is important for cold-water fish to function effectively. (Hint: consider what would happen if they were high in saturated fats.)

12 Butter is much slower to go rancid than margarine. Identify the reason for this with reference to the major types of fats that make up butter and margarine.

13 The figure below shows an incorrect structure for the naturally occurring unsaturated fat linolenic acid. Identify what is incorrect in this structure and redraw the structure to show a correct representation. Explain why the figure below is an incorrect representation of linolenic acid.



10.6 Soaps



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- describe the production of soaps by the base hydrolysis (saponification) of fats (triglycerides)
- recognise that a soap is made of a long hydrocarbon chain with a negatively charged carboxylate group at one end
- describe how the structure of soaps relates to their cleaning action
- relate the inability of soaps to clean in hard water to their structure.

A quick scan of the shelves in a supermarket highlights the importance of soaps and other cleaning products to society. Not only do we consume a significant amount of cleaning products, but the range of products we use is also wide. Soaps have been with us for a very long time with many ancient civilisations, including the ancient Babylonians, making soap by heating fats with a slurry of ashes in water. As shown in Figure 10.6.1, soap manufacturers have been encouraging us to use their products for a long time.



FIGURE 10.6.1 A soap advertisement from 1940

Soaps (and detergents) are used as cleaning agents in a wide range of circumstances including cleaning our bodies, hair, dishes, clothes and surfaces in the home. In this module you will learn about how soaps are manufactured from fats and oils, about their structural features and about the mechanism of their cleaning action.

SAPONIFICATION—THE MANUFACTURE OF SOAP

In Module 10.5 you learnt that fats and oils are triglycerides—ester molecules made from a combination of a glycerol molecule and three molecules of long-chain carboxylic acids called fatty acids—and that triglycerides are made by the condensation reaction between a fatty acid and glycerol (Figure 10.5.3 on page 387). The reaction to make soap is the reverse of this condensation reaction.

Traditionally, soap was made by heating an animal fat or vegetable oil with a strong alkali, such as sodium hydroxide solution. When triglyceride molecules are heated with sodium hydroxide, the three ester links in the triglyceride are hydrolysed. In theory, water can be used for this reaction. Reactions where water is used to break down a compound are known as hydrolysis reactions. In practice, the reaction with water is very slow, so a strong base such as sodium hydroxide or potassium hydroxide is used. The reaction with water in alkaline conditions is known as **base hydrolysis** and when it is applied specifically to esters it is called **saponification**.

The general equation for the base hydrolysis of a triglyceride with sodium hydroxide is shown in Figure 10.6.2. The hydrolysis breaks the three ester bonds between the C atom of the carbonyl carbon and the O atom of the propane chain. The products of the hydrolysis are glycerol and the sodium salts of the three fatty acids. The sodium salts are the main components of soap.

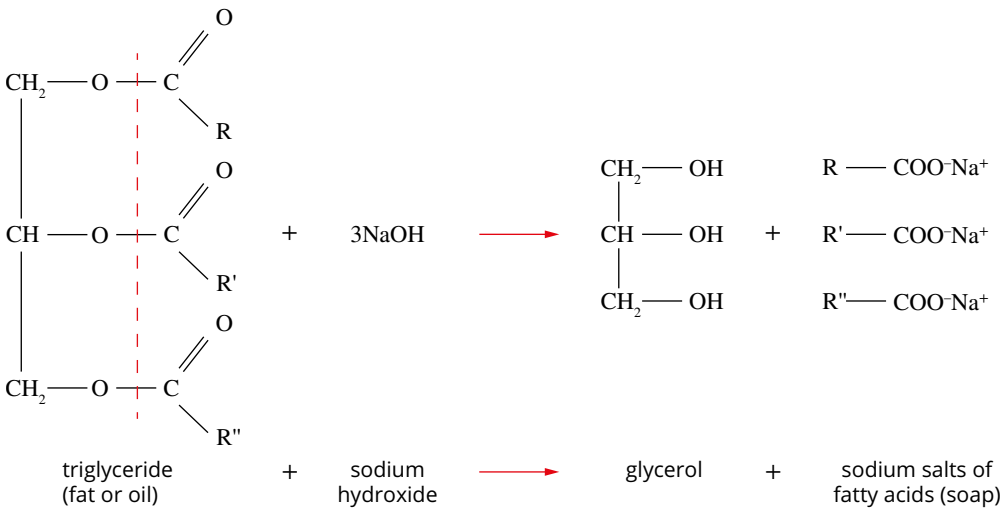


FIGURE 10.6.2 The alkaline hydrolysis of a triglyceride molecule to form glycerol and soap. Base hydrolysis breaks the three ester bonds on the triglyceride along the dotted red line.

Figure 10.6.3 on page 396 shows the base hydrolysis of a triglyceride with three stearate ester groups to produce the soap sodium stearate.

The metal hydroxide used as an alkali can alter the effects of the soap produced. The fatty acid sodium salts produced when sodium hydroxide is used tend to be solids at room temperature. However, if potassium hydroxide is used, the fatty acid potassium salts produce a liquid soap.



FIGURE 10.6.4 Making soap from vegetable oil and sodium hydroxide solution is a relatively easy reaction to perform in the school laboratory.

The saponification reaction can be easily carried out using equipment in your school laboratory, as shown in Figure 10.6.4.

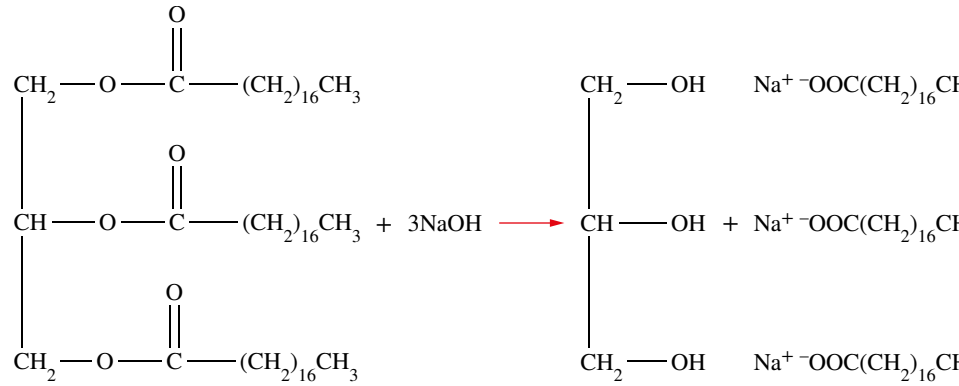


FIGURE 10.6.3 Sodium hydroxide hydrolysis of a triglyceride with three stearate ester groups to produce the soap sodium stearate.

Hydrolysis of triglycerides in the body

When the triglycerides we eat in our foods are digested they undergo a hydrolysis reaction similar to that in soap-making except the products are glycerol and three fatty acids. Triglycerides undergo enzyme-catalysed hydrolysis during digestion. Because triglycerides are insoluble in water their molecules remain intact as they pass through the digestive tract until they reach the small intestine. In the small intestine, **bile** is used to process the triglycerides.

Bile emulsifies fats, breaking them down into smaller particles and dispersing them as small droplets. This process of creating an **emulsion** is similar to how soaps and detergents work on the fat left in a frying pan after cooking fatty food. The effect of emulsification on fats in the small intestine is shown in Figure 10.6.5.

Emulsification of fats increases their surface area so that more triglyceride molecules are exposed to the aqueous environment.

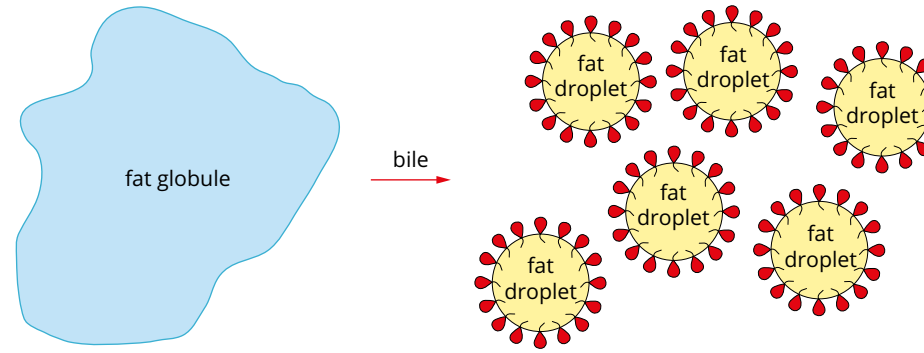


FIGURE 10.6.5 A triglyceride enters the small intestine as a fat globule or an oil globule. The bile turns this globule into an emulsion, consisting of much smaller fat droplets with bile particles embedded in the surface. The surface area of the fat exposed for hydrolysis by the water-soluble lipase enzyme is now much greater.

In your body, the enzyme lipase breaks down triglycerides. However, lipase is a water-soluble protein so it can only interact at the surface of the hydrophobic fat globules. Emulsification of fats by bile increases the surface area of the fats, which means that lipase can access more triglyceride molecules, which increases the rate of hydrolysis.

Lipase enters the intestine from the pancreas. The enzyme catalyses the hydrolysis of the three ester bonds in the triglyceride molecules. You can see in Figure 10.6.6 how the triglyceride molecules undergo hydrolysis to form glycerol and fatty acids.

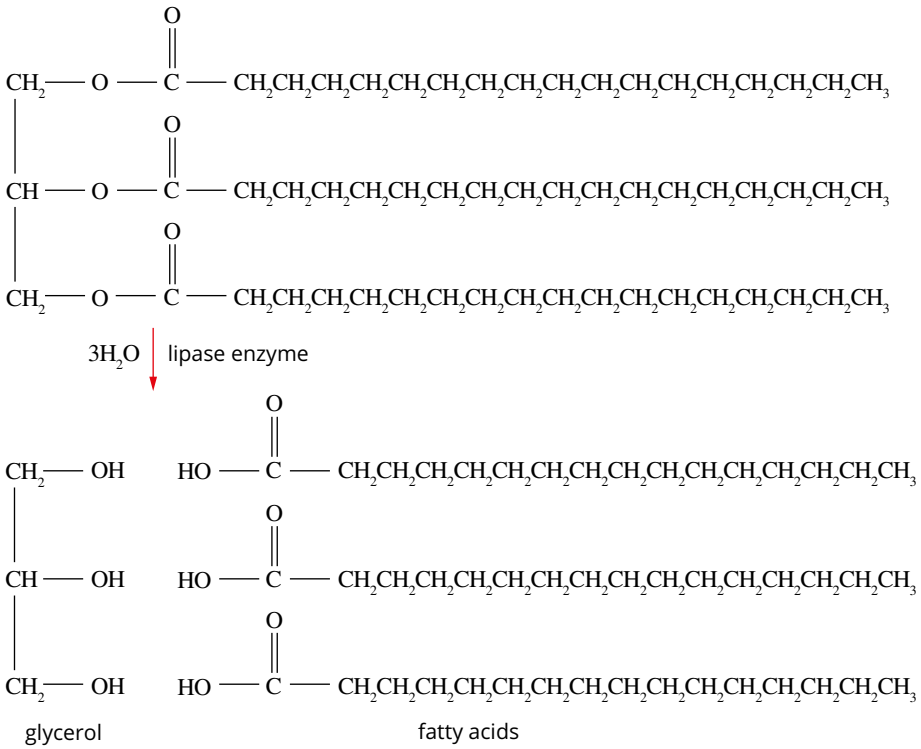


FIGURE 10.6.6 Hydrolysis of a triglyceride to glycerol and three fatty acid units

The three fatty acids will not necessarily have the same structure. Figure 10.6.7 shows a general equation for the hydrolysis of a triglyceride where the letter R is used to represent each fatty acid hydrocarbon chain.

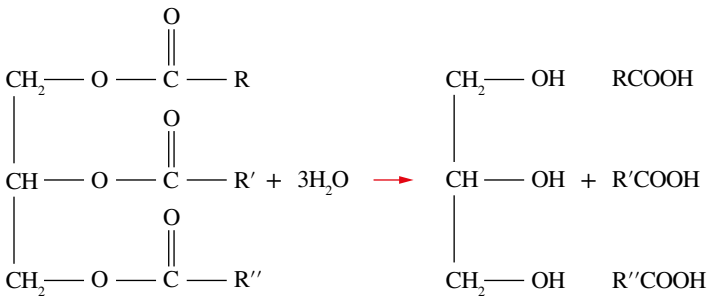


FIGURE 10.6.7 General equation for the hydrolysis of a triglyceride. R, R′ and R″ represent different hydrocarbon chains.

The glycerol and fatty acids that are produced pass into the bloodstream to the liver, where they are re-formed into triglycerides.

THE CLEANING ACTION OF SOAPS

Previously, you have learnt that substances with similar types of intermolecular forces will be miscible, that is they will dissolve in each other. A polar molecule will dissolve in a polar solvent, but a non-polar molecule will not. Similarly, a non-polar molecule will dissolve in a non-polar solvent, but a polar molecule will not. An understanding of solubility is needed to understand how cleaning occurs. The most common stain that you want to remove in the laundry is body oil. Oils are non-polar but water is a polar solvent. From a chemistry point of view, cleaning therefore presents a dilemma. Soaps (and detergents) provide the solution.

Small molecules can usually be described simply as either polar or non-polar. The long fatty acid ions in soap, however, have a non-polar section and a negatively charged carboxylate functional group. This structure, as shown in Figure 10.6.8, allows these ions to form a link between water and oil.

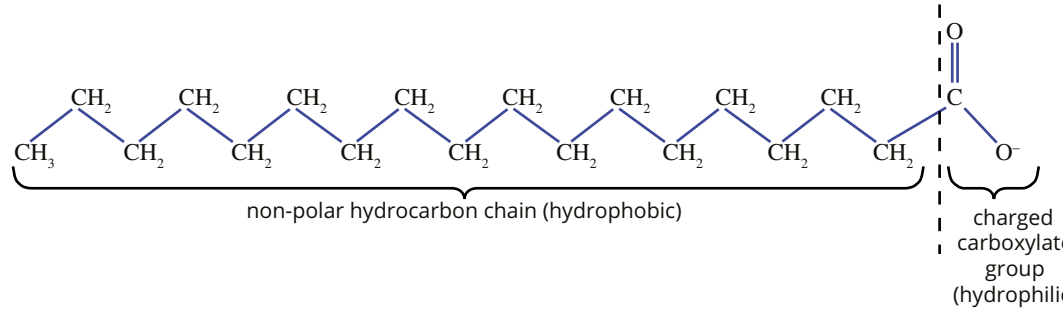


FIGURE 10.6.8 Soap particles have a non-polar hydrocarbon chain and one end that is negatively charged.

Water can bond with the charged carboxylate group at the end of the fatty acid ion. This charged end is referred to as the **hydrophilic** or 'water-loving' end of the ion. This type of bonding is an example of **ion–dipole bonding**.

On the other hand, the non-polar hydrocarbon chain tends not to dissolve in water. It is referred to as **hydrophobic** or 'water-hating'. It will mix readily with oil, due to the weak dispersion forces present. To simplify diagrams with soap particles, the hydrocarbon chain is often shown as a zigzagged line and the charged end as a circle, as shown in Figure 10.6.9.

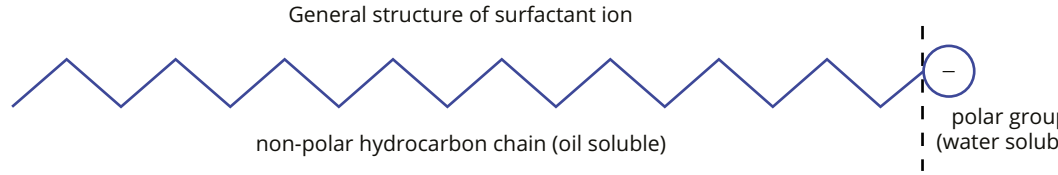


FIGURE 10.6.9 Simplified representation of a soap particle

Soap in water

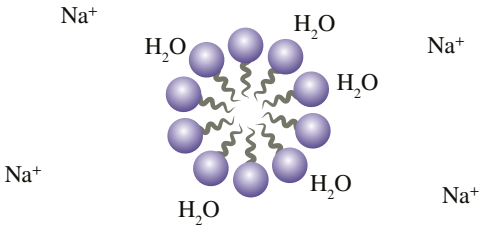


FIGURE 10.6.10 The arrangement of soap particles in a micelle. Micelles have a spherical shape.

In water, soap particles tend to clump together. The hydrophilic ends are on the outer perimeter of these clumps where they will be in contact with the water. The hydrophobic sections of the soap are in the centre of the clump where they are in contact with each other. This is a stable arrangement called a **micelle**, as shown in Figure 10.6.10.

Removing the dirt

During the washing of clothes, vigorous agitation breaks up micelles formed by soap. The non-polar ends of the soap particles are then able to position themselves in drops of oil or grease, leaving the hydrophilic end in the water. As agitation continues, water forms ion–dipole bonds with the negatively charged carboxylate ends of the soap and the oil particle is lifted from the fabric (Figure 10.6.11).

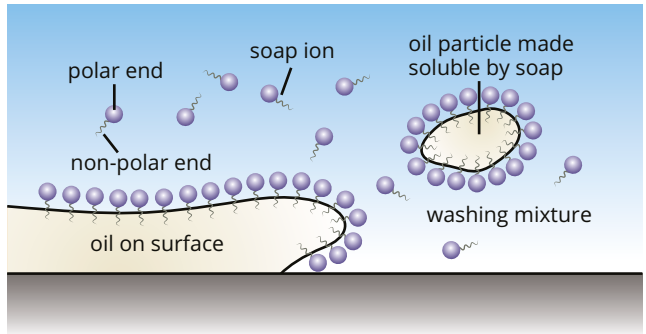


FIGURE 10.6.11 The cleaning action of soap. The non-polar chain of soap particles is embedded in an oil stain while the charged part is in the water.

Once the oil lifts from the fabric, the non-polar sections of the soap embed themselves around the oil. The charged end of the soap protrudes into the water. The oil, surrounded by soap molecules, is a stable arrangement that prevents the stain reattaching to the fabric (Figure 10.6.12). When the water is drained from the wash, the oil stains are drained away as well.

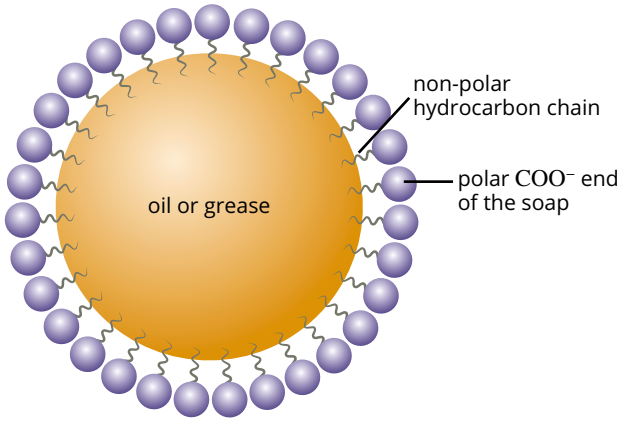


FIGURE 10.6.12 An oil or grease stain that has been lifted from fabric

The non-polar chain and charged end of soap particles enable them to function as cleaning agents. With the addition of soap, a polar solvent can successfully remove non-polar stains. The general term for substances such as soaps is **surfactant**, which is an abbreviation for 'surface acting agent'.

Cleaning in hard water

In some parts of Australia, the effectiveness of soaps is limited. This is because the water supply in these regions contains high levels of metal ions such as Ca^{2+}, Mg^{2+} and Fe^{2+}. Water containing significant concentrations of metal ions is described as **hard water**.

When a typical soap, such as sodium stearate, is added to hard water, the stearate ions react with the calcium and magnesium ions. While sodium stearate is soluble, calcium and magnesium stearates are not and they precipitate from the wash as an unsightly scum. This reaction is illustrated by the equation:

$$2CH_3(CH_2)_{16}COONa(aq) + Ca^{2+}(aq) \rightarrow (CH_3(CH_2)_{16}COO)_2Ca(s) + 2Na^+(aq)$$

The net effect of using soap in hard water is:

- poorly washed clothes
- blocked drains from soap scum
- grey precipitate (scum) in wash tubs
- unsightly stains around basins and taps (as evident in Figure 10.6.13).

To obtain a satisfactory result when washing with soap in hard water, either extra soap needs to be used to create an excess of fatty acid ions or some of the metal ions need to be removed. Metal ions can be removed through the addition to the soap of other negative ions such as carbonate ions. The carbonate ions soften the water by precipitating the calcium ions as calcium carbonate. An equation for the precipitation of unwanted magnesium ions through the addition of sodium carbonate is:

$$Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MgCO_3(s)$$

Another solution to the problem of the limited cleaning action of soaps in hard water is to use a detergent. The cleaning mechanism of a detergent is similar to that of soap but it does not precipitate out in hard water. This modification is discussed in Module 12.2.



FIGURE 10.6.13 Damage to a sink caused by metal ions present in hard water

10.6 Review

SUMMARY

- Soaps are manufactured from the base hydrolysis of fats and oils (triglycerides). The reaction is called saponification.
- The base hydrolysis of triglycerides produces glycerol as well as soap.
- Digestion of triglycerides is also a hydrolysis reaction. The reaction in the body is catalysed by enzymes. The products are glycerol and the fatty acids from which the triglyceride was originally made.
- Digestion of triglycerides occurs in the small intestine where bile emulsifies the fat, which is then hydrolysed by the enzyme lipase.
- A soap molecule consists of a long, non-polar hydrocarbon chain with a negatively charged carboxylate functional group at one end.
- This charged end is referred to as hydrophilic ('water-loving'), while the non-polar hydrocarbon chain is referred to as hydrophobic ('water-hating').
- The cleaning action of soap can be explained in terms of its non-polar hydrocarbon chain and its charged group:
  - the non-polar chain dissolves in the non-polar oil or grease
  - the charged carboxylate group forms ion–dipole bonds with water molecules to link the oil or grease with water
  - agitation of the water then allows the oil or grease to be lifted from the surface that is being cleaned.
- Soaps are less effective than detergents in hard water due to the formation of insoluble metal salts.

KEY QUESTIONS

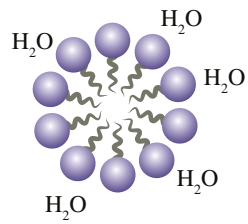
Retrieval

1 Recall the correct words in order to complete the following sentences about saponification.

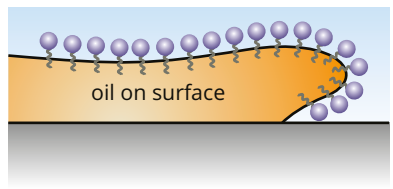
In a saponification reaction, a _____ undergoes _____ _____ to form the _____ of a _____ _____. The other product of saponification is _____.

2 Soap is added to water in a washing machine and washing begins. Indicate the order of the following images to show the correct sequence for a grease stain lifting from the fabric and floating in the water.

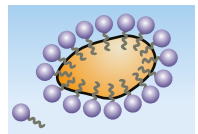
A



B



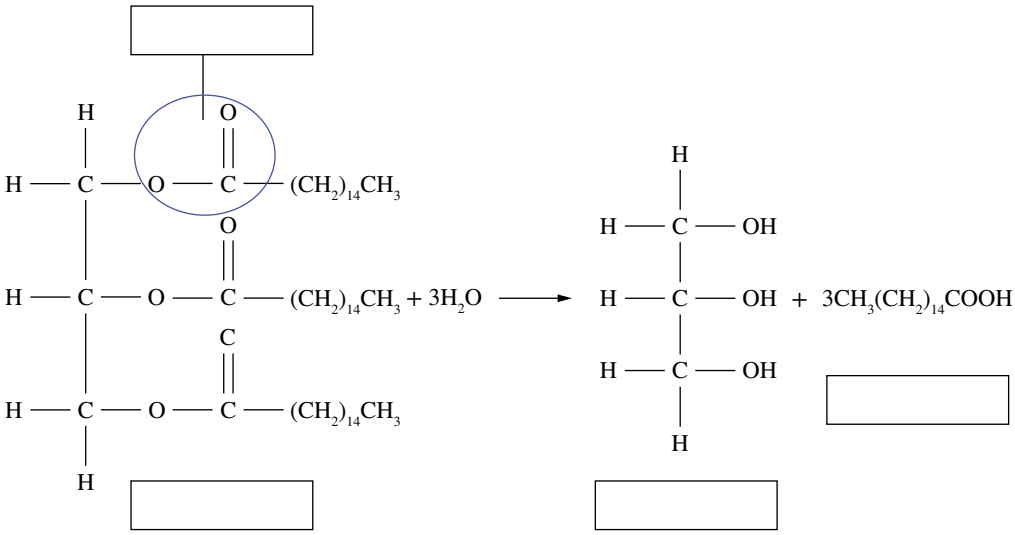
C



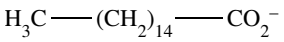
3 Describe an advantage that detergents have over soaps.

Comprehension

4 Show the hydrolysis of a triglyceride during digestion by labelling the parts of the diagram below.



5 The particle shown below is a fatty acid ion, called the palmitate ion, derived from the triglyceride in palm oil. Show where the hydrophilic section of the palmitate ion is by circling it.

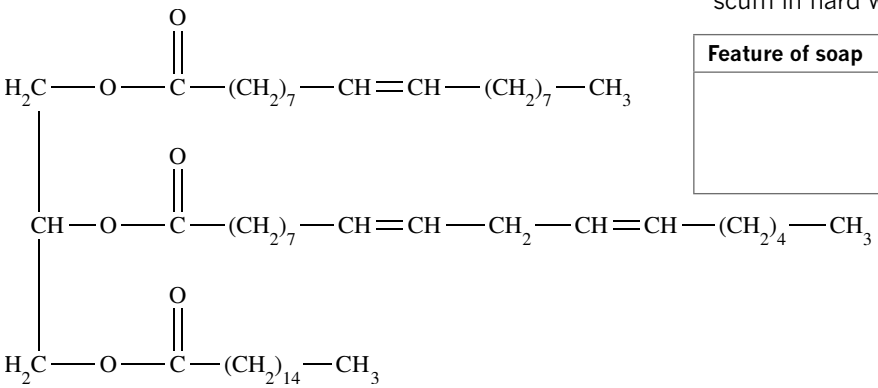


6 Explain what limits the effectiveness of soaps in hard water.

7 Oil spills in waterways can be a major ecological disaster. One of the ways that may be used to deal with an oil spill is to add chemical dispersants to the spill to break down the oil into droplets, which can lead to an increase in the rate of its natural biodegradation. Describe the properties that you would expect a dispersant to have and explain how they improve the miscibility of the oil and water.

Analysis

8 The triglyceride below is heated with a solution of sodium hydroxide. Determine what the formulas of the soap molecules produced from this saponification reaction are.



9 Compare and contrast the hydrolysis of triglycerides in the body and the hydrolysis of triglycerides during a saponification reaction.

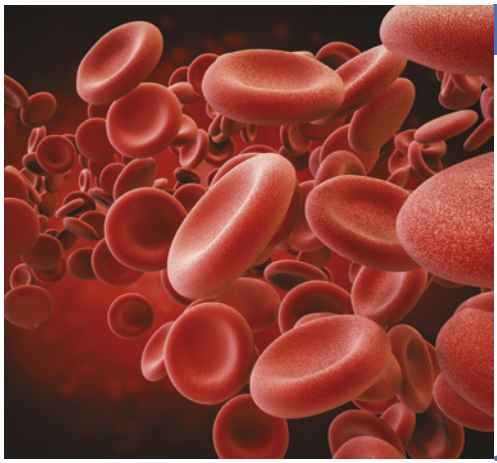
10 Hydrolysis of triglycerides is the reverse of the condensation reaction between glycerol and fatty acids that make a triglyceride. Hydrolysis in water is slow so the hydrolysis of triglycerides to make soap is done using a hydroxide solution. Although hydroxide mediated hydrolysis is much faster than hydrolysis in water, the hydroxide is not a catalyst. Deduce why hydroxide is not considered a catalyst in this reaction.

11 Consider the following list of statements and classify them as features of soaps or detergents or both in the table below.

- contains a hydrocarbon chain
- produced from renewable resources
- does not form a scum in hard water
- forms a scum in hard water
- is a surfactant
- contains a charged end
- forms micelles
- produced from petroleum
- contains a metal ion

Feature of soap	Feature of detergent	Feature of both

10.7 Carbohydrates



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- recognise that monosaccharides contain either an aldehyde group (aldose) or a ketone group (ketose) and several –OH groups and these monosaccharides have the empirical formula CH_2O
- describe the condensation reaction of monosaccharides to form disaccharides and polysaccharides
- recognise a glycosidic bond
- understand that polysaccharides are formed when monosaccharides monomers are joined by glycosidic bonds
- distinguish between α-glucose and β-glucose
- compare and explain the structural properties of starch and cellulose.







FIGURE 10.7.1 (a) The sago palm is found in rainforest areas of Asia. (b) As the sago palm ages, the centre softens and forms a product that is harvested. These women are beating the soft centre into a pulp. (c) The soft centre of the sago palm is the main ingredient in many desserts such as sago pudding.

There are millions of organic chemicals on Earth, and you do not need to look further than the plants and trees around you to find them. Figure 10.7.1 shows the sago palm, which is a common plant in the rainforest areas of Asia. Like many trees, the sago palm is a source of timber but, unlike most trees, its centre forms the basis of a popular dessert—sago pudding.

The main structural component of all plants, including the sago palm, is the polymer cellulose. Over half the world's organic carbon is bound up in trees and other plants in the form of cellulose.

The soft centre of the sago palm tree is a form of starch. Starch is the main component of flour, an essential ingredient of foods such as bread, cakes, sauces and pastry.

Cellulose and starch belong to a class of compounds called **carbohydrates**. In this module, you will learn about the chemical structure of common carbohydrates and their importance to nature and society.

MONOSACCHARIDES

Carbohydrates are made from the elements carbon, hydrogen and oxygen. Carbohydrates usually have the general formula $C_x(H_2O)_y$, where x and y are whole numbers. Carbohydrates range in size from small molecules, with relative molecular masses between 100 and 200, to very large polymers, with molecular masses greater than one million.

One of the simplest carbohydrates, glucose ($C_6H_{12}O_6$), is formed in the cells of green plants through the process of **photosynthesis**. Photosynthesis takes place in the presence of light and the process can be represented by the equation:

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

Photosynthesis is an **endothermic** reaction, in which the Sun's energy is transformed into chemical potential energy in glucose. Living organisms use glucose as a source of energy. Animals cannot perform photosynthesis so they need to consume plants or animals in their diet to meet their energy needs.

The smallest carbohydrates are the **monosaccharides**. They are white, sweet-tasting solids that are highly soluble in water. The structures of the three most common monosaccharides, glucose, galactose and fructose, are shown in Figure 10.7.2. Note that these monosaccharides all have the same molecular formula of $C_6H_{12}O_6$, which means they are isomers.

The structures of the monosaccharides look very similar, particularly glucose and galactose. However, the positions of the hydroxyl (–OH) groups in glucose and galactose are different. These slight variations in structure lead to significant differences in their functions in living organisms.

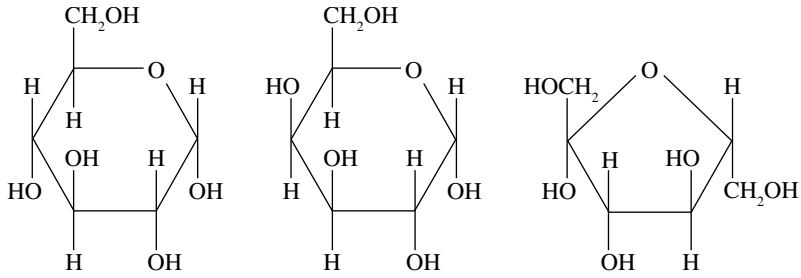


FIGURE 10.7.2 Structural formulas of glucose, galactose and fructose. Carbon atoms in the rings have been omitted for simplicity. There is a carbon atom at each corner of the ring structures except where an oxygen atom is shown.

When there are four different groups around a carbon atom, the molecule has a chiral centre. Glucose and galactose have five chiral centres. Although all the atoms in these molecules are connected in the same way, the groups are arranged differently around one of the chiral centres. It is this difference that causes the molecules to behave differently in living organisms.

All three monosaccharides contain a number of polar hydroxyl groups, which means they can form hydrogen bonds with water. As a result, monosaccharides are highly soluble in water.

Glucose is found in all living things, especially in the juice of fruits, the sap of plants and the blood and tissue of animals. As a product of photosynthesis, glucose functions as a key energy source in most forms of life.

Fructose is found in many fruit juices and honey. Its main role in the body is as an energy source, where it is used in much the same way as glucose. Figure 10.7.3 shows some fruits with high fructose contents.

Galactose is not found free in nature. However, it occurs as a component of larger carbohydrates like lactose, the main sugar found in milk.

Glucose, fructose and galactose are structural isomers. They have the same molecular formula but different molecular structures. The differences in their structures appear slight but they are of great importance to living organisms.



FIGURE 10.7.3 Fructose is the most common sugar in fruit, especially berries.

Carbohydrates in solution

The behaviour of some carbohydrates when they are dissolved in water can be quite complex. For example, monosaccharides can exist as isomers in equilibrium. Glucose isomers are shown in Figure 10.7.4.

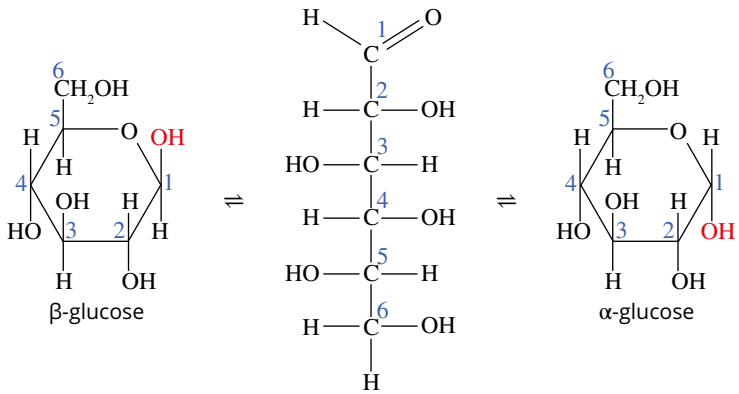


FIGURE 10.7.4 Glucose exists in solution in equilibrium between three isomers. Note the aldehyde in the straight-chain form.

The existence of these three isomers of glucose in solution allows scientists to understand why two different forms of glucose can be found in many organisms. Figure 10.7.4 shows that β-glucose can be converted to α-glucose, and vice versa, via the straight-chain form.

When the straight chain closes to make a ring, the –OH group bonded to carbon number 1 (C1) can be above the ring or below the ring. At equilibrium, the majority (approximately 99%) of glucose in solution is in cyclic form, with the ratio of α-glucose to β-glucose at room temperature about 36:64.

WS 4.1.8

In their straight-chain form, monosaccharides are classified as either **aldoses** or **ketoses** depending on their carbonyl group. The straight-chain form of glucose has an aldehyde functional group on C1 so it is classified as an aldose. The straight-chain form of fructose has a ketone functional group so it is classified as a ketose (Figure 10.7.5).

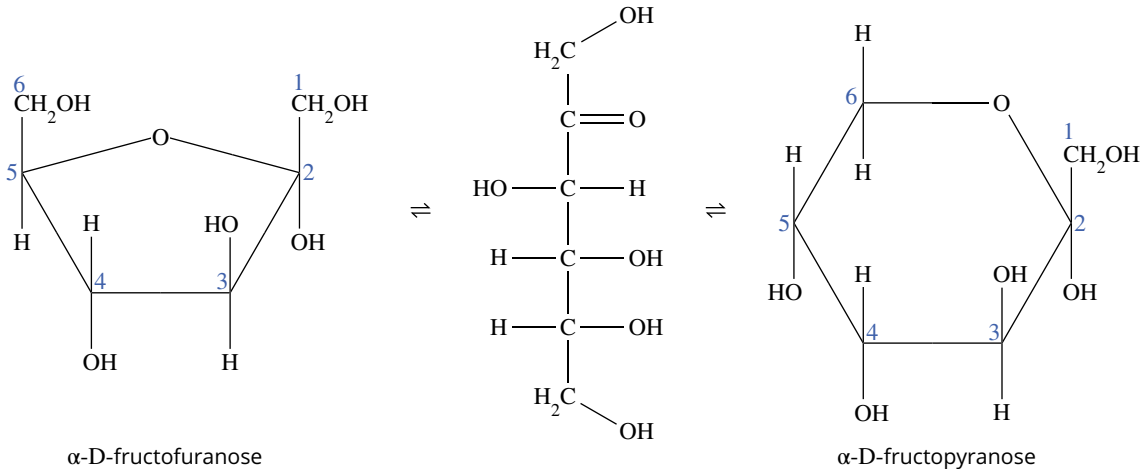


FIGURE 10.7.5 Fructose exists in solution in equilibrium between a number of isomers, three of which are shown here. Note the ketone in the straight-chain form.

DISACCHARIDES AND POLYSACCHARIDES

Two monosaccharides can join to form **disaccharides** or multiple monosaccharides can link with each other to produce a polymer, a **polysaccharide**.

Disaccharides

Disaccharides are carbohydrates formed from the reaction between two monosaccharide molecules. A condensation reaction occurs between the hydroxyl functional groups on neighbouring molecules and a water molecule is formed as a by-product.

The two monosaccharides are joined by an oxygen atom. The connection between the monosaccharide units is called an **ether bond** (or **glycosidic bond** in carbohydrates). Figure 10.7.6 shows the formation of two important disaccharides, maltose and sucrose.

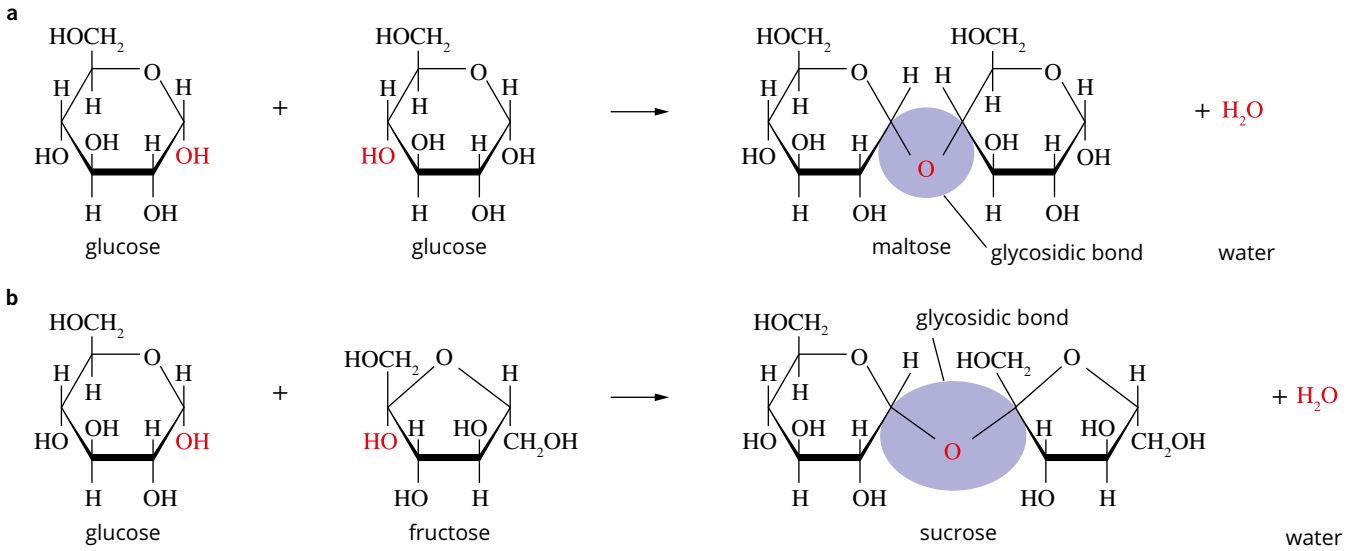


FIGURE 10.7.6 (a) The condensation of two glucose molecules forms maltose. (b) The condensation of glucose and fructose molecules forms sucrose. The glycosidic bonds are highlighted.

Maltose is added to foods as a sweetener and is used in the brewing industry as a raw material for fermentation into beer.

Sucrose is commonly referred to as table sugar. It is the most popular sweetener among the simple sugars. Sucrose is found in high concentrations in crops such as sugar beet and sugar cane, as shown in Figure 10.7.7.





FIGURE 10.7.7 (a) Germinating barley seeds are a source of maltose. (b) The juice of sugar cane has a high sucrose content.

Sweetness

Monosaccharides and disaccharides are often referred to as sugars because of their sweet taste. It is this sweetness that is often blamed for the dietary issues of many Australians. The lure of a sweet taste can lead people to eat more food than they require. The excess foods consumed are converted to fats, which are stored in the body.

Similar to the requirement that the shape of a substrate molecule match the shape of the active site in an enzyme (Module 10.4) for the substrate to react, the sweetness of some substances is thought to be due to the shape of their molecules matching the shapes of the molecules that form the surface of our taste buds. To taste sweet, molecules seem to need three sites that can form bonds with taste buds on the surface of the tongue. Provided the bonds are of the correct type and the three sites are certain distances apart, your brain recognises a substance as tasting sweet.

Two of these bonds to the taste buds are hydrogen bonds, and the third is formed with a non-polar site. The so-called 'triangle of sweetness' needed in the molecule is shown in Figure 10.7.8. Some molecules have many such triangles that can 'lock on to' the taste buds for long periods. Substances that are several thousand times sweeter than glucose exist. Table sugar (sucrose) is twice as sweet as glucose.

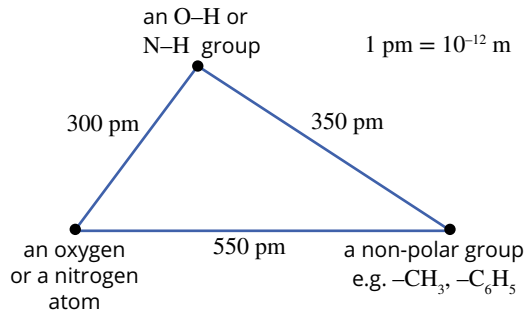


FIGURE 10.7.8 It is thought that this 'triangle of sweetness' must be present in a molecule for it to taste sweet.

Monosaccharides and disaccharides are not the only substances to have the required shape needed to impart a sweet taste to foods. Artificial sweeteners such as cyclamates, sugar alcohols and aspartame are available to the food industry. These products are significantly sweeter than sugars.

Concerns about the intake of sugars by humans have seen an increase in the use of artificial sweeteners. Table 10.7.1 compares the energy released when these substances are metabolised in 'diet' versions of a popular soft drink compared with the regular version.

TABLE 10.7.1 Comparisons of the energy content of Coke® and its 'diet' versions

Product	Main ingredients	Energy (kJ/100 mL)
diet Coke®	carbonated water, caramel, aspartame, phosphoric acid, potassium benzoate, caffeine	1.5
coke Zero®	carbonated water, caramel, aspartame, phosphoric acid, potassium benzoate, caffeine	1.4
coke®	carbonated water, cane sugar, caramel, food acid, phosphoric acid, caffeine	180

When two monosaccharides react, a disaccharide is formed. This is another example of a condensation reaction because a small molecule, such as water, is produced as a by-product. The bond formed between the two monosaccharides is called either an ether or a glycosidic bond.

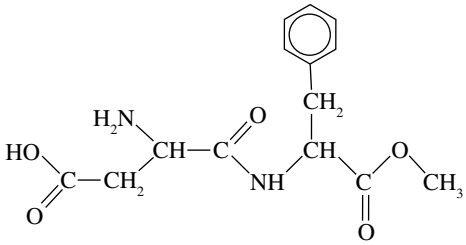


FIGURE 10.7.9 Aspartame, also known as food additive 951, is used as an artificial sweetener in diet soft drinks and as sugar-substitute tablets. It has different functional groups and a different structure from carbohydrates.

The use of artificial sweeteners has proved a popular way of reducing the amount of sugar added to foods. One of the most common sweeteners is aspartame, which is sold under the trade names NutraSweet® and Equal®. Although the metabolism of similar masses of aspartame and sucrose release about the same amount of energy (about $17\,kJ\,g^{-1}$), aspartame can be used in much smaller quantities than sugar because it is nearly 200 times sweeter (Figure 10.7.9). Neotame, another artificial sweetener, is over 50 times sweeter than aspartame!

Sweetness is commonly measured through comparison with sucrose. Sucrose is assigned an arbitrary value of 1 for sweetness. Table 10.7.2 lists other common sugars and sweeteners for comparison.

Table 10.7.2 shows that, despite the similar structures of sugars, their sweetness varies. Lactose has about one-sixth the sweetness of sucrose. Presumably the bonds in sucrose match the triangle of sweetness better than those of lactose. The table also shows why smaller proportions of artificial sweeteners are needed in processed foods to achieve the same sweetness as sugars.

TABLE 10.7.2 Comparison of common sugars and their sources

Sweetener	Sweetness value	Source
lactose	0.16	milk, sugar
galactose	0.32	component of lactose
glucose	0.74	formed in photosynthesis
sucrose	1.00	table sugar
fructose	1.74	fruit sugar
cyclamate	30	artificial sweetener
aspartame	100–150	artificial sweetener
saccharin	450	artificial sweetener
neotame	7000–13 000	artificial sweetener

POLYSACCHARIDES

A condensation reaction between monosaccharides does not necessarily stop with the formation of a disaccharide. Reactions with other monosaccharides can continue to produce a polymer, a polysaccharide. A polysaccharide can contain thousands of glucose units.

Polysaccharides are generally insoluble in water and have no taste. The three most important biological polysaccharides are starch, cellulose and glycogen. Simplified models of these polysaccharides can be seen in Figure 10.7.10.

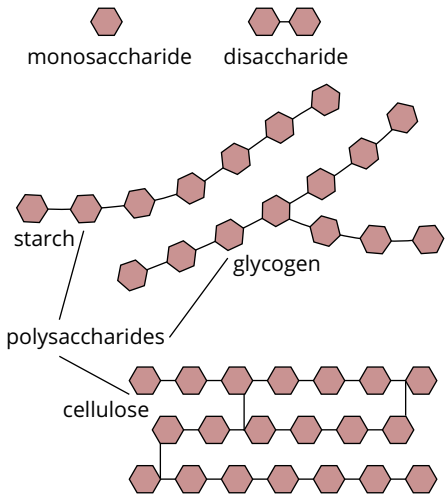


FIGURE 10.7.10 Representations of different carbohydrate molecules

The properties of starch, cellulose and glycogen are very different from each other, yet they are all polymers of the same monomer—glucose. How can three different substances be formed from the one monomer? The answer to this is found from a closer inspection of the structure of glucose. There are two forms of glucose. These are α-glucose and β-glucose, as shown in Figure 10.7.4 on page 403. The orientation of the hydroxyl groups is different in the two forms.

Starch

Plants are able to produce and polymerise α-glucose molecules to form starch. Polymerisation is a condensation reaction, forming glycosidic bonds between each glucose molecule. This also produces many water molecules as a by-product. Plants store starch so that it can later be **metabolised** to produce energy. When energy is needed, the plant can break down the starch back into glucose and react the glucose with oxygen to produce energy to maintain its functions. This reaction is respiration and can be summarised by the equation:

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

Foods such as potato and sago have a high starch content. If the starch forms a linear polymer, it is known as **amylose** (Figure 10.7.11).

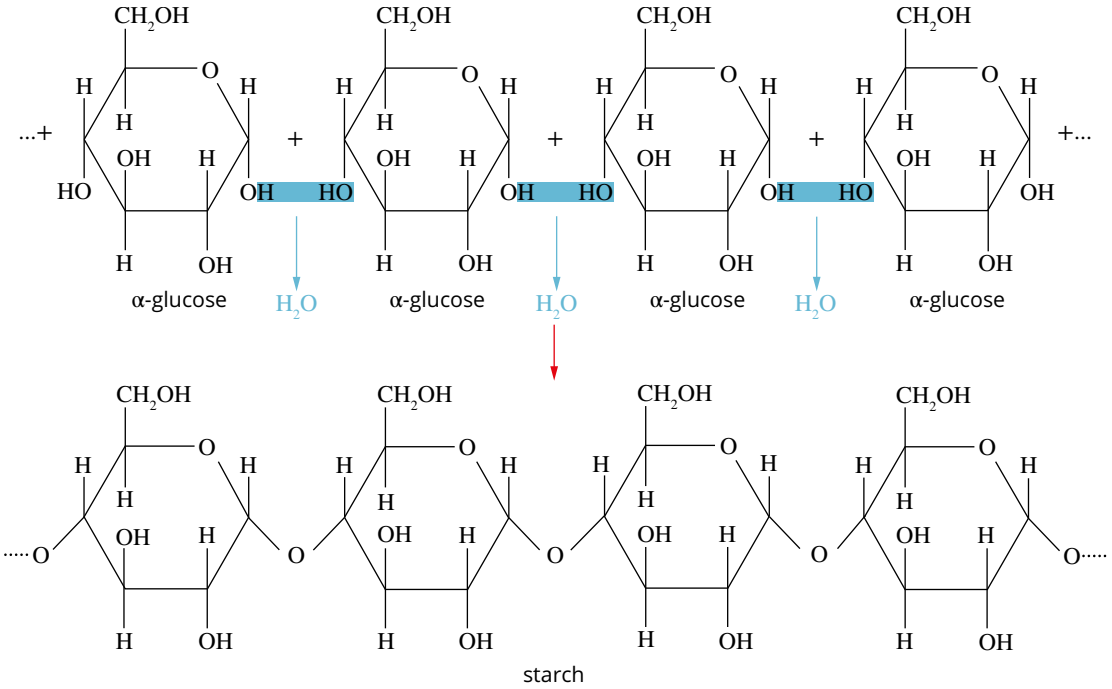


FIGURE 10.7.11 The condensation polymerisation of α-glucose to produce amylose, which is a form of starch

A second form of starch, known as **amylopectin**, can form if some of the α-glucose molecules undergo condensation reactions between hydroxyl groups at different positions around the glucose rings. In this way, occasional branches occur in the structure. Figure 10.7.12 shows that the branches along the polysaccharide chains occur after about 20–24 glucose units.

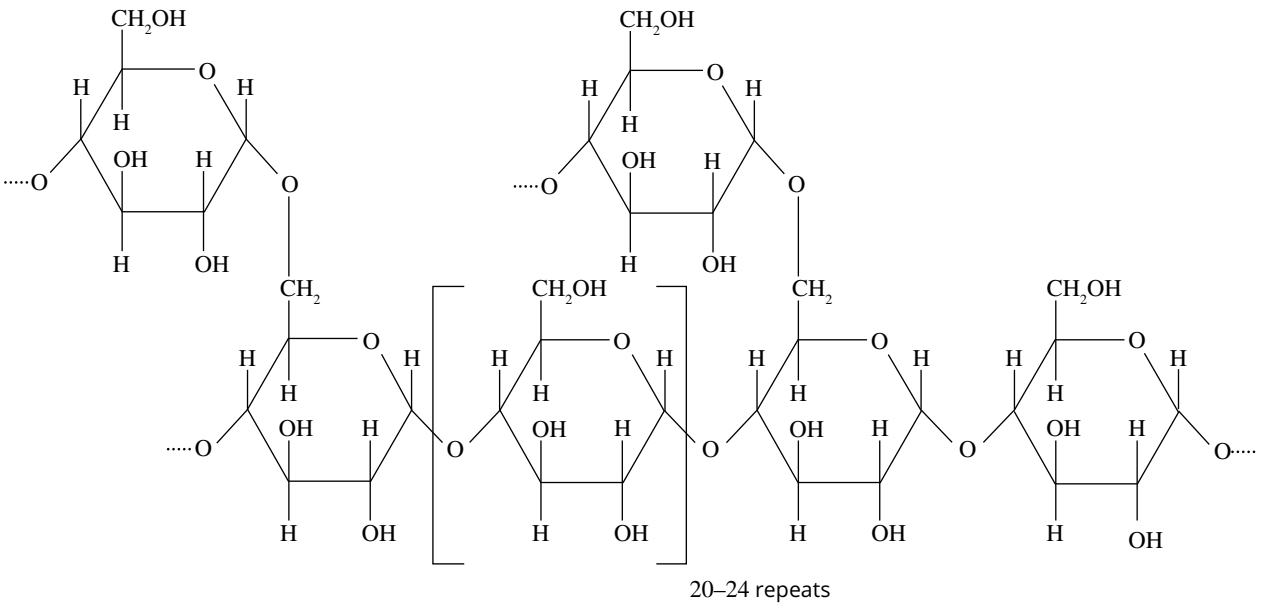


FIGURE 10.7.12 Amylopectin is a form of starch that has occasional branches along the glucose chains.

Amylose and amylopectin have different solubilities in water. The long molecules of amylose coil into spiral-like helices and pack together tightly, with many –OH groups inside the helices and away from contact with water. Therefore, amylose is largely insoluble in cold water. However, in the case of amylopectin, the branching of its molecules restricts the coiling of the polymer, leaving many more –OH groups exposed so that it dissolves in water.

Cellulose

Cellulose is the main structural material in plants. It is the most abundant molecule in living tissue and is found in the walls of plant cells. Cotton is almost pure cellulose, while wood is around 50% cellulose. Wood also contains other polysaccharides and a significant percentage of lignin, another type of complex organic polymer.

Cellulose is a very large, straight-chain polymer formed from the polymerisation of β-glucose. The chain of glucose molecules in cellulose looks similar to that of starch. However, as Figure 10.7.13 shows, there is a different arrangement of the glucose units.

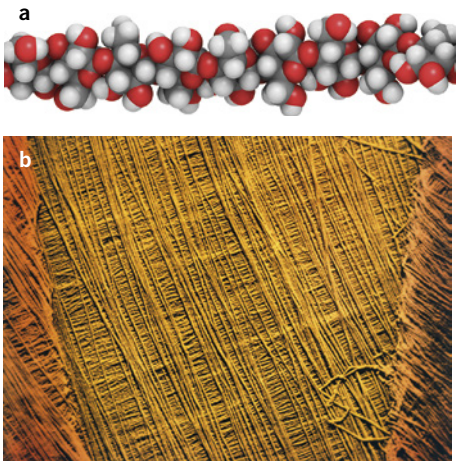


FIGURE 10.7.14 (a) This model shows the linear nature of a cellulose molecule. The oxygen atoms in the hydroxyl groups are coloured red. (b) A scanning electron microscope image shows the cellulose fibres in the walls of algae cells.

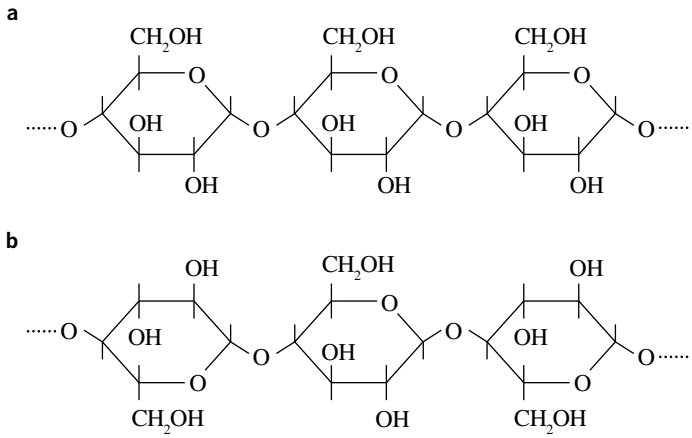


FIGURE 10.7.13 Sections of (a) starch and (b) cellulose polymers. Note the different orientations of the $-CH_2OH$ groups on adjacent glucose monomers.

The alternating nature of the $-CH_2OH$ group in cellulose allows for good alignment of hydroxyl groups between neighbouring cellulose molecules. The result is hydrogen bonding between the molecules, resulting in a strong material that gives the plant support and rigidity. The linear nature of cellulose fibres is shown in Figure 10.7.14.

Glycogen

The third polysaccharide formed from polymerisation of glucose is **glycogen**. Glycogen is a polymer of α-glucose but is highly branched in a similar fashion to amylopectin, as shown in Figure 10.7.15.

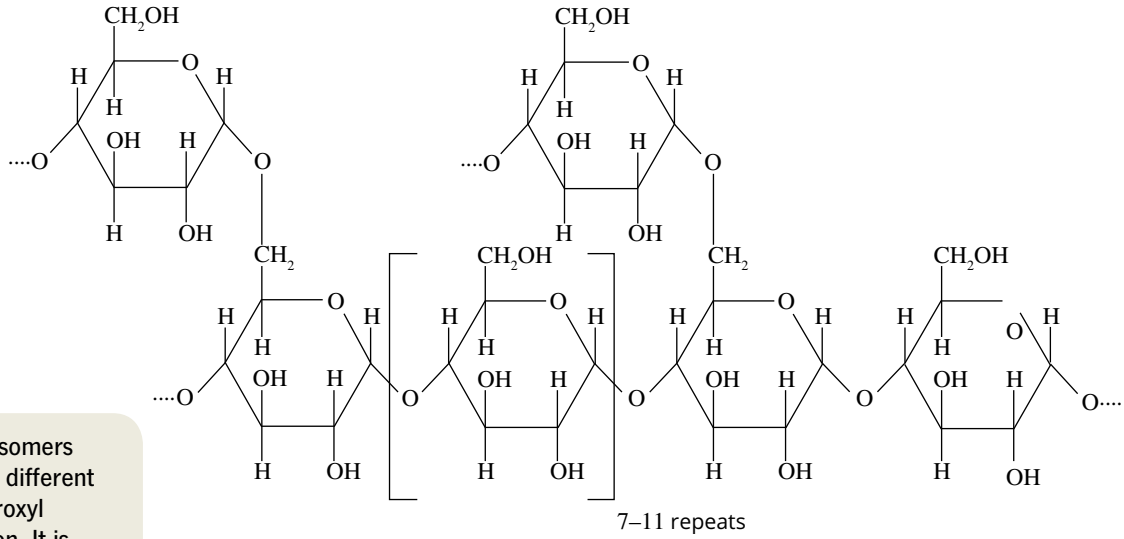


FIGURE 10.7.15 Glycogen is a highly branched polymer of α-glucose.

Animals store glycogen that will metabolise to provide energy when glucose levels are low. Glycogen is formed from excess glucose and stored in the liver or muscle tissue. If energy is needed, the glycogen can be broken down to glucose, which can then be used in cellular respiration.

i Glucose can form two isomers (α- and β-glucose) with different orientations of the hydroxyl group on the first carbon. It is because of these two forms that three of the most important polysaccharides found in living organisms exist—starch, cellulose and glycogen.

10.7 Review

SUMMARY

- Carbohydrates are made from the elements carbon, hydrogen and oxygen and usually have the formula $C_x(H_2O)_y$, where x and y are whole numbers.
- The main role of carbohydrates is as a source of energy for living things. Energy from the Sun is transformed to chemical potential energy in carbohydrates.
- The smallest carbohydrates are monosaccharides.
- Glucose is an important monosaccharide. It is synthesised in plants through the process of photosynthesis.
- Monosaccharides are highly soluble in water as they contain several polar hydroxyl groups, allowing them to form hydrogen bonds with water molecules.
- Disaccharides are formed from condensation reactions between two monosaccharide molecules. The bonds formed between monosaccharides are known as ether or glycosidic bonds.
- Monosaccharides and disaccharides are often referred to as sugars because of their sweet taste.
- Glucose can undergo condensation reactions to form a range of important polymers known as polysaccharides. The polysaccharides have different properties owing to the different orientations of the hydroxyl groups on the glucose units and the extent of branching in the polymer chain.
- Cellulose is a structural material in plants, starch is stored in plants and glycogen is stored in animals for later metabolism into energy.
- Important carbohydrates are listed in Table 10.7.3.

TABLE 10.7.3 Composition and source of important carbohydrates

Carbohydrate		Composition	Source
monosaccharides	glucose	$C_6H_{12}O_6$	fruit juices
	fructose	$C_6H_{12}O_6$	fruit juices, honey
	galactose	$C_6H_{12}O_6$	not found naturally in its free form
disaccharides	maltose	formed from glucose + glucose	germinating grain
	sucrose	formed from glucose + fructose	sugar cane, sugar beet
	lactose	formed from glucose + galactose	milk
polysaccharides	glycogen	polymer of α-glucose	stored in animals in the liver and muscles to be metabolised for energy
	starch	polymer of α-glucose	stored in plants to be metabolised for energy—abundant in wheat, corn, potatoes etc.
	cellulose	polymer of β-glucose	plant fibre—in plant cell walls

KEY QUESTIONS

Retrieval

1 Select the correct statements about starch. (Hint: there may be more than one answer.)

A Starch is a disaccharide.
B Starch is a polymer of sucrose.
C There are two common forms of starch.
D Starch is an energy storage molecule in plants.
E Starch is composed of relatively large molecules.
F Many glycosidic bonds are formed when glucose reacts to form starch.
G All forms of starch are highly soluble in water owing to the large number of hydroxyl groups.

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10.7 Review *continued*

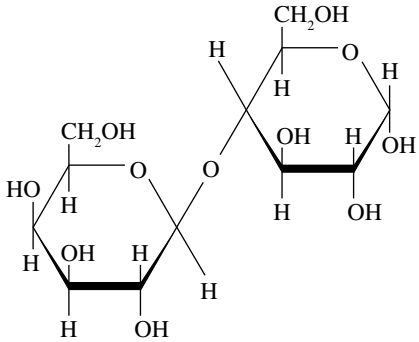
2 Name the carbohydrate that is:
- **a** a structural material in plants
- **b** stored in animals so that it can later be metabolised to provide energy
- **c** stored in plants so that it can later be metabolised to provide energy
- **d** a disaccharide found in milk.

Comprehension

3 Glucose is the most abundant monosaccharide. Draw a structural formula for glucose and use it to explain why it is highly soluble in water.

4 Glucose is described as a monosaccharide, maltose as a disaccharide and glycogen as a polysaccharide.
- **a** Explain the difference between these three types of carbohydrates.
- **b** Determine the type of reaction involved in converting glucose to maltose and then to glycogen.
- **c** Determine the functional group in the molecule involved in these reactions.

5 The structure of lactose is shown below. Lactose undergoes hydrolysis during digestion.



- **a** Explain the term ‘hydrolysis’.
- **b** Show a hydroxyl group and a glycosidic bond in the molecule.

6 Explain the difference between α-glucose and β-glucose.

7 Partial hydrolysis of cellulose produces the disaccharide cellobiose. Draw the structure for this disaccharide. Refer to Figure 10.7.13b on page 408 to assist you.

Analysis

8 Glucose has the molecular formula $C_6H_{12}O_6$ and is classified as an aldohexose. Fructose has the molecular formula $C_6H_{12}O_6$ and is classified as a ketohexose. Xylose is a monosaccharide classified as an aldopentose.
- **a** Determine the molecular formula for xylose.
- **b** Draw a straight-chain formula for xylose.

Chapter review

10

KEY TERMS

2-amino acid
α-helix
active site
aldose
amino acid
amylopectin
amylose
β-pleated sheet
base hydrolysis
C-terminal
carbohydrate
cellulose
chiral carbon
cis-arrangement
complementary proteins
dipeptide
dipolar ion
disaccharide
disulfide bridge
emulsion
enantiomers
endothermic
enzyme–substrate complex
essential amino acid
ester link
ether bond
glucose
glycogen
glycosidic bond
hard water
hydrophilic
hydrophobic
ion–dipole bonding
ketose
lipid
metabolised
micelle
monosaccharide
N-terminal
non-essential fatty acid
omega carbon
omega-3 fatty acid
omega-6 fatty acid
peptide link
polypeptide
polysaccharide
primary structure
protein
protein sequencing
quaternary structure
R group
saponification
secondary structure
side chain
starch
substrate
surfactant
tertiary structure
trans-isomer
tripeptide
zwitterion

KEY QUESTIONS

Retrieval

1 Select the correct statement about amino acids.

A Amino acids contain only the elements C, H, O and N.

B Amino acids may contain more than one nitrogen atom.

C The functional group on an amino acid side chain is always non-polar.

D All 20 amino acids needed by humans are known as essential amino acids.

2 Identify two functional groups that are present in all amino acids.

3 Select the false statement about proteins.

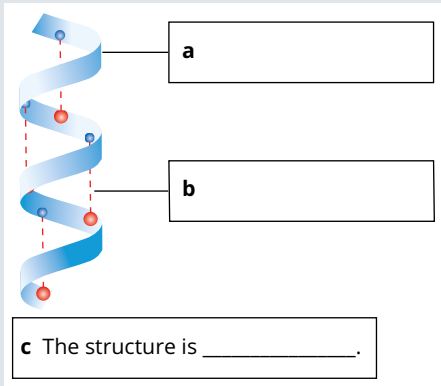
A A peptide bond can be broken by hydrolysis.

B Proteins typically contain more than 50 amino acids.

C Water is released when two amino acids form a peptide bond.

D The C-terminal amino acid in the polypeptide Asn-Cys-Gly-Leu-Phe-Glu is asparagine.

4 Identify the type of bonding represented by labels **a** and **b** in the diagram below. Identify the type of secondary structure in **c**.



5 Describe how β-pleated sheets form in a protein.

6 Some proteins exhibit a quaternary structure. Select the statement that describes this level of structure.

A The sequence (number, order and type) of amino acids in a polypeptide chain.

B An association of two or more polypeptide chains joined by peptide links between the chains.

C An association of two or more polypeptide chains held together by dispersion forces and other bonds.

D A single polypeptide chain twisted into a series of helices by hydrogen bonding between peptide links.

7 The enzyme glucokinase catalyses the first step in the oxidation of sugar in human liver cells, in a process called glycolysis. Select the statement about this process that is correct.
- **A** Glucokinase is a protein.
- **B** Many other enzymes can also catalyse this reaction.
- **C** Glucokinase is able to catalyse many other reactions.
- **D** Glucokinase increases the activation energy of this reaction.

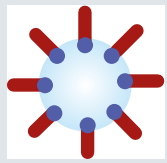
8 Select the molecule that would have the lowest melting point.
- **A** $C_{17}H_{31}COOH$
- **B** $C_{19}H_{39}COOH$
- **C** $CH_3(CH_2)_{16}COOH$
- **D** $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

9 Select the best reason for ensuring that you include omega-3 fatty acids and omega-6 fatty acids in your diet.
- **A** They are oils, rather than solid fats.
- **B** They are needed as an energy source.
- **C** They are the best form of energy storage.
- **D** Some cannot be made in the body.

10 Select the statement that best describes the process of saponification.
- **A** Concentrated acid is heated with a triglyceride.
- **B** Glycerol is reacted with fatty acids in alkaline conditions.
- **C** A concentrated base solution is heated with a triglyceride.
- **D** Fatty acids are precipitated from concentrated base solutions.

11 Select the best explanation for why aspartame is used in diet foods in place of sugar.
- **A** Aspartame molecules absorb energy in the human body.
- **B** Aspartame molecules do not release energy in the human body.
- **C** Aspartame is many times sweeter than sugar so less can be used.
- **D** A given mass of aspartame releases less energy than an equivalent mass of sugar.

12 Select the statement that is best represented by the diagram below.



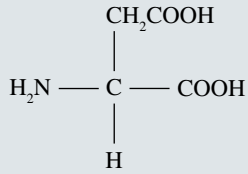
- **A** Soap particles forming a micelle in water.
- **B** Soap particles aligned in a drop of water that is in oil.
- **C** Soap particles aligning in a drop of oil that is in water.
- **D** Soap particles in a drop of oil that has lifted from fabric in a wash.

13 Recall which carbohydrate is sometimes referred to as animal starch and why.

Comprehension

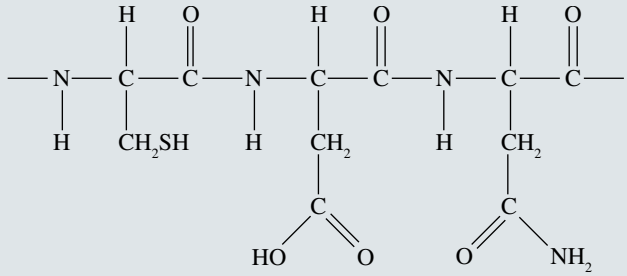
14 Draw the general structure of an amino acid. Label the amino group and the carboxyl group.

15 Aspartic acid is one of the non-essential amino acids shown below. It exists mainly as a zwitterion at pH 2.8.



- **a** Name the:
  - **i** acidic functional group
  - **ii** basic functional group.
- **b** Explain what is meant by the term 'zwitterion'.
- **c** Draw the structure of the molecule as it is most likely to exist in a solution at:
  - **i** pH much greater than 2.8
  - **ii** pH much less than 2.8
  - **iii** pH 2.8.

16 Draw a circle around the parts of the polypeptide segment below that might be involved in forming bonds responsible for the tertiary or quaternary structures of the protein molecule.



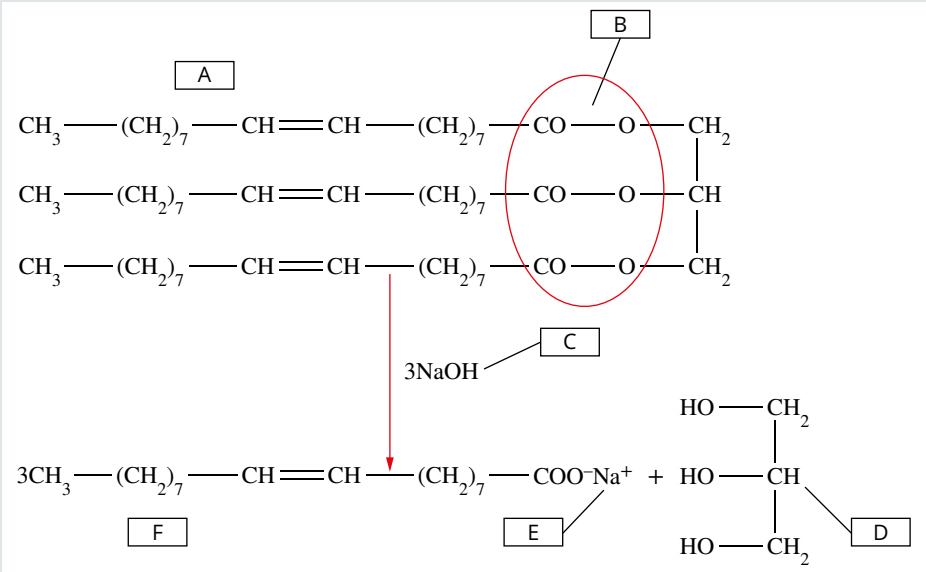
17 Explain what is meant by the primary, secondary and tertiary structures of a protein.

18 Enzyme activity is influenced by changes in pH. Changing pH can alter the charge on some functional groups because they act as weak acids or bases. The R groups of a polypeptide chain are important in maintaining the enzyme's tertiary structure. Complete the following table for each of the R groups listed.

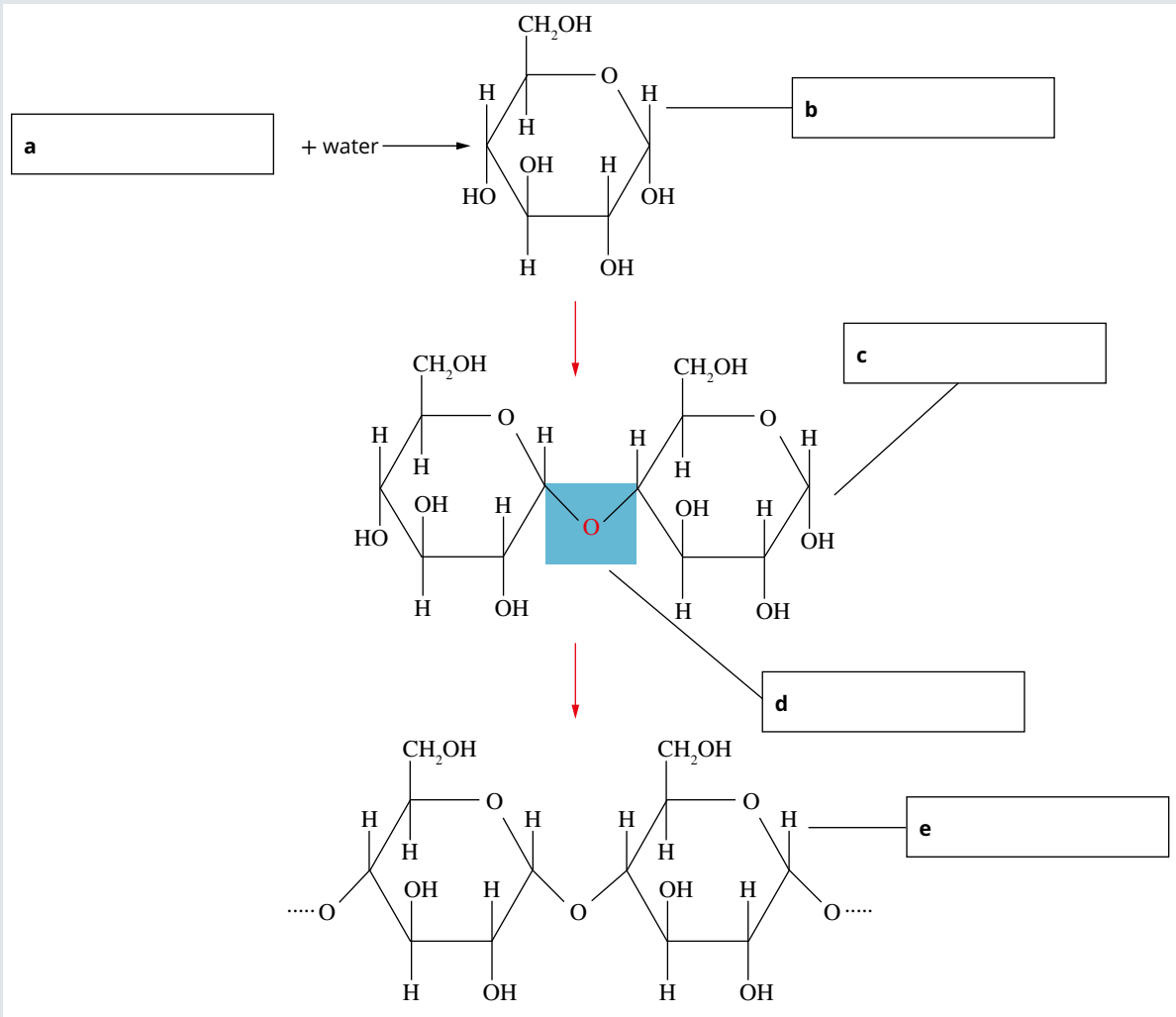
Structure of R group	Is the R group acidic or basic or neither?	Is the R group positively charged, negatively charged or neutral?	
		In a solution of pH 2	In a solution of pH 11
$-CH_2COOH$			
$-CH_2CH(CH_3)_2$			
$-CH_2OH$			
$-(CH_2)_4NH_2$			

19 Explain the difference between an omega-3 fatty acid and an omega-6 fatty acid.

20 Select from the following terms to label the A–F in the following diagram of a saponification reaction.
metal ion, base, ester, glycerol, triglyceride, fatty acid, catalyst



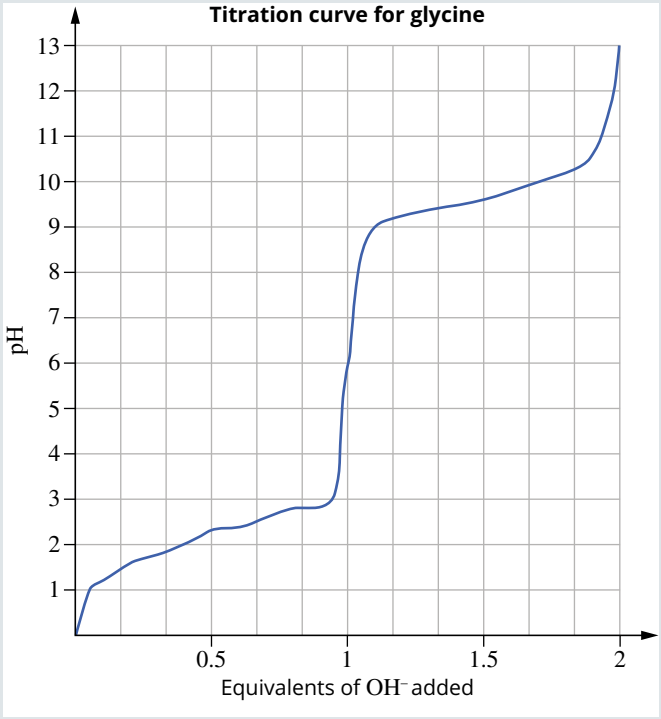
21 Use the following terms to complete labels **a**–**e** in the diagram below, which shows the formation of a polysaccharide.
polysaccharide, disaccharide, carbon dioxide, glycosidic link, glucose



Analysis

22 In its solid state, the amino acid alanine is crystalline and has a melting point of 258°C, while propanoic acid as a solid is waxy and has a melting point of –20°C. Explain the difference in the nature of these two substances as solids and their melting points.

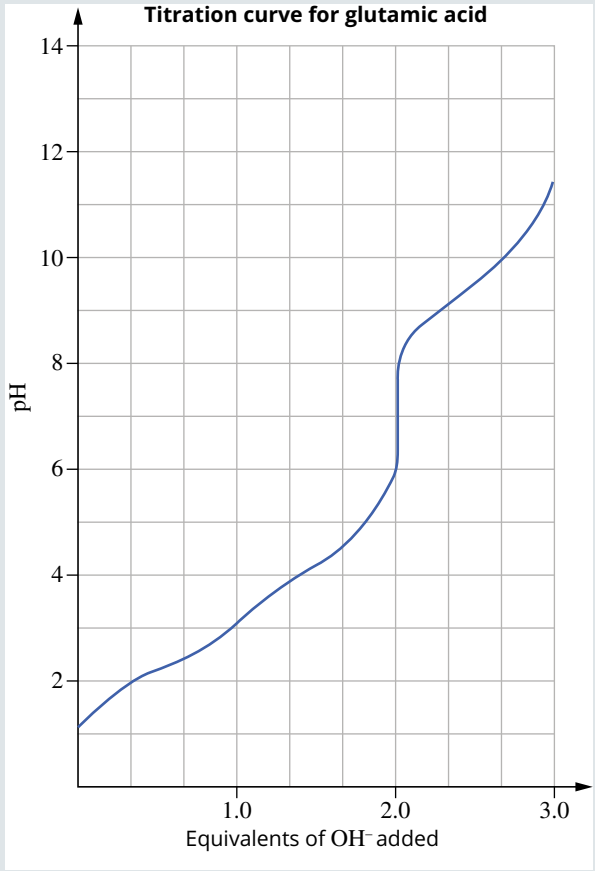
23 When an aqueous solution of glycine (H_2NCH_2COOH) has sodium hydroxide solution added to it, the titration curve shown below is obtained. It shows the pH of the solution against the equivalents of hydroxide ion added to the solution. For example, an equivalents of 0.5 means there is 0.5 the number of moles of OH^- present in the solution compared to the number of moles of glycine.



Draw structures for the forms in which the glycine exists in solution in the following pH ranges, and explain the changes in the species present as the pH increases.

- **a** 1–3
- **b** 3–9
- **c** 9–10.5

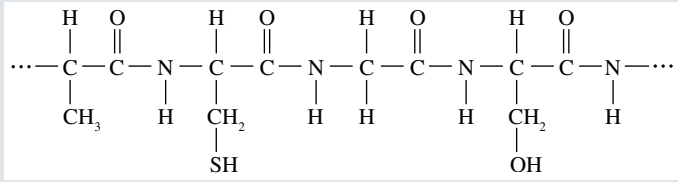
24 The following graph shows the titration curve for glutamic acid. A significant change in pH from approximately 6 to 8 occurs when two equivalents of hydroxide ion have been added to a glutamic acid solution. This contrasts with a significant change in pH from approximately 3 to 9 for addition of one equivalent of hydroxide ion for glycine (refer to the figure in question **23**). With reference to the structures of these amino acids, explain the difference in equivalents of hydroxide ion for a significant pH change. See Table 10.1.1 on page 358 for structures of the amino acids.



25 Draw structural formulas to show the hydrolysis of maltose.

26 When alanine and glycine (see Table 10.1.1 on page 358) react, two different dipeptides can be formed.

- **a** Construct the condensed structural formula of each dipeptide.
- **b** Determine the number of tripeptides that can be formed from three amino acids.
- **c** Proteins are formed using 20 different amino acids and can be hundreds of amino acid units in length. On the basis of your answers to parts **a** and **b**, state a conclusion about the number of different proteins possible.
- **d** Show the peptide links in the section of a protein chain shown below.



- **e** Construct the formulas of the amino acids that make up this section of the chain.

27 If the amino acids alanine and cysteine are mixed together and reacted in a condensation reaction, four dipeptides could form—Ala-Cys, Cys-Ala, Ala-Ala or Cys-Cys. To synthesise a dipeptide with a particular sequence, it is therefore necessary to prevent the amino functional group and the carboxylic acid functional group on appropriate amino acids from reacting. One way of doing this is to convert the carboxylic acid group to an ester and convert the amine to what is called a 'Boc' group. These are described as protecting groups and can be removed after the polypeptide is formed without affecting the peptide bond.

a Identify which ends of the amino acids glycine and phenylalanine (Table 10.1.1 on page 358) would need to be protected to form the dipeptide Phe-Gly.

b Describe the steps that could be used to make the tripeptide Ala-Gly-Phe. It can be broken into seven steps, including the final step of removing protecting groups to give the tripeptide. The first step is to protect the amino group of alanine with Boc.

28 Electrostatic interactions of different types between the side chains on amino acid residues contribute to a protein's tertiary structure. Identify two amino acids that could form the following interactions with each other in a protein chain. You will need to refer to the table of 2-amino acids (Table 10.1.1 on page 358) to complete this question.

a dispersion forces only

b hydrogen bonding

c ionic attraction

29 Keratin is a protein found in the fibres of hair and wool and has a very low solubility in water. Based on its low solubility in water, predict the arrangement of the R groups of the amino acids in keratin when it folds to form the tertiary structure. Explain your prediction.

30 The enzyme carbonic anhydrase catalyses the decomposition of carbonic acid molecules to carbon dioxide and water in the lungs. When heated above 60°C, the enzyme becomes inactive. Deduce why the enzyme loses its activity at 60°C. State what happens to the primary structure of the carbonic anhydrase enzyme when heated.

31 Mutations can cause the wrong amino acid to be inserted into an enzyme, which is a protein chain, when it is being assembled. In some instances such a mistake has no effect on the function of the enzyme but in others it disables it. Determine how a single change in an enzyme's primary structure could cause such dramatically different results.

32 A dessert of jellied pineapple cannot be made by using gelatine and fresh pineapple because an enzyme in the pineapple causes molecules in the gelatine to break down instead of setting. Explore how jellied pineapple might be prepared. Explain your answer.

33 The structure of the fatty acid linoleic acid is:

$$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$$

a Name the chemical needed to react with linoleic acid to form a triglyceride.

b Draw the structure of the triglyceride made from linoleic acid.

c Name and circle the functional groups in the triglyceride molecule.

d Classify the triglyceride as saturated, monounsaturated or polyunsaturated.

e Deduce whether this triglyceride is likely to be a solid or liquid at room temperature. Provide a justification for your deduction.

34 Chocolates typically have a fat content ranging from 20 to 55% depending on the type of chocolate. The chocolate in bars is solid. Deduce why saturated fats are more important than unsaturated fats in the composition of a chocolate bar.

35 Analyse the list of substances below and list all the combinations of substances that can be used to make a soap.

A $CH_3(CH_2)_{16}COOH$

B $CH_2OHCHOHCH_2OH$

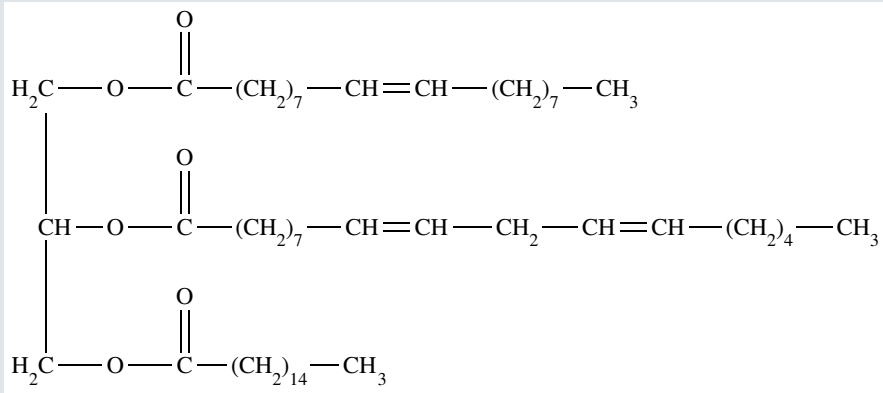
C CH_3OH

D NaOH

E $CH_3(CH_2)_4CHCHCH_2CHCH(CH_2)_7COO^-Na^+$

F KOH

G (figure below)



36 Many oven cleaners include sodium hydroxide as one of their major ingredients. Explain how the sodium hydroxide can contribute to the cleaning action of an oven cleaner.

37 The human brain relies almost exclusively on glucose as an energy source. Normal functioning of the brain depends on a constant supply of glucose from the blood. Explain how your body maintains a fairly constant concentration of glucose in the blood even though you do not eat foods that supply glucose constantly throughout the day.

38 **a** Contrast condensation reactions and hydrolysis reactions.

b Explain the importance of these reaction types in the human body.

c Construct equations for condensation reactions between:

i two glucose molecules

ii a glycerol molecule and three palmitic acid molecules

iii two alanine molecules.

39 Bread making involves interactions between carbohydrates, enzymes and proteins. Cereal flours contain the enzymes α-amylase and β-amylase, which will break down the starches in flour. α-amylase will break down the amylopectin into glucose, maltose and smaller chain polysaccharides called dextrins. β-amylase breaks down the amylose and dextrins to maltose.

Proteins from flour have an important role in helping the bread to rise. When flour is mixed with water the proteins glutenin and gliadin absorb water and form bonds with each other to form an elastic matrix called gluten. This elastic matrix traps gases, which helps the bread rise.

a Name the type of bond that links the monosaccharides in the polysaccharides and disaccharides, and name the reaction type responsible for their breakdown.

b Use structural formulas to construct equations to show the changes that occur to the starch in flour during bread making.

c Name the type of bonds and attractive forces that can link the proteins glutenin and gliadin to each other.

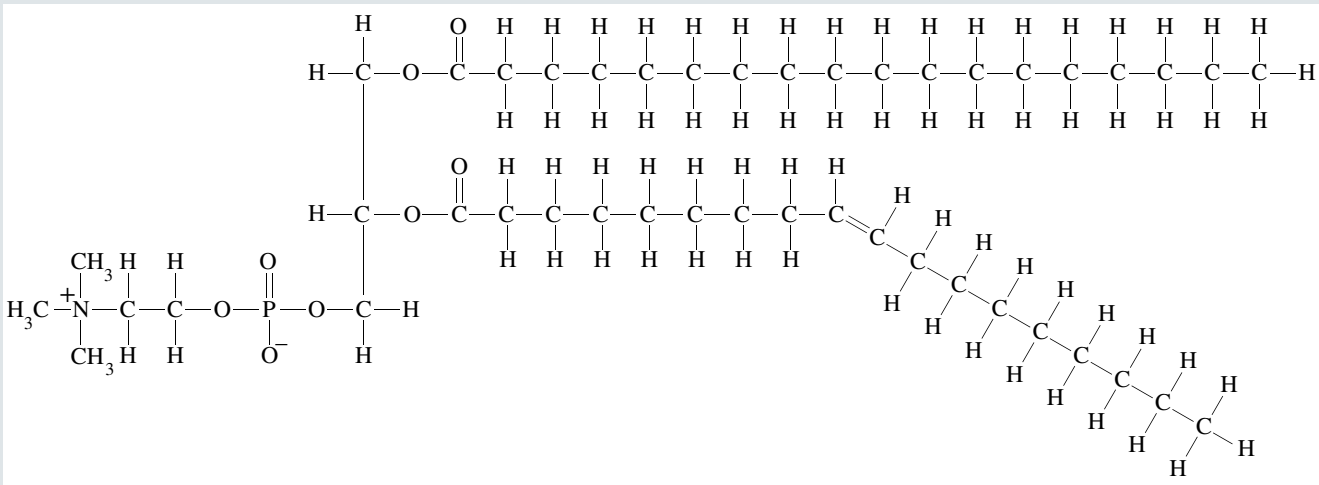
d Name the type of attractive force that allows the glutenin and gliadin to absorb water.

Knowledge utilisation

40 Glycogen is a polysaccharide made of linked α-glucose molecules and cellulose is a polysaccharide made of linked β-glucose molecules. Humans can digest glycogen but have very little ability to digest cellulose. Propose reasons for the difference in digestion of these polysaccharides.

41 Seeds usually have oils in them. The function of these oils is to provide energy for the seed's germination and early growth. These oils need to be liquid to be available when germination occurs. Predict what you would expect to observe in the ratio of saturated, monounsaturated and polyunsaturated fats in seeds from plants going from the equator towards the polar regions. Explain the reason for your prediction.

42 Phospholipids are a class of lipids with the structure shown below. Compare their structure to that of a triglyceride. Predict the way in which phospholipid molecules behave in water. Justify your prediction.



CHAPTER

11 Analysis of organic compounds



In Units 1 and 2, you were introduced to instrumental methods of chemical analysis such as chromatography, mass spectrometry and atomic absorption spectroscopy. These methods are based on the chemical and physical properties of substances, and help analytical chemists to determine how much of a substance is present in a sample.

The properties of substances can also be used to determine their identity. Analytical chemists combine knowledge of the properties of chemicals with instrumental methods to identify and quantify substances. Analytical instruments coupled with computers are extremely accurate and are able to detect and identify very small amounts of complex substances.

In this chapter, you will learn about five instrumental techniques used to identify and determine the structure of organic compounds—chromatography, electrophoresis, mass spectrometry, X-ray crystallography and infrared spectroscopy. You will also analyse data from these techniques to identify an organic compound and determine its structure.

Syllabus subject matter

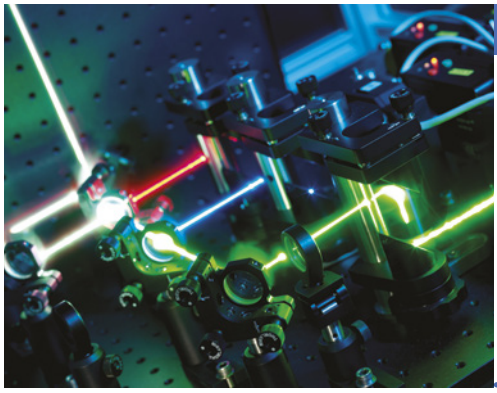
Topic 1 • Properties and structure of organic materials

ANALYTICAL TECHNIQUES

- explain how proteins can be analysed by chromatography and electrophoresis
- select and use data from analytical techniques, including mass spectrometry, X-ray crystallography and infrared spectroscopy, to determine the structure of organic molecules
- analyse data from spectra, including mass spectrometry and infrared spectroscopy, to communicate conceptual understanding, solve problems and make predictions.

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11.1 Chromatography



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- explain how mixtures can be separated by chromatography
- outline the principles of chromatography and how proteins are separated through high-performance liquid chromatography (HPLC)
- explain, using intermolecular forces, the adsorption and desorption of components in a mixture
- quantitatively analyse chromatograms and compare to known standards
- qualitatively analyse chromatograms by calculating the retardation factor of components in a mixture.

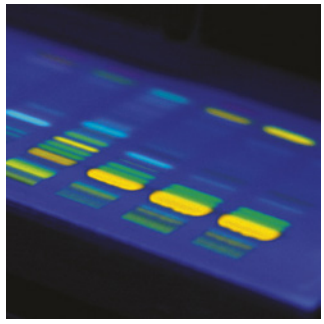


FIGURE 11.1.1 These glowing bands, viewed under fluorescent lighting, are individual chemical components that have been separated from a mixture by a form of thin-layer chromatography. The individual components can then be identified by mass spectrometry.



FIGURE 11.1.2 Paper chromatography can be used to separate mixtures of inks into their separate components.

The term 'adsorption' describes the adhesion of molecules or substances to the surface of a solid or liquid. This is why the stationary phase in chromatography is either a solid or a liquid. The mobile phase is in either a liquid or a gas state.

Chromatography is a widely used technique for separating and analysing complex mixtures of organic compounds. Food, petrochemicals, perfumes and pharmaceuticals are all mixtures that can be separated by chromatography. A feature of chromatography is that it can be performed on very small samples and for low concentrations. When separated, the various components often appear as distinct bands, as seen in Figure 11.1.1.

PRINCIPLES OF CHROMATOGRAPHY

You can perform a simple chromatography experiment by putting spots of ink from felt-tip pens near one end of a strip of filter paper. The filter paper can then be suspended so the end closest to the ink spots is just immersed in water with the water level below the ink spot. This is an example of **paper chromatography**. In the laboratory, paper chromatography is performed with high-quality absorbent paper, similar to filter paper.

The original position of the ink spots on the paper is called the **origin**. The inks are a mixture of different-coloured chemicals. As the water soaks up the paper, the **components** of the inks are carried upwards at different rates and separate into spots of different colours, as seen in Figure 11.1.2.

Each spot contains one of the components that are present in the ink mixture. The pattern of bands or spots is called a **chromatogram**.

All methods of chromatography have a:

- **stationary phase**
- moving or **mobile phase**.

In the simple experiment using inks and paper, the stationary phase is a thin layer of water adsorbed to the paper and the mobile phase is the water that is moving up the filter paper.

As the components in the ink are swept upwards over the stationary phase by the solvent, they undergo a continual process of **adsorption** (onto the stationary phase), followed by **desorption** and dissolving (into the mobile phase). The components of a mixture undergo the processes of adsorption and desorption at different rates, so the components separate as they move over the stationary phase.

The rate of movement of each component mainly depends on:

- how strongly the component adsorbs onto the stationary phase
- how readily the component dissolves in the mobile phase.

In this example the mobile phase was water. Since water is a polar solvent, the more polar components tend to move more quickly than the less polar components. These more soluble components move further up the paper in a given time interval.

Thin-layer chromatography (TLC) is similar to paper chromatography. In TLC, a thin layer of a fine powder, such as alumina (aluminium oxide), is spread on a glass or plastic plate, which acts as the stationary phase.

Qualitative analysis is used to determine the identity of chemicals present in a mixture. Both paper chromatography and TLC are useful for qualitative analysis. They can indicate which chemicals are present in the mixture but cannot give their specific concentration.

Although the components of inks can be seen easily in chromatograms, most compounds are colourless and must be made visible. Many organic compounds fluoresce and appear blue when viewed under ultraviolet light. Another way to make colourless components visible is to spray them with a chemical that reacts to form coloured or fluorescent compounds.

Interpreting chromatograms

The components in a mixture can be identified by including standards of known chemicals on the same chromatogram as the unknown sample or calculating the **retardation factor (R_f)** of the sample (see Skillbuilder below for calculation of R_f).

Suppose you wish to find out whether a lolly contains the sugars fructose and glucose. You could place a sample of the lolly on the same chromatogram as a pure sample of each of fructose and glucose (the 'standards'). If spots from the lolly sample move the same distance from the origin as the spots from the pure samples, then the lolly is likely to contain the sugars, as shown in Figure 11.1.3.

For this method, you need to have an idea of the chemical that might be present in the sample. The sample and standards are 'run' on the same chromatogram because the distances moved from the origin will depend on the solvent used as the mobile phase and the distance moved by the **solvent front**. The further the solvent front is allowed to travel, the further the spots travel.

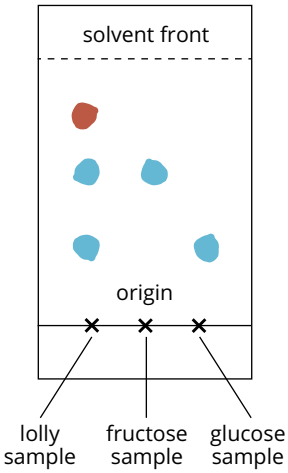


FIGURE 11.1.3 Identification of sugars in a lolly using paper or thin-layer chromatography. The lolly is likely to contain fructose and glucose, as well as a brown-coloured component.

'Solvent front' is the term used to describe the movement of the solvent during chromatography. It is visible as the wet moving edge of the solvent as it travels along the stationary phase.

SKILLBUILDER

Calculating R_f values

The retardation factor (R_f) for a component can be used to identify the components of a mixture by calculating the distance they travel up the stationary phase compared to the distance travelled by the solvent front. This is expressed as a retardation factor (R_f) for a component:

$$R_f = \frac{\text{distance the component travels from the origin}}{\text{distance the solvent front travels from the origin}}$$

The R_f values are always less than one, which means that the component most strongly adsorbed onto the stationary phase moves the shortest distance and has the lowest R_f value.

Each component has a characteristic R_f value for the conditions under which the chromatogram was obtained. By comparing the R_f values of components of a particular mixture with the R_f values of known substances determined under identical conditions, you can identify the components present in a mixture.

This means the R_f values of unknown spots can be compared against a table of R_f values of common materials.

Using Figure 11.1.4, calculate the R_f value of the blue and red component.

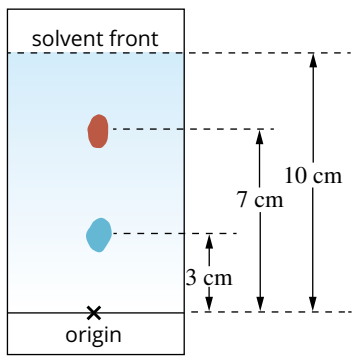


FIGURE 11.1.4 A thin-layer chromatogram of a sample with two components. The distances from the origin enable you to calculate R_f.

Step 1: Record the distance the component has moved from the origin and the distance the solvent front has moved from the origin.

The distance the solvent front has moved from the origin is 10 cm.

The distance the blue component has moved from the origin is 3 cm.

The distance the red component has moved from the origin is 7 cm.

Step 2: Calculate the R_f value of the blue component using the following formula:

$$R_f = \frac{\text{distance the component travels from the origin}}{\text{distance the solvent front travels from the origin}}$$

$$R_f(\text{blue component}) = \frac{3.0}{10}$$
$$= 0.30$$

$$R_f(\text{red component}) = \frac{7.0}{10}$$
$$= 0.70$$

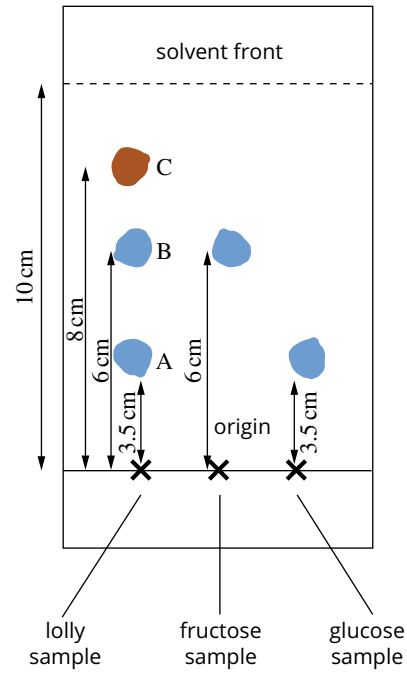
Step 3: Compare R_f values of unknown substances with the R_f values of common materials and identify the components.

Worked example 11.1.1

CALCULATING R_f VALUES

For the R_f value of a component to be comparable to a set of standard R_f values, they must be determined under identical conditions.

Using the following figure, calculate the R_f values of the different components of a lolly. Using qualitative and quantitative data, show that the lolly contains glucose.



Thinking	Working
Record the distance component A has moved from the origin, the distance the glucose sample has moved from the origin, and the distance the solvent front has moved from the origin.	The distance that component A has moved from the origin is 3.5 cm. The distance the glucose sample has moved from the origin is 3.5 cm. The distance the solvent front has moved from the origin is 10 cm.

Calculate the R_f value of the glucose sample and component A using the following formula: $R_f = \frac{\text{distance the component travels from the origin}}{\text{distance the solvent front travels from the origin}}$	$R_f\,(\text{glucose}) = \frac{3.5}{10}$ $= 0.35$ $R_f\,(\text{component A}) = \frac{3.5}{10}$ $= 0.35$
Compare R_f values of unknown substances with the R_f values of common materials and identify the components.	The lolly sample's component A and glucose both increased by the same proportion and the calculated R_f values were the same. Thus the sample does contain glucose.

➤ Try yourself 11.1.1

CALCULATING R_f VALUES

Using the figure in Worked example 11.1.1, calculate the R_f values of the different components of a lolly. Using qualitative and quantitative data, show that the lolly contains fructose.

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

High-performance liquid chromatography (HPLC) is a modern instrumental chromatographic technique based on column chromatography.

In **column chromatography**, the solid stationary phase is packed into a glass column, as shown in Figure 11.1.5. The sample mixture is applied carefully to the top of the packed solid, and a solvent, which acts as the mobile phase, is dripped slowly onto the column from a reservoir above. A tap at the bottom of the column allows the solvent, which is now called the **eluent**, to leave the column at the same rate as it enters it at the other end.

As the components are carried down the column, they are repeatedly adsorbed to the stationary phase and desorbed back into the mobile phase. The components of a mixture undergo the processes of adsorption and desorption to different degrees, so the components separate as they move downwards (Figure 11.1.6).

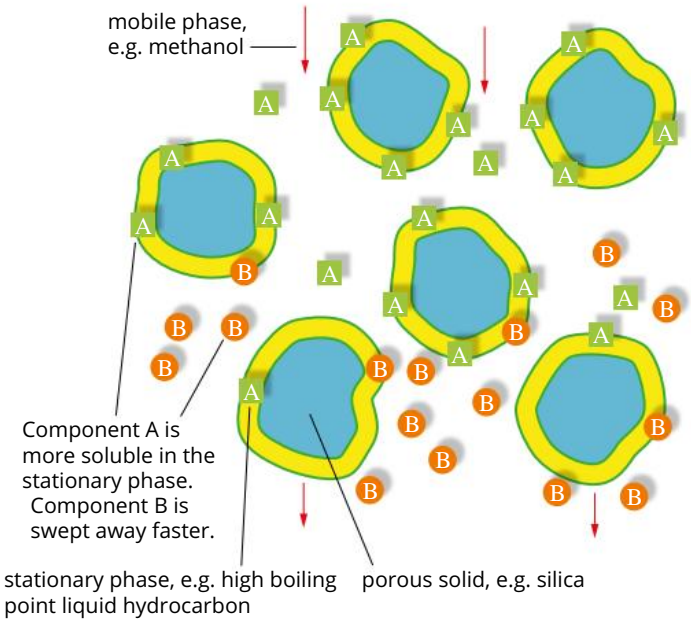
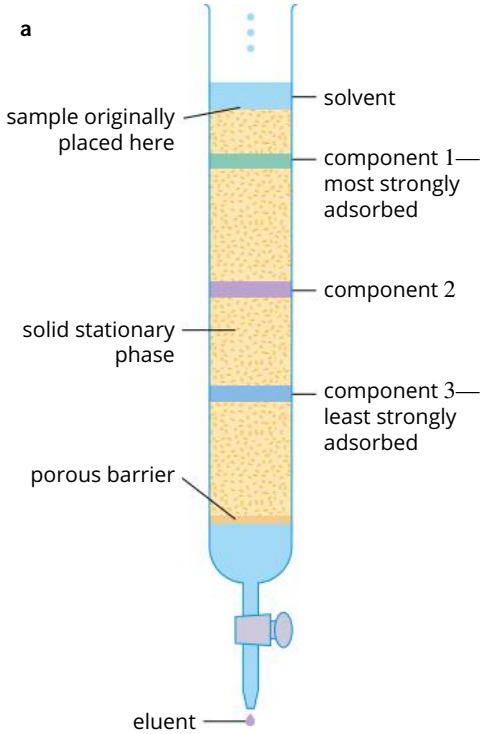


FIGURE 11.1.6 Organic compounds are separated based on different adsorption and desorption rates between the mobile and stationary phases.



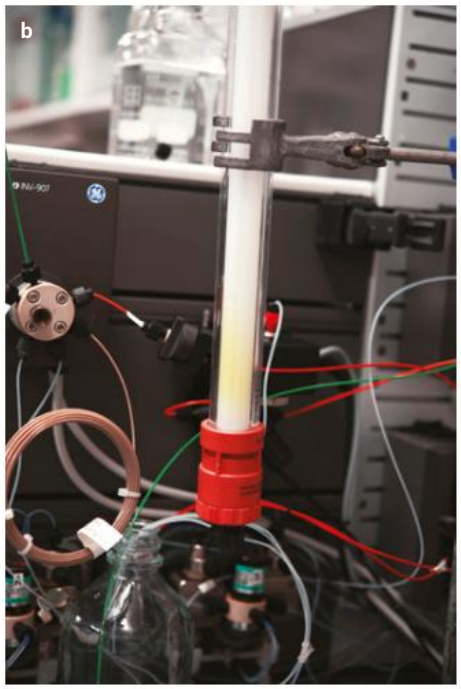


FIGURE 11.1.5 Column chromatography is used to separate the components in a mixture. (a) Diagram illustrating the separation of components in a liquid mixture. (b) Protein (yellow) separation according to similar physical properties. This technique can also be used to purify samples.

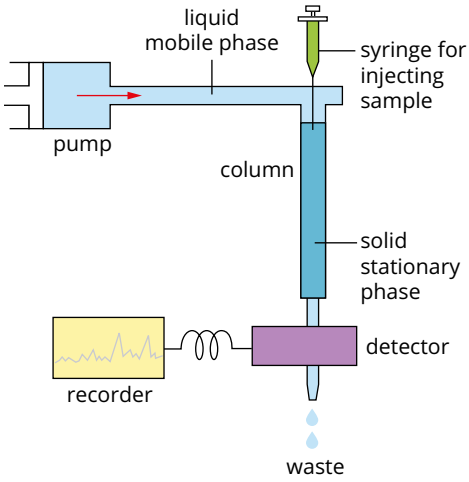


FIGURE 11.1.7 The construction of a high-performance liquid chromatograph

High-performance liquid chromatography (HPLC) is sometimes also referred to as high-pressure liquid chromatography.

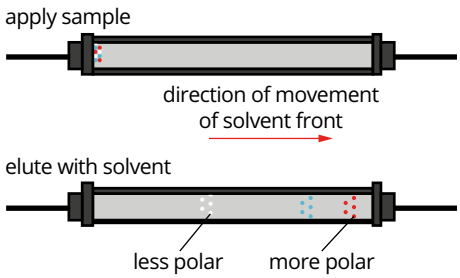


FIGURE 11.1.8 A diagram showing how HPLC can be used to separate and collect different components

A detector is attached to the bottom of the column to measure the response as a function of time, as shown in Figure 11.1.5b. The chromatogram shows the response of the detector against time. The response of the solvent is constant and gives a flat baseline. As components pass through the detector, the response changes and a peak is formed. The sample is injected into the column at time zero. Different chemicals show different strengths of attraction for the stationary phase and the mobile phase, and so pass through the column at different rates.

HPLC allows scientists to perform extremely sensitive analyses of a wide range of mixtures. It is commonly used for the separation and identification of very complex mixtures of similar compounds, such as proteins, drugs in blood and hydrocarbons in oil samples. Compounds in trace concentrations as low as parts per trillion (ppt) may easily be identified.

Figure 11.1.7 shows the apparatus used for HPLC. The basic principles of HPLC are the same as for column chromatography. The main difference between simple column chromatography and HPLC is the particle size of the solids used in the columns. The smaller particles are responsible for a greater surface area, therefore giving much better separation of similar organic compounds like proteins and peptides. The small particle size creates a considerable resistance and therefore the solvent is pumped through the column under high pressure.

A range of solids is available for use in HPLC columns, including alumina (Al_2O_3) and silica (SiO_2). Some solids also have chemicals specially bonded to their surfaces to improve the separation of proteins.

In the most common form of HPLC, called **reversed-phase HPLC**, the stationary phase is silica. The silica used has been modified to make it non-polar by attaching long hydrocarbon chains to its surface. A polar solvent, such as a mixture of water and methanol, is used as the mobile phase.

Polar molecules in the sample form relatively strong hydrogen bonds and dipole–dipole attractions with solvent molecules but are only weakly adsorbed to the non-polar stationary phase. Therefore, polar molecules in the sample spend most of their time moving with the solvent.

On the other hand, non-polar compounds in the sample tend to adsorb to the non-polar stationary phase by dispersion forces. They are also less soluble in the solvent because they cannot form hydrogen bonds with the polar mobile phase. Non-polar compounds spend less time in solution, so they move through the column more slowly than polar molecules.

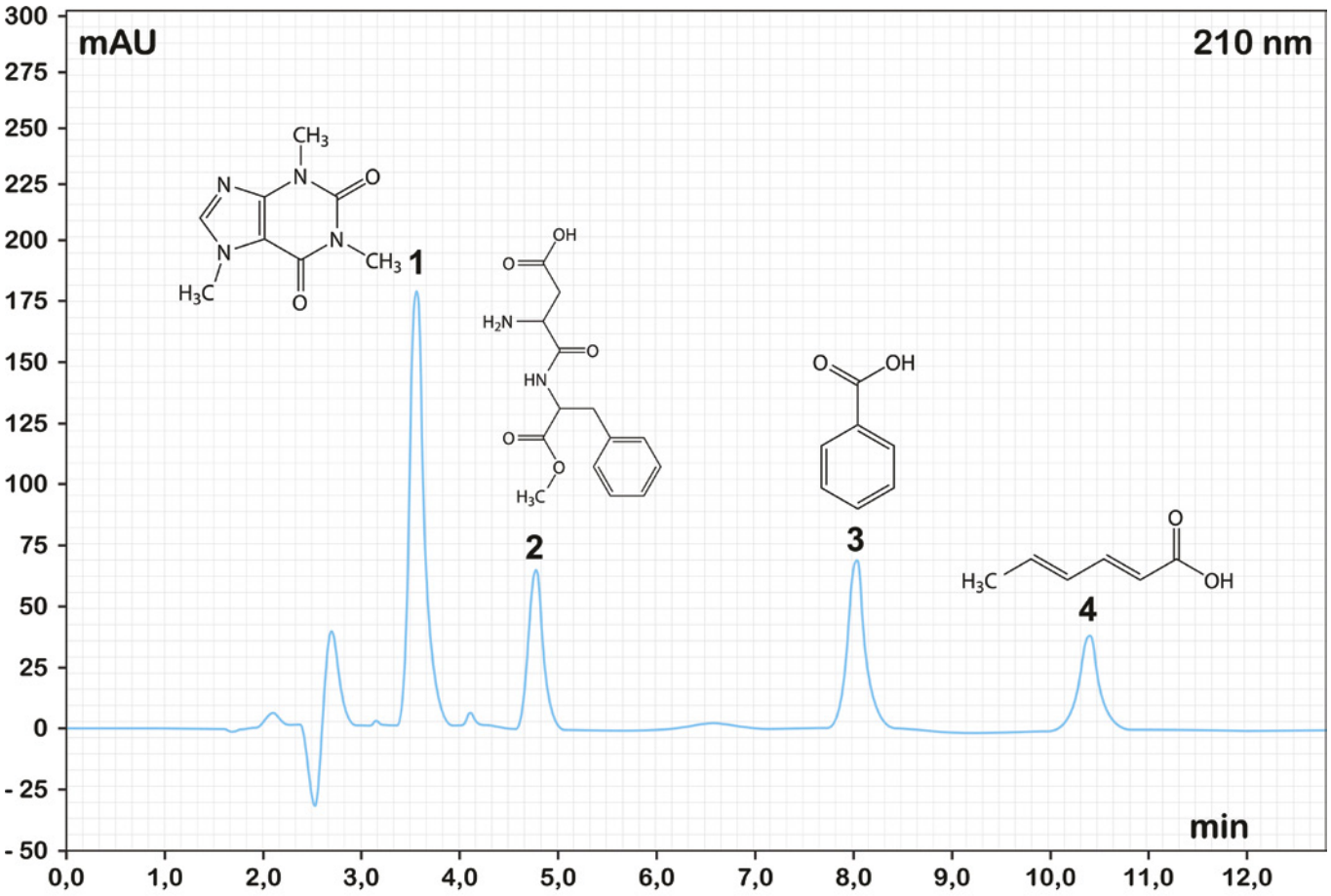
An example of this is the separation of peptides from digested **proteomes** and the purification of protein therapeutic drugs. Proteins can be separated according to their solubility into the mobile phase and ability to adsorb to the stationary phase. The separation of proteins occurs as components elute in order of solubility. The way this separation occurs can be seen in Figure 11.1.8.

In HPLC, the components are usually detected by passing the eluent stream through a beam of ultraviolet (UV) light. Many organic compounds absorb UV light. When an organic compound passes in front of the beam of light, a reduced signal is picked up by a detector. The amount of light received by the detector is converted into an absorbance measurement and recorded on a chart that moves at a constant speed or on a computer. The resulting graph (trace) is called a chromatogram.

The time taken for a component to pass through the column is called the **retention time (R_t)** and this is characteristic of the component for the conditions of the experiment. It is similar to the R_f value in paper chromatography and thin-layer chromatography.

Retention times are used to identify the components associated with the peaks on a chromatogram (qualitative analysis). The relative amounts of each component in a mixture may be determined by comparing the areas under each peak with areas under the peaks for standard samples (quantitative analysis). Quantitative analysis uses peak areas or heights to determine the concentration of a compound in the sample.

In Figure 11.1.9 you can see an example of the component peaks found in an HPLC chromatogram.



No.	Peak name	Ret. time, min	Area, mAU*min	Height, mAU	Amount, mg/L
1	Caffeine	3.560	26.5392	181.783	22.461
2	Aspartame	4.787	10.0363	68.106	51.107
3	Benzoic acid	8.053	15.8525	70.416	5.053
4	Sorbic acid	10.511	9.9644	38.081	5.098

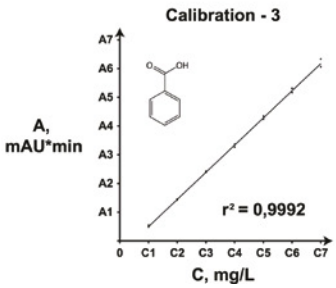


FIGURE 11.1.9 HPLC chromatogram of food additives, with calibration curve to calculate concentration of each component

Paper chromatography and thin-layer chromatography provide qualitative analysis of components in a mixture. That is, the components that make up a mixture can be identified.

HPLC provides qualitative and quantitative analysis of components in a mixture. The size of the peaks is due to the amount of light absorbed by each component, and this can be used to calculate the relative amount (concentration) of each component within the mixture.

Qualitative analysis

In HPLC the same compound gives the same retention time, providing the conditions (temperature, mobile phase, stationary phase, flow rate, pressure etc.) remain the same. Each component forms one peak in the chromatogram.

A chromatogram produced by HPLC of a sample of body fluid can be seen in Figure 11.1.10. The smaller, more polar components are more soluble in the solvent used and are eluted more quickly. Therefore, these components have a lower retention time.

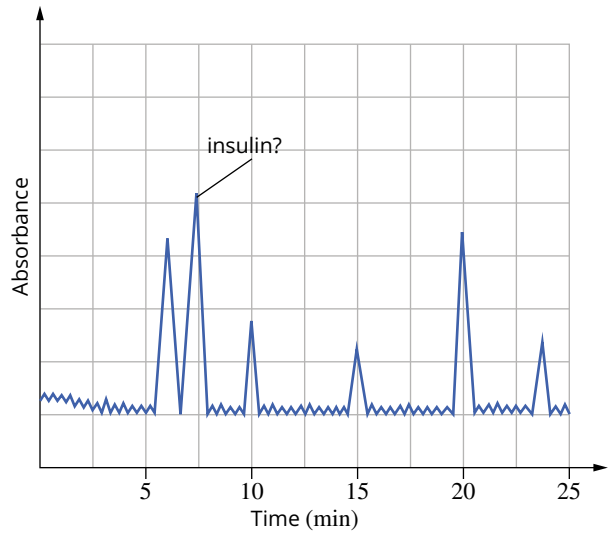


FIGURE 11.1.10 A chromatogram of a body fluid sample

The peaks can be tentatively identified by running a sample containing a known pure compound (such as insulin) under exactly the same conditions as the sample (Figure 11.1.11).

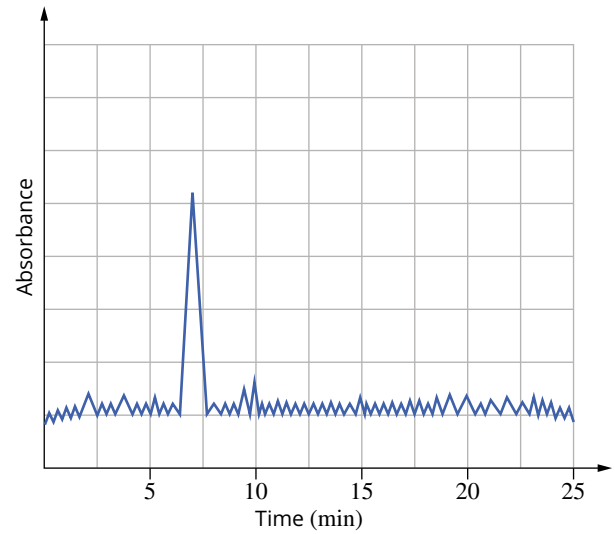


FIGURE 11.1.11 A chromatogram of a reference sample containing insulin

A component can also be tentatively identified by adding a known compound to the sample (**spiking**). Figure 11.1.12 shows the sample spiked with insulin. Insulin was added to the sample and the spiked chromatogram shows the second peak to be larger than it was in the unspiked sample. There are no extra peaks, indicating that insulin is very likely to have been present in the sample.

The larger second peak shows a concentration difference because of the added insulin. This can be used to quantify the amount of insulin in the original sample by spiking with increasing amounts of insulin to create a standard additions calibration curve.

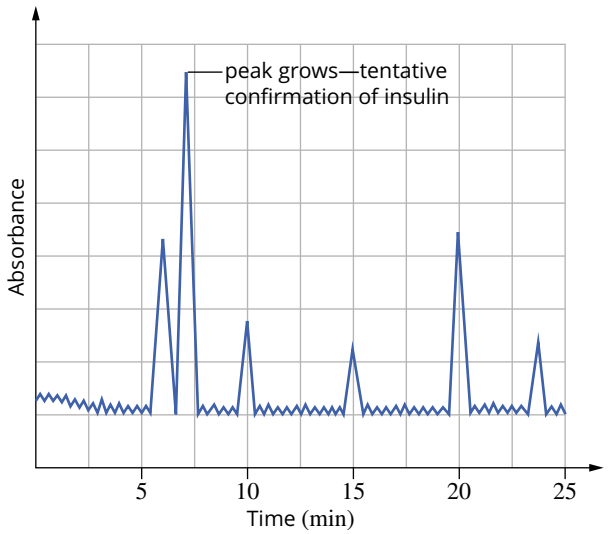


FIGURE 11.1.12 A chromatogram of a body fluid sample spiked with insulin

Quantitative analysis

To determine the concentration of an individual component in a mixture, its peak area is compared with the peak areas of samples of the same chemical at known concentrations. A solution with an accurately known concentration is called a standard solution.

By plotting the peak areas against the concentrations of the standard solutions, you can draw a **calibration curve** and use it to determine unknown concentrations.

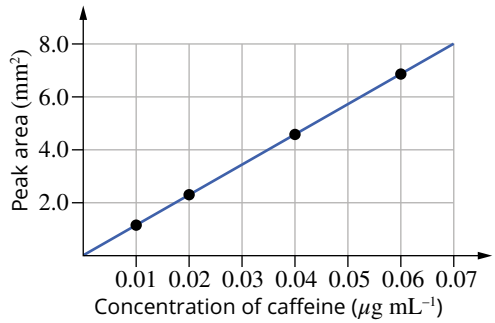
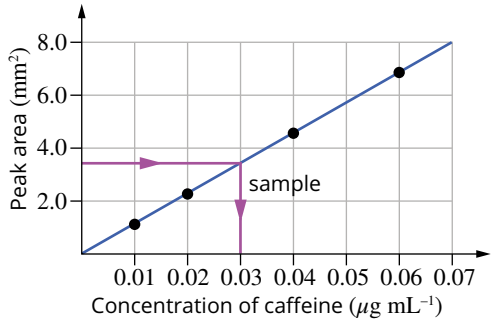
Worked example 11.1.2

CONCENTRATION OF A COMPONENT IN A MIXTURE

The concentration of caffeine in an energy drink was determined by HPLC. Chromatograms of standards with accurately known concentrations of caffeine were also obtained under the same conditions as the sample.

The peak areas of the sample and the standards are shown in the following table. Calculate the concentration of caffeine in the sample.

Caffeine standards ($\mu g\ mL^{-1}$)	Peak area (mm^2)
0.010	1.0
0.020	2.4
0.040	4.6
0.060	7.0
sample	3.6

Thinking	Working
Construct a calibration curve by plotting peak area versus concentration.	
Use the calibration curve to find the concentration corresponding to the peak area of the sample.	A line (purple) can be drawn on the calibration curve from the peak area of the sample to find the corresponding concentration on the graph.  The concentration of caffeine in the energy drink is 0.030 μg mL^{-1}.

➤ Try yourself 11.1.2

CONCENTRATION OF A COMPONENT IN A MIXTURE

Trinitrotoluene (TNT) is often blended with other explosives to suit particular applications. A sample from a solution of an explosive mixture was injected into an HPLC column using a water/methanol mobile phase. The peak corresponding to TNT had an area of 8.8 mm^2. The peak areas for three standard solutions were also measured, as shown in the following table.

Determine the concentration of TNT in the sample solution in μg mL^{-1}.

TNT standards (μg mL^{-1})	Peak area (mm^2)
1.0	2.9
5.0	14.5
2.0	5.8
4.0	11.6
6.0	17.4

Gourmet cooks value olive oil for its distinctive taste and aroma. Nutritionists favour it because it is rich in monounsaturated triglycerides, which are believed to lower blood cholesterol levels and reduce the risk of heart disease. But some of the companies that process and distribute olive oil succumb to the temptation to mix their olive oil with less expensive oils such as corn, peanut and soybean oil.

A European company sent a shipment of olive oil to the United States. A routine sample was taken and HPLC was used to separate the oils into their component triglycerides (an example of the chromatograms obtained can be seen in Figure 11.1.13). The oil in the suspect sample had too much of the polyunsaturated triglycerides, confirming that the imported sample was diluted with corn oil.

HPLC can be combined with another analytical technique called mass spectroscopy (MS). Together, the techniques allow chemists to determine smaller and smaller quantities and identify a wider range of materials.

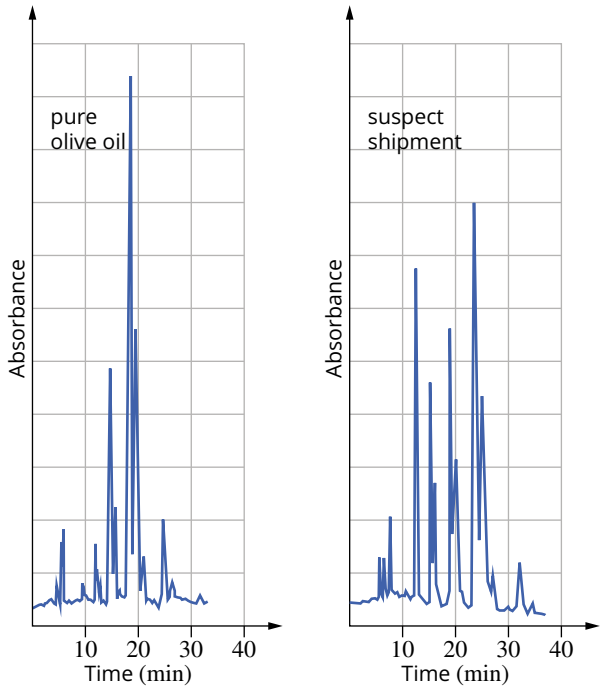


FIGURE 11.1.13 Peaks in the chromatogram of the suspect oil indicate the presence of compounds found in corn oil, rather than olive oil.

11.1 Review

SUMMARY

- The components in a mixture can be separated and identified by chromatography.
- Two simple forms of chromatography are paper chromatography and thin-layer chromatography.
- A mobile phase and a stationary phase are present in all forms of chromatography.
- The components of a mixture separate during chromatography as a consequence of how strongly they adsorb to the stationary phase and desorb back into the mobile phase.
- Paper and thin-layer chromatography can be used to identify the components in a mixture by comparing them with known standards or by determining their R_f values.
- High-performance liquid chromatography (HPLC) is a very sensitive technique and is used for qualitative and quantitative analysis.
- In HPLC the mobile phase is a liquid under pressure.
- In HPLC retention time is used to identify components in a mixture.
- The concentration of an individual component in a mixture can be determined by comparing its peak area on a chromatogram with the peak areas of samples with known concentrations of the same chemical.
- Organic compounds are separated based on different adsorption and desorption rates between the mobile and stationary phases.
- The peak areas of standard solutions are used to construct a calibration curve, which can be used to determine unknown concentrations.

continued over page

11.1 Review *continued*

KEY QUESTIONS

Retrieval

1 Describe how the rate of adsorption and desorption of a component that appears at the top of a paper chromatogram compares to that of a component that appears at the bottom of a chromatogram.

2 Describe how an R_f value is calculated.

3 Identify the mobile phase and the stationary phase for each of the following types of chromatography.

- **a** paper chromatography
- **b** thin-layer chromatography
- **c** high-performance liquid chromatography

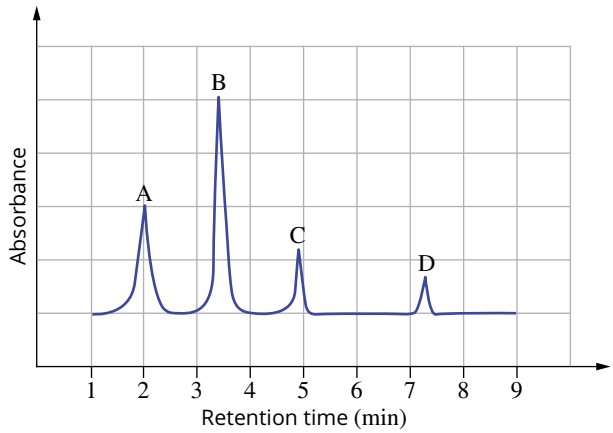
Comprehension

4 Explain why it is necessary to construct a calibration curve to determine the concentration of a component in a mixture that has been analysed by HPLC.

5 Determine which feature of a chromatogram obtained during an HPLC analysis is:

- **a** used to identify the components of a mixture
- **b** least affected by a change in concentration of the sample components
- **c** used to determine the concentration of each component in a mixture.

6 A mixture was composed of four primary alcohols with the formula ROH, where R is a straight-chain alkyl group. The mixture was analysed by HPLC using a non-polar stationary phase and a blend of water and methanol as the mobile phase. The following chromatogram was obtained.

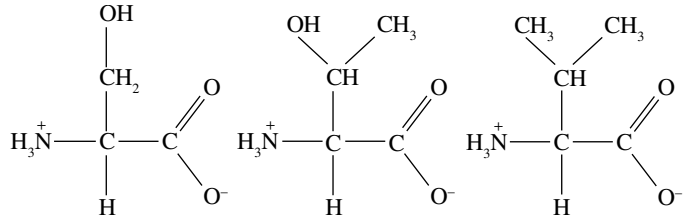


- **a** Determine the order from smallest to largest molar mass of the primary alcohols found in peaks A to D.
- **b** List the primary alcohols in order of lowest to highest concentration according to their peak height.

7 Explain why paper or thin-layer chromatography might be used as the initial investigation of a mixture rather than HPLC.

Analysis

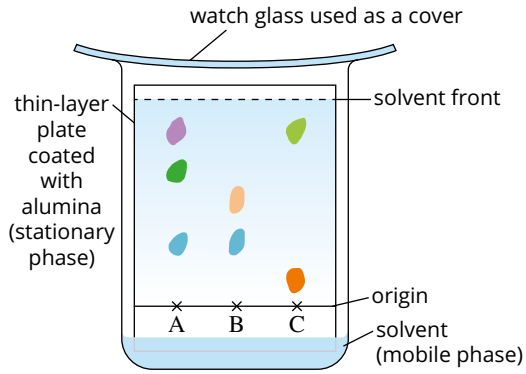
8 Reversed-phase HPLC uses a polar mobile phase and a non-polar stationary phase. A mixture of the amino acid molecules serine, threonine and valine, as shown in the figure below, was analysed by reversed-phase HPLC. Sort the amino acids in the order that they would reach the detector.



9 **a** Consider the diagram below showing a thin-layer chromatogram of three different samples (A, B and C) and:

- **i** determine how many different components are present in sample B
- **ii** select which colour of sample A is least strongly adsorbed on the stationary phase
- **iii** show which samples are likely to have one component in common.

b The green spot in sample A is 8.0 cm above the origin. The R_f value of this green spot is 0.74. The orange and green spots of sample C are 3.0 cm and 9.0 cm above the origin, respectively. Calculate the R_f values of each component of sample C. Give your answer to two decimal places.



10 EPO is a protein hormone produced by the kidneys. Although banned, some endurance athletes use it to improve their performance because it increases the body's oxygen-carrying capacity. Athletes are routinely tested for EPO levels by HPLC. The peak areas produced from an HPLC analysis of an athlete's blood and the peak areas of a number of standard solutions of EPO are shown in the table below.

	EPO (μg mL^{-1})	Relative EPO peak area
blood sample	?	5.6
standard 1	2.0	1.6
standard 2	4.0	3.2
standard 3	6.0	4.8
standard 4	8.0	6.4

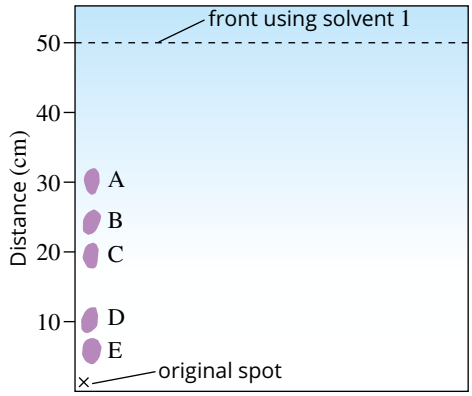
a Draw a calibration curve of the relative peak area against concentration of EPO (μg mL^{-1}).

b Determine the concentration of EPO in the blood sample correct to one decimal place.

11 The amino acids present in a sample of fruit juice can be detected by thin-layer chromatography. R_f values of some amino acids in two separate solvents are given in the table below.

Amino acid	Solvent 1 R_f	Solvent 2 R_f
lysine	0.12	0.55
leucine	0.58	0.82
proline	0.39	0.88
valine	0.40	0.74
2-aminobutyric acid	0.28	0.58
threonine	0.21	0.49
hydroxyproline	0.21	0.67
phenylalanine	0.50	0.86
isoleucine	0.57	0.81
alanine	0.24	0.55
serine	0.19	0.34
glutamic acid	0.25	0.33
glycine	0.20	0.40
arginine	0.13	0.60
taurine	0.12	0.33
tyrosine	0.38	0.62

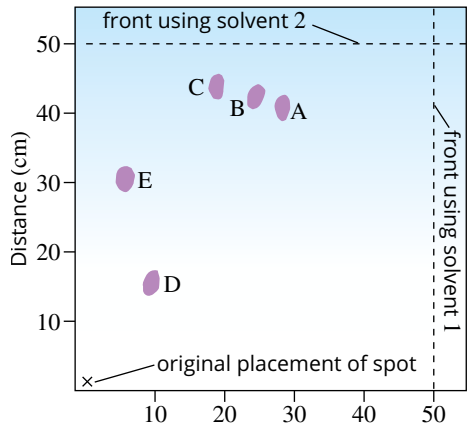
To achieve better separation of the complex mixture of substances present in the juice, a 'two-way' chromatogram was prepared. The first step in this procedure was to run a chromatogram using solvent 1. The results of this chromatogram are shown in the following figure.



a Calculate the R_f value of each spot on the chromatogram.

b Use the information in the table to determine the amino acids responsible for each spot.

The TLC plate was then turned around so that it lay at a right angle to the original and a second chromatogram was produced using solvent 2. The figure below shows the appearance of the TLC plate after some time.



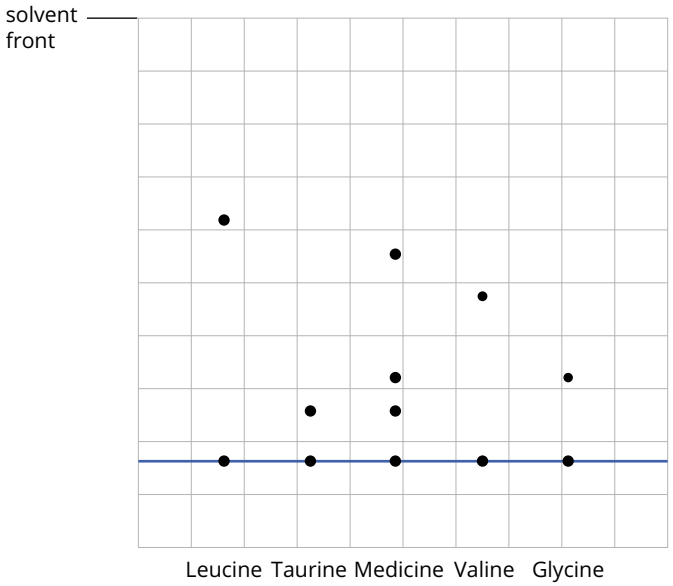
c Using the information in the table, determine each component in the mixture.

d Evaluate the advantage of a two-way chromatogram.

continued over page

11.1 Review *continued*

12 The figure below shows a thin-layer chromatogram obtained for individual amino acids and a medicine. Refer to this figure and the table in the previous question to complete the following.



a The following materials are commonly used in chromatography: water, ethanol, paraffin wax, glass sheets, paper strips, powdered alumina, nitrogen gas and hexane. Choose a suitable stationary phase and mobile phase from the list to use in the analysis of amino acids by thin-layer chromatography.

b Calculate the distance moved by the sample of leucine if the solvent front moves 13 cm from the origin.

c The separation of taurine and glycine on the chromatogram is not very great. Determine what would happen to the R_f values of the two amino acids if the separation was carried out for a longer period so the solvent front moved 20 cm instead of 13 cm from the origin. Explain your answer.

d Determine which amino acids are present in the medicine.

13 A chemist working for a sports anti-doping agency analyses the testosterone levels of an athlete's blood by HPLC.

a List the steps that the chemist would undertake in the analytical process.

b The chemist obtained the results shown in the table for four testosterone standards and the athlete's blood sample. The concentrations of the standards were measured in nanograms per litre. Determine the testosterone concentration in the athlete's blood.

Concentration (ng L^{-1})	Peak area (mm^2)
20.0	0.12
40.0	0.22
60.0	0.36
80.0	0.46
blood sample	0.28

14 A government department used HPLC to analyse some imported olive oil and found that the oil was impure as it contained chemicals found only in corn oil. The peak area of one of the corn oil components in the chromatogram of a sample of the impure oil was 15.5 mm^2. The peak areas of four standard solutions of the component were also measured, as shown in the following table.

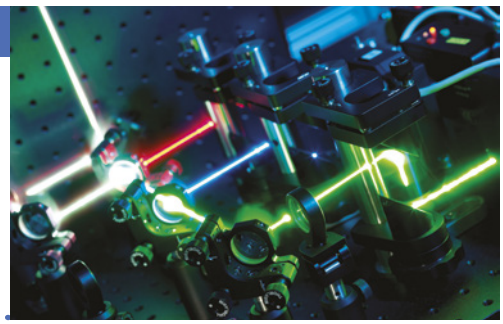
Determine the concentration of the corn oil component in the sample.

Corn oil component standards (%)	Peak area (mm^2)
1.0	5.8
2.0	11.6
3.0	17.6
4.0	23.0

11.2 Electrophoresis

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- explain the purpose and use of protein gel electrophoresis
- outline the principles of gel electrophoresis
- select protein bands in the lane(s) of interest to be analysed
- estimate molecular masses of unknown proteins in a complex mixture
- note intensity of staining that reflects the relative abundance of individual proteins.



Gel electrophoresis is a technique used for separating proteins and nucleic acids (DNA and RNA). Most organic molecules carry a net charge and will migrate at a rate proportional to their charge. When an electric current is applied to the gel, the negatively charged molecules in the gel move towards the positive terminal. Small molecules move faster than large ones, causing them to separate based on their size.

PRINCIPLES OF GEL ELECTROPHORESIS

Proteins are **amphoteric** and can therefore carry a charge depending on the pH of the environment. An amphoteric compound can act as an acid or a base, by donating or accepting hydrogen ions.

The gel used has a jelly-like texture and is usually composed of **agarose** (a purified form of agar) or the more popular precast **polyacrylamide gels (PAGE)**. Agarose gel has big pores and is used to separate DNA, and PAGE has smaller pores and is used to separate smaller proteins. The gels consist of a three-dimensional network of solid material and pores which act as a molecular sieve for protein molecules.

Coomassie blue dye or fluorescent stains is added to the gel and the separated proteins are visible by eye as blue bands, as shown in Figure 11.2.1. Bright coloured bands are observed wherever there are proteins present in the gel. The intensity of the staining reflects relative abundance of individual proteins.

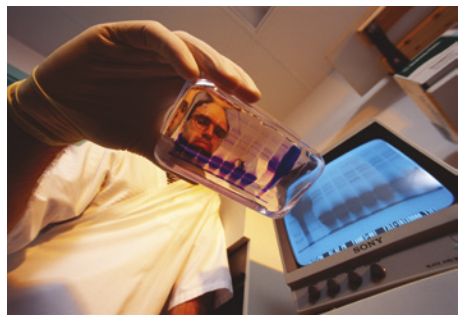


FIGURE 11.2.1 A researcher in an agricultural research laboratory studies bands of proteins in an electrophoresis gel tray.

Proteins are separated according to molecular mass (size).

Proteins are treated with **sodium dodecyl sulfate** (SDS, an anionic detergent soap) to break up (**denature**) and coat proteins with a negative charge. Boiling proteins with SDS breaks the weak bonds (hydrogen bonds and disulfide bridges) in the protein, therefore loosening the secondary and tertiary structures. The charge on each protein is now negative and can be separated by size.

A high voltage battery is used to force a current through the SDS-PAGE. The battery is attached to the negative terminal of the gel and allowed to move through the gel by adding a buffer solution that conducts electricity. The smaller proteins (fragments) will travel furthest, while the larger proteins are too big to move far.

The following steps outline the process of protein gel electrophoresis that is represented in Figure 11.2.2 on page 432.

1 An electrophoresis gel is prepared. The gel is rectangular and contains small wells (holes) at one end.
2 The gel is placed into a gel electrophoresis chamber with the wells situated at the negative terminal of the chamber.
3 Each sample is loaded into one of the wells within the gel.
4 A standard protein mixture (called a protein ladder) is also run on the gel for comparison with the samples. This allows the protein to be identified.
5 The gel is placed in an electrophoresis bath where it is covered with a controlled pH solution (buffer) that contains ions to conduct an electric current.
6 A power source is attached to the electrophoresis bath and switched on. The electrical current causes the negatively charged proteins to migrate through the gel towards the positive terminal of the chamber.

7 Smaller proteins move faster through the gel, so they migrate further through the gel than larger proteins in a given period of time. This sorts the proteins by size.
8 The proteins are detected by applying Coomassie blue dye, which is included in the gel.

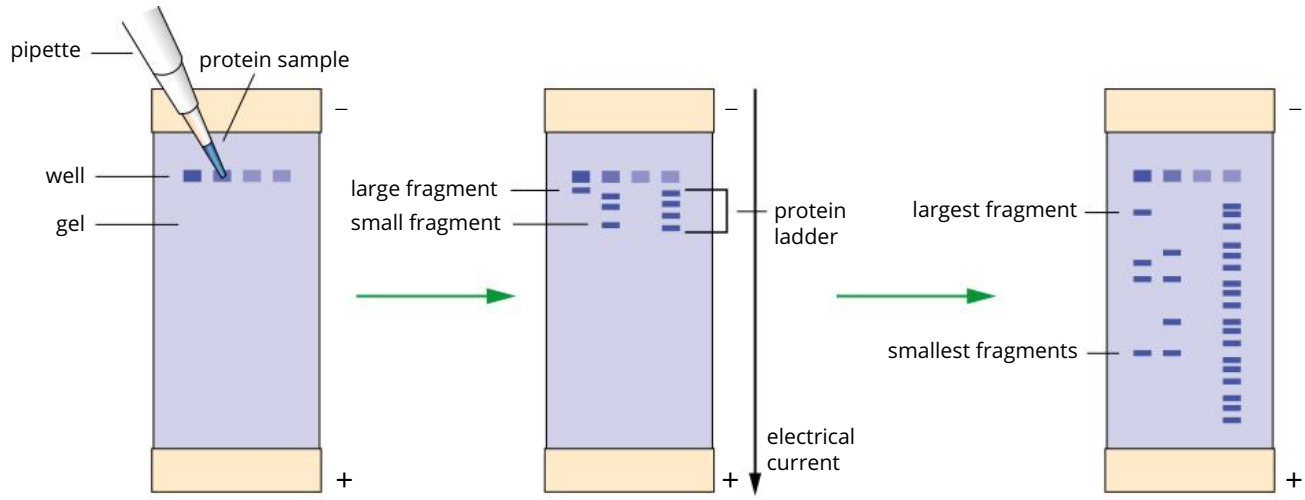


FIGURE 11.2.2 The process of gel electrophoresis, showing two unknown protein samples being loaded into wells and migration of the proteins through the wells based on their size. The last well contains a protein ladder for comparing and estimating which proteins the two unknown samples contain.

INTERPRETATION OF GEL ELECTROPHORESIS

The main purpose for using protein gel electrophoresis is separation of proteins and to study the presence or absence of proteins in a sample.

The size of the protein bands of various samples can be determined by comparing them against a standard (protein ladder), which contains known fragments of proteins. Protein standards are used to monitor separation as well as estimate the size and concentration of the separated proteins. When doing DNA testing, the DNA ladder is run on the gel next to the samples to determine the approximate length of each fragment. This can be seen in Figure 11.2.3.

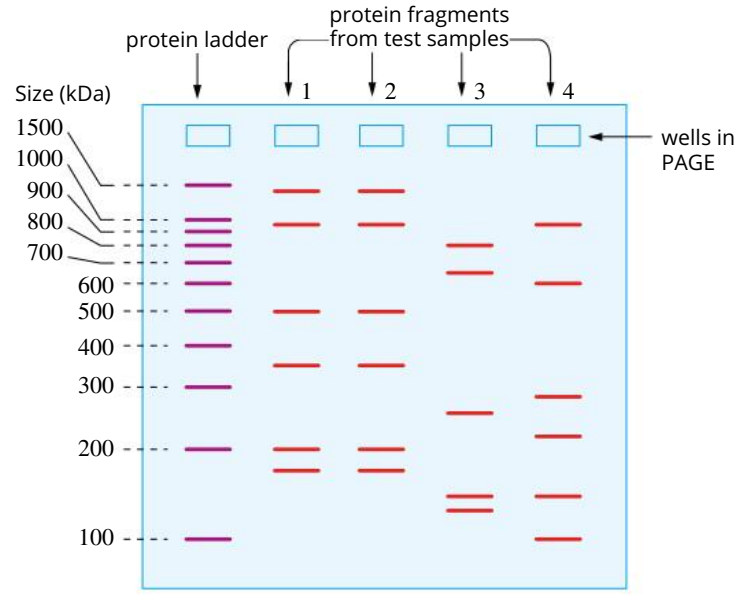


FIGURE 11.2.3 The results from gel electrophoresis of a protein can be shown as a diagram that can be analysed. Particular fragments can be identified and compared.

Fragment lengths are measured in base pairs (bp) to compare DNA fragments but proteins are compared according to molecular weight expressed in kDa (kilo Daltons, where one **Dalton** is the mass of a hydrogen atom, 1.66×10^{-24}g). The molecular weight of a protein can be estimated by comparing it to the known standard that is run on the gel for comparison.

Figure 11.2.4 shows the protein profile of three different snake venoms. The protein ladder is used as a size standard in protein electrophoresis and can be seen on the left-hand side of the gel.

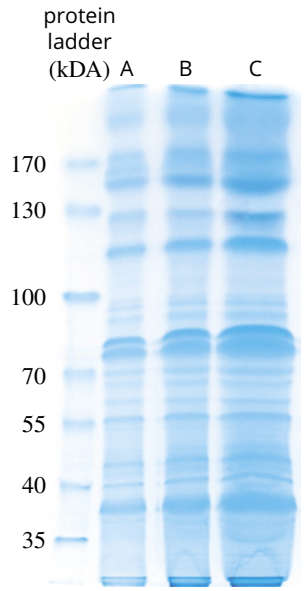


FIGURE 11.2.4 Protein profile of venom showing the different proteins (blue bands) contained in a sample

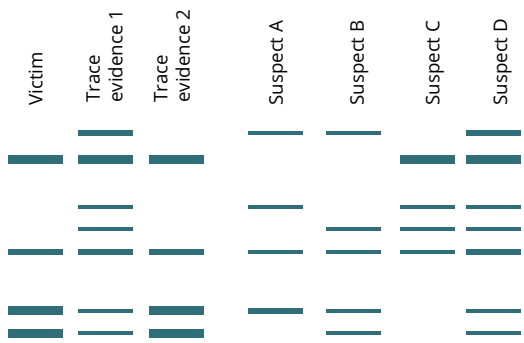
Worked example 11.2.1

COMPARING PROTEIN BANDS TO STANDARD MARKERS

Use the following figure to identify the origin of:

a trace evidence 1

b trace evidence 2.



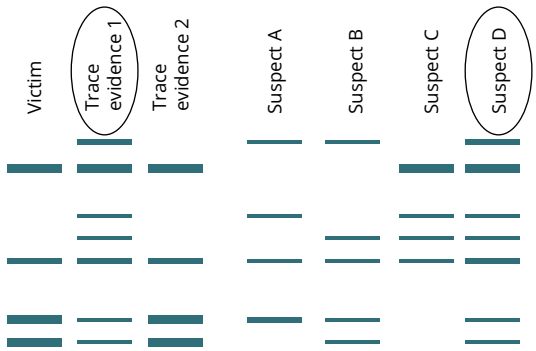
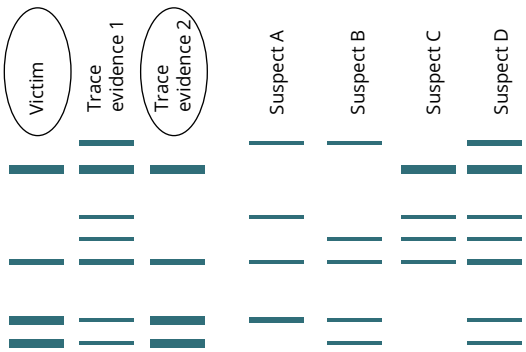
Thinking	Working
a Compare the protein bands from trace evidence 1, victim and suspects. Circle the suspect that has the same bands as trace evidence 1.	
State finding.	Trace evidence 1 is comparable with suspect D.
b Compare the protein bands from trace evidence 2, victim and suspects. Circle the suspect that has the same bands as trace evidence 2.	
State finding.	Trace evidence 2 is comparable to the victim.

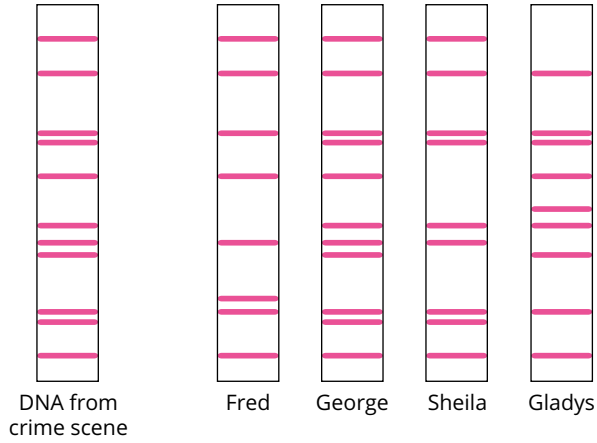


FIGURE 11.2.5 Researcher cutting separated proteins out of gel for further testing.

➤ Try yourself 11.2.1

COMPARING PROTEIN BANDS TO STANDARD MARKERS

Analyse the following figure to identify from which suspect the DNA found at the crime scene was most likely to have come from.



Gel electrophoresis separates proteins by molecular weight but does not distinguish between molecules with the same molecular weight. Further testing can be done by extracting separated proteins from the gel by physically cutting them out, as shown in Figure 11.2.5. Proteins can be analysed and identified further through mass spectrometry to differentiate between species with the same molecular mass and different functional groups.

11.2 Review

SUMMARY

- Gel electrophoresis is a technique that separates fragments of negatively charged DNA by length, and proteins by size.
- Each DNA sample is loaded into a different well in an agarose gel.
- Each protein sample is loaded into a different well in a polyacrylamide gel (PAGE).
- Sodium dodecyl sulfate is used to denature proteins and cover them with a negative charge.
- The wells are located at the negative end of a gel electrophoresis chamber.
- The gel is submerged in a buffer solution and the electricity is switched on.
- Negatively charged DNA or protein migrates through pores in the gel towards the positive terminal. Smaller fragments move faster and therefore further through the gel than longer fragments in a given time.
- The electricity is switched off and the gel is viewed to identify the number and size of DNA and protein fragments. DNA and protein fragments are visible as bands in a stained gel.
- The location of a band directly correlates with its specific length or molecular weight, so visible fragments can be identified and measured by comparing their position to the DNA or protein ladder.

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KEY QUESTIONS

Retrieval

1 **a** Define gel electrophoresis.

b Describe what gel electrophoresis reveals about protein fragments.

2 Proteins are amphoteric. Recall what amphoteric substances are.

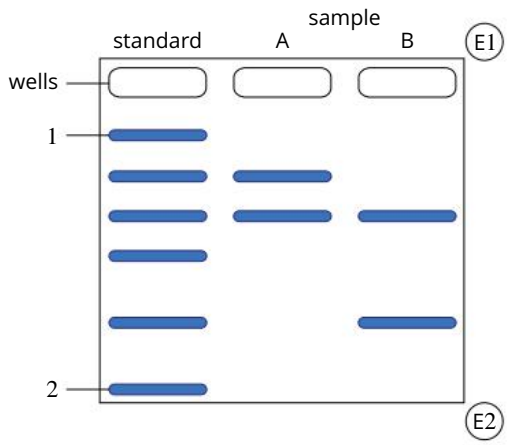
Comprehension

3 A protein ladder is used in gel electrophoresis. Explain what a protein ladder is and its purpose.

4 Explain the purpose of boiling proteins in SDS prior to molecular weight determinations using PAGE.

Analysis

5 Gel electrophoresis was conducted with a standard and two samples (A and B). The resulting gel is illustrated in the following diagram.



a Identify what the numbers 1 and 2 indicate.

b E1 and E2 represent the electrodes. Identify the positive electrode.

c Determine the direction in which protein fragments migrate through the gel when an electric current is applied.

d Distinguish how many protein fragments are in:

i the standard (protein ladder)

ii sample A

iii sample B.

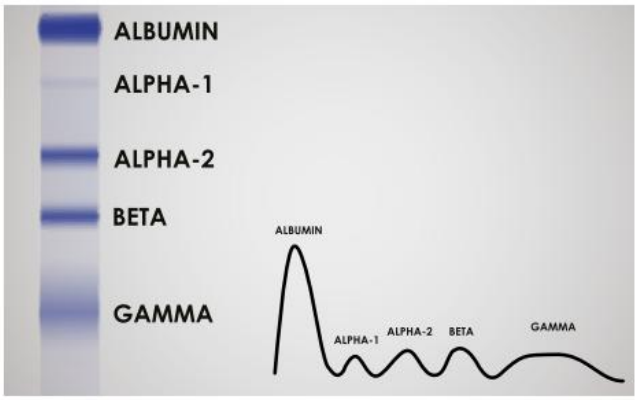
e You have been given information about the protein ladder. The sizes of the fragments are 600, 500, 400, 300, 200 and 100 kDa. Deduce the sizes of the fragments in samples A and B.

6 Snake venom contains a mixture of proteins and polypeptides. Snake venom affects platelet plug formation by interacting with the proteins that cause blood to coagulate. The proteins that inhibit coagulation have a molecular weight of 35 kDa and 70 kDa. Use Figure 11.2.4 on page 433 to answer the following questions.

a Identify how many of the samples contain these proteins.

b Conclude what assumption can be made about the toxicity of the three snakes.

7 Serum protein electrophoresis is a test used to measure albumin and globulin in blood. These two groups of proteins can be separated into five fragments, as shown in the following figure. This test is sometimes referred to as a 'total serum protein' test. (Computer analysis of protein gel electrophoresis is shown on right-hand side, including comparison between curve height and band intensity.)



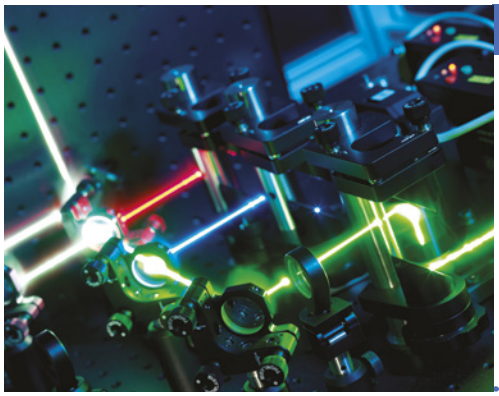
a Gamma globulin, also called antibodies, helps to fight infection in the body. Explain why gamma would be at the bottom of the protein ladder.

b Sort the size of the protein fragments in decreasing order.

c Identify which protein has the highest concentration in blood.

d During an acute inflammatory state, alpha-2 globulin will increase and gamma globulin will decrease. Determine what would happen to the patterns on electrophoresis gel.

11.3 Mass spectrometry



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- briefly outline principles of mass spectrometry
- explain the fragmentation of molecules when placed in a mass spectrometer
- identify the base peak and molecular ion on a mass spectrum
- analyse and interpret the mass spectrum of organic molecules
- use data given to interpret a mass spectrum and identify the organic molecules tested
- determine the identity of an organic compound based on the molecular ion seen in the mass spectrum and fragmentation pattern.



FIGURE 11.3.1 Curiosity, a robotic rover, on the surface of Mars

Mass spectrometry is one of the most commonly used analytical tools. It is used to analyse samples of solids, liquids and gases. It is a very sensitive quantitative technique that can detect concentrations in the parts per billion to parts per trillion range.

In Unit 1 you studied the use of mass spectrometry in the analysis of isotopes. Mass spectrometry can also be applied to the study of molecules. Each molecule produces its own unique mass spectrum, so a molecule can be identified by comparing its mass spectrum with the mass spectra held in a database.

Mass spectrometry is used to determine the structure of proteins and drugs. It can also detect molecules that are common markers for diseases such as cancer. **Mass spectrometers** have also been used in space exploration to analyse the atmosphere on Mars and on the moons of Saturn. The Mars rover Curiosity, shown in Figure 11.3.1, is a robotic laboratory that NASA landed on Mars in 2012. Curiosity carries a number of miniaturised analytical instruments, including a mass spectrometer.

Mass spectrometry is often combined with other instrumental techniques, in particular chromatography, for the analysis of complex mixtures.

PRINCIPLES OF MASS SPECTROMETRY

Figure 11.3.2 outlines the components of a mass spectrometer. It shows:

- ions are formed in the ionisation chamber where the sample is exposed to high voltages
- the ions are separated in a magnetic field on the basis of their mass-to-charge ratio (m/z)
- the number of ions with different m/z values are measured by a detector and the data is recorded as a **mass spectrum**.

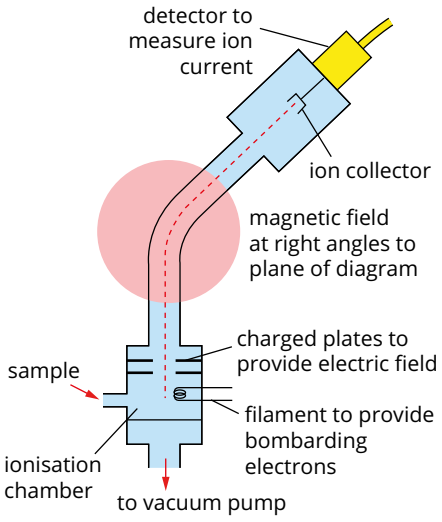


FIGURE 11.3.2 A representation of the components of a mass spectrometer

Features of a mass spectrum

A mass spectrum of a sample of pentane is shown in Figure 11.3.3. It is a plot of the abundance, measured as **relative intensity**, of ions of different m/z. This spectrum shows the positive ions formed when a sample of pentane was injected into the mass spectrometer.

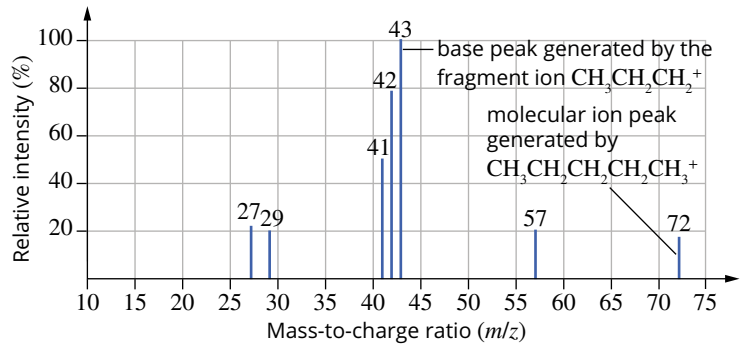


FIGURE 11.3.3 A mass spectrum of pentane ($CH_3CH_2CH_2CH_2CH_3$)

The mass spectrometer gives very accurate information about the mass of positive ions formed in the instrument.

The peak at $m/z = 72$ in pentane's mass spectrum is caused by the **molecular ion**. A molecular ion is formed when the entire molecule loses an electron and becomes positively charged. When ions are singly charged, meaning $z = 1$, then the m/z ratio is the same as the molecular mass of the ion. In most cases, the peaks in a mass spectrum are generated by singly charged ions.

The other peaks in the spectrum, which have smaller m/z values than the molecular ion, represent fragment ions. These are formed when the high-energy electrons in the ionisation chamber cause bonds to break, which then causes the molecule to break into pieces.

The most intense peak, $m/z = 43$, is called the **base peak** and is produced by the most abundant fragment ion. The base peak is assigned a relative intensity of 100%. The intensity of all the other peaks are measured relative to the base peak. In some spectra, the peak with the highest intensity is also the molecular ion. In other spectra, the base peak may correspond to a smaller fragment (Figure 11.3.3). The relative intensities of the peaks in the spectrum depend on the:

- energy of the ionising electrons
- ease with which fragments can be formed
- stability of the fragment ions formed.

Fragmentation

Inside the ionisation chamber, high-energy electrons ionise the sample by knocking off or adding an electron, leading to a positive or negative molecular ion. Because covalent bonds are formed from the sharing of electrons, the addition or removal of electrons can cause the bonds to weaken and break.

The **fragmentation** of the molecule into smaller pieces is represented in the mass spectrum by peaks with an m/z smaller than the molecular ion. Fragments can be produced by the breaking of almost any bond in the molecular ion. They may represent single atoms, small groups of atoms or large sections of the parent molecule.

The m/z values and formulas of some common fragment ions in mass spectra of organic molecules are listed in Table 11.3.1.

TABLE 11.3.1 Common positive fragment ions

m/z	Formula
15	CH_3^+
17	OH^+
29	$CH_3CH_2^+$, CHO^+
31	CH_3O^+
35 and 37	$^{35}Cl^+$, $^{37}Cl^+$
42	CH_2CO^+
43	$CH_3CH_2CH_2^+$, CH_3CO^+
45	$COOH^+$
60	CH_3COOH^+
79, 81	$^{79}Br^+$, $^{81}Br^+$

INTERPRETATION OF MASS SPECTRA

The information that is provided by mass spectrometry can be illustrated by examining the mass spectrum of ethanoic acid.

Ethanoic acid (CH_3COOH) can be ionised in a mass spectrometer by removing an electron in the following process:

$$CH_3COOH + e^- \rightarrow CH_3COOH^+ + 2e^-$$

The molecular ion, CH_3COOH^+, is unstable and can break into a number of fragment ions, as shown in Figure 11.3.4.

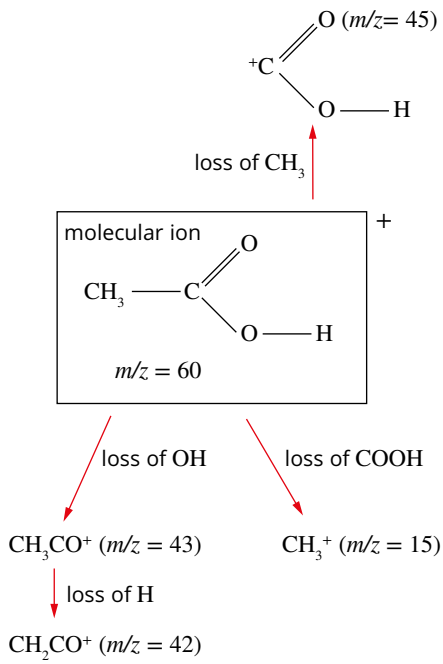


FIGURE 11.3.4 Formation of fragment ions from ethanoic acid

The molecular and fragment ions generate peaks in the mass spectrum of ethanoic acid, as shown in Figure 11.3.5.

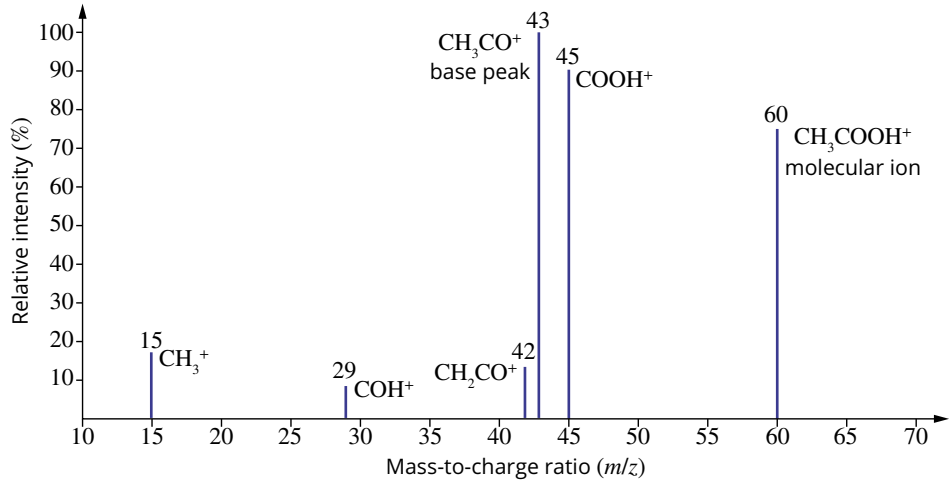


FIGURE 11.3.5 Mass spectrum of ethanoic acid

The mass spectrum of ethanoic acid indicates that the molecular ion has a mass of 60. The mass of the molecular ion is the same as the relative molecular mass of the ethanoic acid molecule. The fragment ions provide information about the structure of the ethanoic acid molecule, as shown in Table 11.3.2.

TABLE 11.3.2 Identity of peaks in ethanoic acid mass spectrum

m/z	Ion identity	
60	CH_3COOH^+	molecular ion caused by loss of an electron
45	$COOH^+$	loss of CH_3 from molecular ion
43	CH_3CO^+	loss of OH from molecular ion
42	CH_2CO^+	loss of H from CH_3CO^+
29	COH^+	loss of an O atom from $COOH^+$
15	CH_3^+	loss of COOH from molecular ion

Worked example 11.3.1

DETERMINING THE IDENTITY OF A COMPOUND FROM ITS MOLECULAR ION

The mass spectrum of an unbranched alkane has a molecular ion peak of $m/z = 86$. Determine the molecular formula of the alkane and give its name.

Thinking	Working
The *m/z* value of the molecular ion is equal to the relative molecular mass of the molecule.	The relative molecular mass of the alkane is 86.
Identify the general formula for the molecule.	The general formula for an alkane is C_nH_{2n+2}.
Use the general formula to construct an equation linking the relative molecular mass to the relative atomic masses of the constituent atoms.	$M_r(C) = 12$ $M_r(H) = 1$ $(12 \times n) + (1 \times (2n + 2)) = 86$
Solve the equation for *n*.	$12n + 2n + 2 = 86$ $14n + 2 = 86$ $14n = 84$ $n = 6$
Use the value of *n* to find the molecular formula and the name.	C_6H_{14}, which is hexane.

➤ Try yourself 11.3.1

DETERMINING THE IDENTITY OF A COMPOUND FROM ITS MOLECULAR ION

The mass spectrum of an unbranched alkane has a molecular ion peak of $m/z = 58$. Determine the molecular formula of the alkane and state its name.

Differentiating between the same molecular ions

Methyl propanoate and ethyl ethanoate are both esters and have the same molecular formula, $C_4H_8O_2$. The molecular ion for both molecules is the same, therefore fragment ions have to be used to provide information about identifying the molecules by mass spectrum.

Methyl propanoate and ethyl ethanoate both have a molecular ion at $m/z = 88$. The fragment ions differ slightly for each molecule, as seen in the mass spectra in Figure 11.3.6.

WS 4.1.9

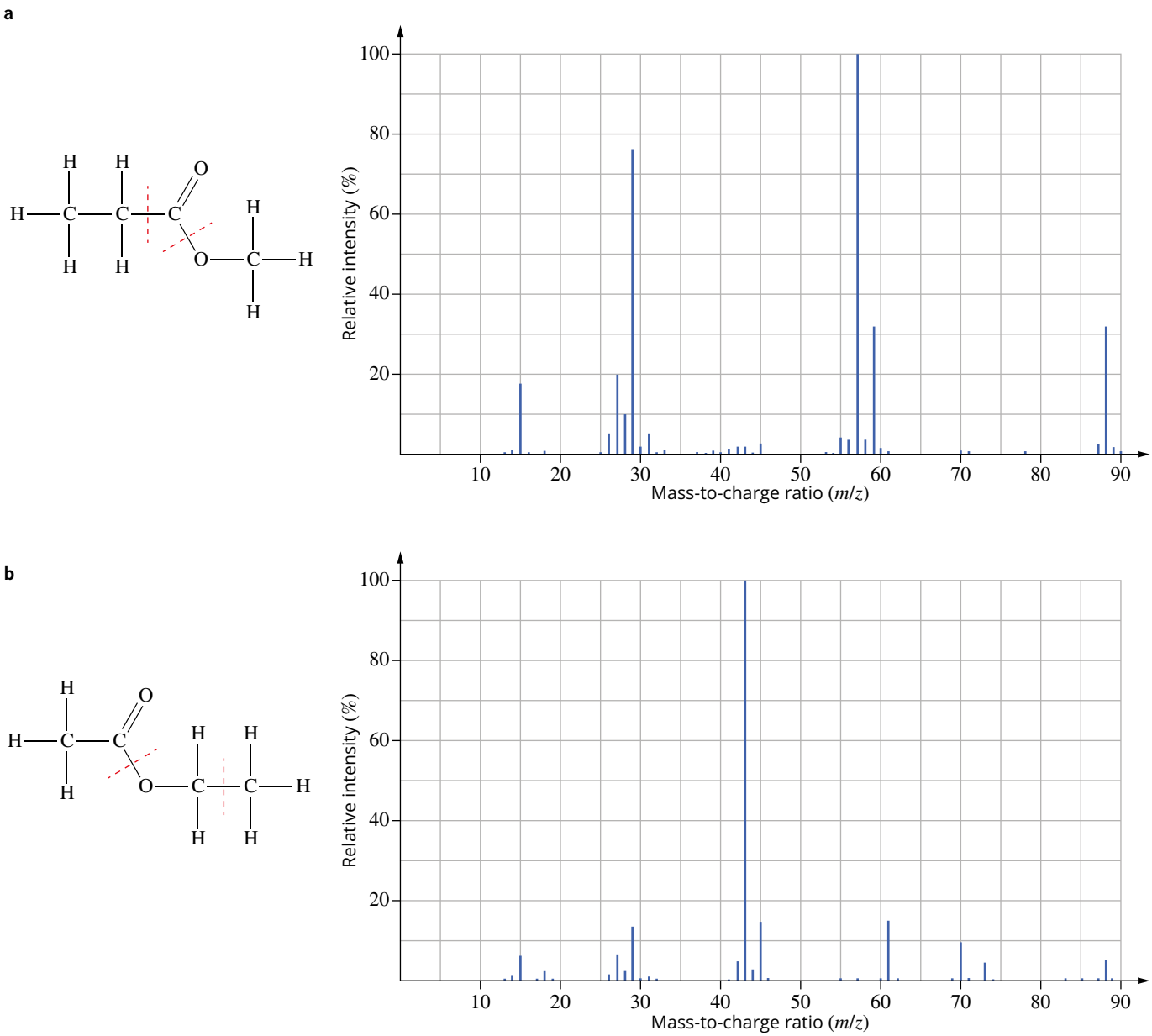


FIGURE 11.3.6 The structural formula and mass spectrum of (a) methyl propanoate and (b) ethyl ethanoate

The mass spectrum of methyl propanoate has the following distinguishing fragment ions.

- The peak at $m/z = 57$ is due to fragment ion $CH_3CH_2CO^+$.
- The peak at $m/z = 29$ is due to fragment ion $CH_3CH_2^+$.

The mass spectrum of ethyl ethanoate has the following distinguishing fragment ions.

- The peak at $m/z = 43$ is due to fragment ion CH_3CO^+.
- The peak at $m/z = 45$ is due to fragment ion OCH_2CH_3.
- The peak at $m/z = 73$ is due to fragment ion $CH_3COOCH_2^+$.

Isotope effects

Most elements exist as mixtures of **isotopes**, as shown in Table 11.3.3. The presence of isotopes in molecules leads to the appearance of additional peaks in a mass spectrum.

TABLE 11.3.3 Isotopes of some atoms and their percentage abundance

Element	Isotope	Isotopic mass	Percentage abundance	Isotope	Isotopic mass	Percentage abundance
hydrogen	^{1}H	1.0	99.98	^{2}H	2.0	0.02
carbon	^{12}C	12.0	98.93	^{13}C	13.0	1.1
oxygen	^{16}O	16.0	99.76	^{18}O	18.0	0.2
chlorine	^{35}Cl	35.0	75.00	^{37}Cl	37.0	24.2
bromine	^{79}Br	79.0	50.69	^{81}Br	81	49.3

The percentage abundance of ^{2}H, ^{13}C and ^{18}O in samples is very small, so ions containing them only produce very small peaks in the mass spectra. The presence of these isotopes can be ignored in most instances. However, chlorine and bromine have high proportions of each isotope, and so samples that contain them have significant peaks for each isotope in their mass spectra.

The mass spectrum of chloromethane (CH_3Cl) shows peaks for two molecular ions (Figure 11.3.7).

- The peak at $m/z = 50$ is due to the molecular ion containing ^{35}Cl.
- The peak at $m/z = 52$ is due to the other molecular ion containing ^{37}Cl.

The relative heights of these peaks reflect the relative abundance of the two isotopes.

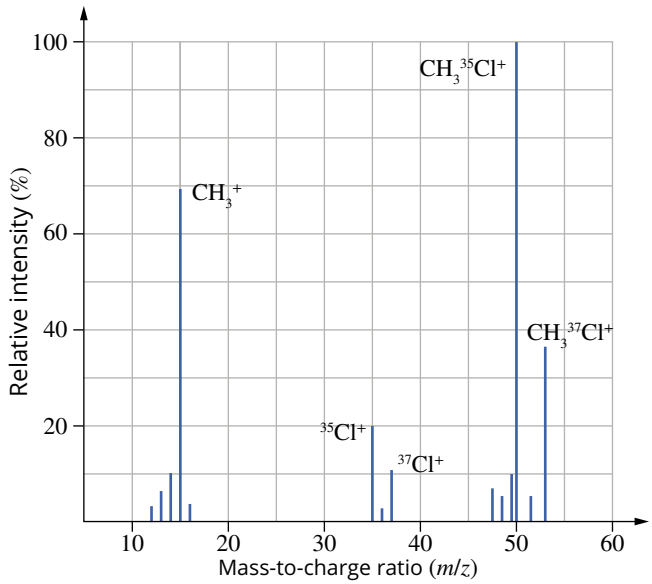


FIGURE 11.3.7 The mass spectrum of chloromethane (CH_3Cl). Note the two molecular ion peaks due to the isotopes of chlorine.

As the number of atoms that have significant proportions of isotopes increases, the mass spectrum can become more complex. The mass spectrum of dichloromethane (CH_2Cl_2) shows three **molecular ion peaks** (Figure 11.3.8).

- The peak at $m/z = 84$ is due to the molecular ion containing two ^{35}Cl atoms.
- The peak at $m/z = 86$ is due to the molecular ion containing one ^{35}Cl atom and one ^{37}Cl atom.
- The peak at $m/z = 88$ is due to the molecular ion containing two ^{37}Cl atoms.

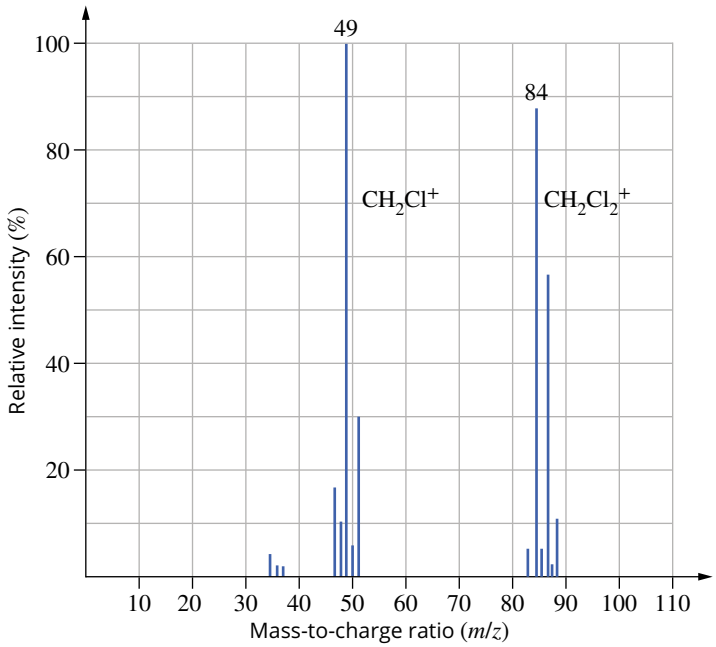


FIGURE 11.3.8 The mass spectrum of dichloromethane (CH_2Cl_2). Note the three molecular ion peaks $m/z = 84$, 86 and 88 due to the isotopes of chlorine.

11.3 Review

SUMMARY

- A mass spectrometer measures the mass-to-charge ratio, m/z, of ions.
- The peak that has the highest m/z is usually caused by the entire molecule becoming ionised and is called the molecular ion peak.
- The molecular ion can break into pieces called fragment ions.
- Fragmentation of a molecule in a mass spectrometer can help to determine its molecular structure.
- Each compound has a unique mass spectrum that can be used to identify it.
- The mass spectrum of a compound containing chlorine or bromine atoms has significant additional peaks due to the isotopes of chlorine and bromine.

KEY QUESTIONS

Retrieval

1 Define the following terms.
- **a** molecular ion
- **b** base peak
- **c** mass-to-charge ratio

2 Recall what additional peaks next to the main molecular ion peak in the mass spectrum indicates.

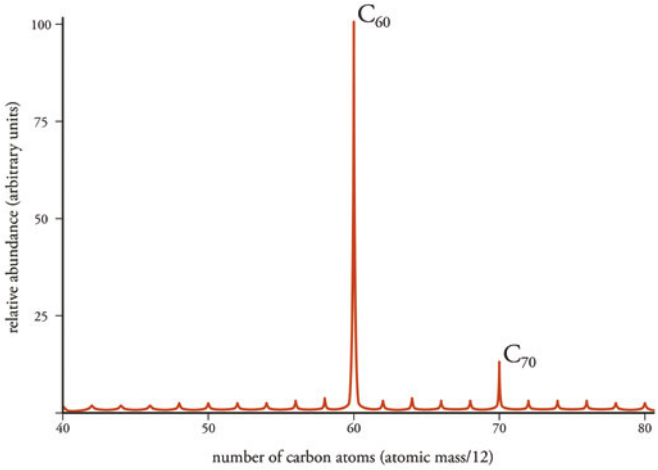
Comprehension

3 Identify the molecular ions (including different isotopes) that would be found in the mass spectrum of 1,1-dibromoethane.

continued over page

11.3 Review *continued*

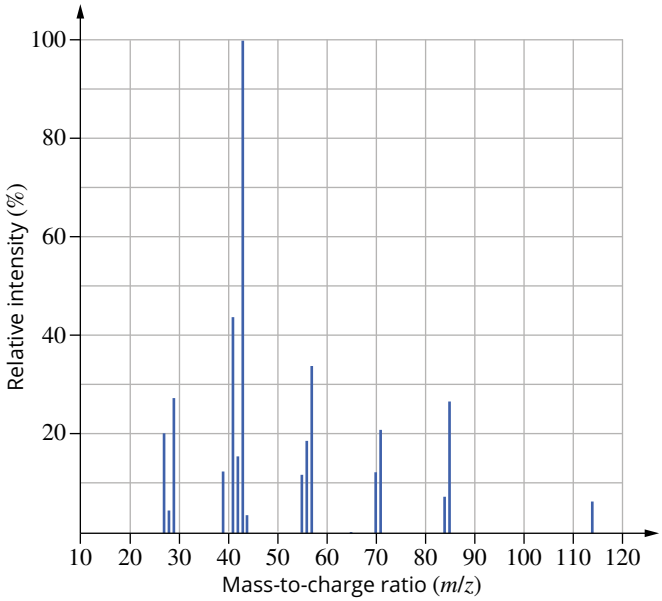
4 The following figure shows fullerene (allotrope) formation in the mass spectrum of graphite (a form of carbon).



a Define what a fullerene is.
b Identify the fullerenes shown in the mass spectrum.
c Explain what the other peaks represent.

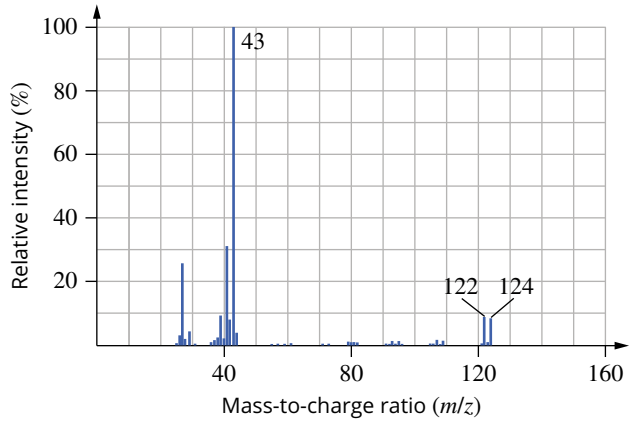
Analysis

5 The following mass spectrum is of a straight-chain alkane.



a Determine the relative molecular mass of the compound.
b Determine the *m/z* value of the base peak.
c Determine the formula for the fragment ion with an *m/z* value of 85.
d Identify the name of the alkane represented.

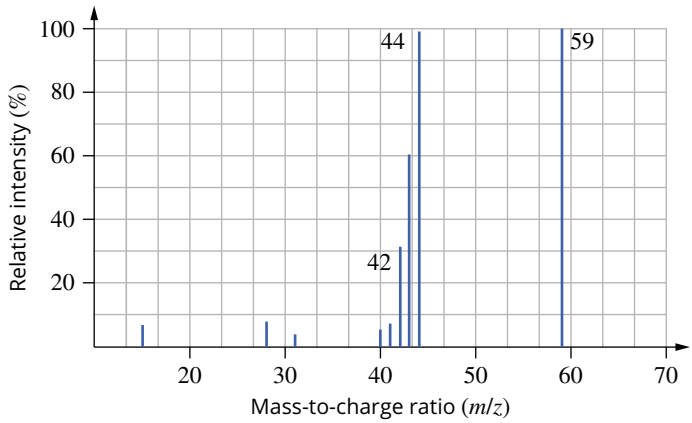
6 The mass spectrum of a bromoalkane is shown below.



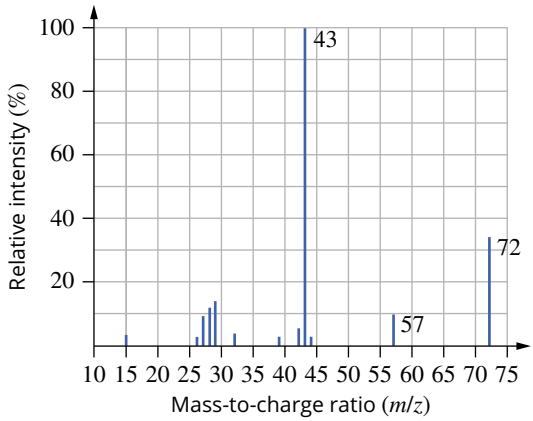
a Determine the formula of the bromoalkene.
b Explain why the mass spectrum has two peaks at *m/z* = 122 and *m/z* = 124.
c Explain the relative heights of these two peaks.
d Determine the ion responsible for the peak at *m/z* = 43 by writing a possible formula.

7 Determine the identity of the molecules using the following mass spectra.

a Figure A represents an unknown amide.



b Figure B represents an unknown ketone.

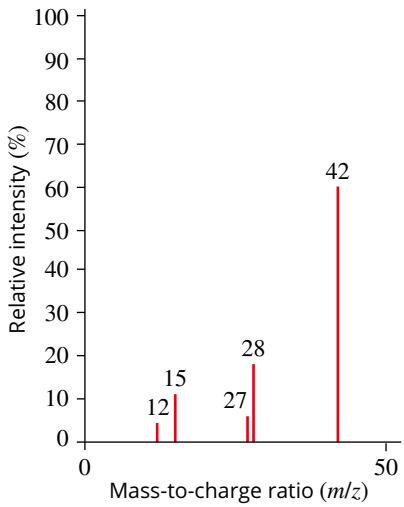


8 The mass spectrum of an unknown alkene is shown below.

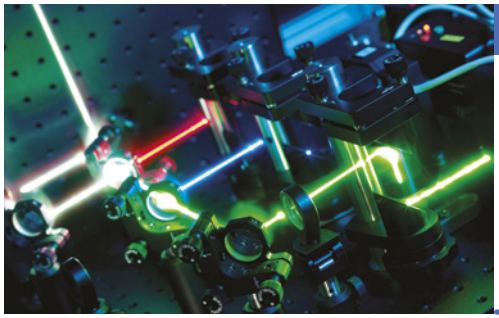
a Identify the molecular ion peak.

b State the relative molecular mass of the unknown alkene.

c Determine the molecular formula of the alkene and state its name.



11.4 X-ray crystallography



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- outline the process of X-ray crystallography
- state crystal conditions required for X-ray diffraction
- use electron density maps to determine element position in molecular structure
- determine the structure of organic molecules through interpretation of electron density maps.

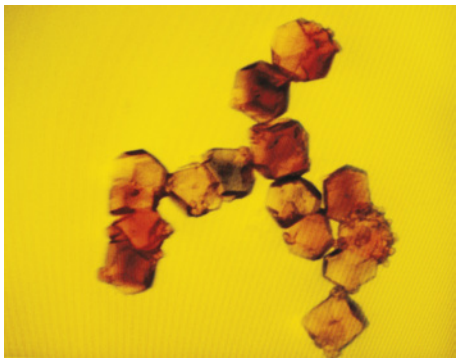


FIGURE 11.4.1 Light microscope view of crystals of DNA grown for analyses by X-ray diffraction. Each crystal is approximately 60 microns across and contains 10 base-pair sections of DNA.

Scientists use a technique called **X-ray crystallography** to determine the three-dimensional structure of large molecules such as DNA, proteins, enzymes and viruses. The technique measures the angles and intensities of diffracted X-ray beams to determine the position of atoms in a **crystal**.

The knowledge of accurate molecular structures is important in drug design and the development of effective therapeutic agents.

The first step in X-ray crystallography is producing large enough quantities of a molecule in order for it to be purified. A single molecule is not large enough to be analysed by this technique, so scientists produce crystals in which the molecules are arranged in a regular pattern to magnify the signal. This can be seen in Figure 11.4.1.

In the next step, an intense beam of X-rays is shone through the crystal. The crystalline structure causes the X-rays to diffract in many directions. The pattern formed and the relative brightness of the dots can be analysed to determine the density of electrons within the crystal.

Computer programs then use this **electron density map** to determine the position of each atom in three-dimensional space.

INTERPRETATION OF X-RAY CRYSTALLOGRAPHY

For **diffraction** to occur, photons must have a wavelength that is approximately equal to the distance between atoms (bond length) in the crystal. X-rays are used because their wavelength (about 10^{-8} cm) is comparable to the bond length (spacing about 10^{-8} cm) between molecules. Figure 11.4.2 shows an X-ray diffraction image of a molecule of DNA.

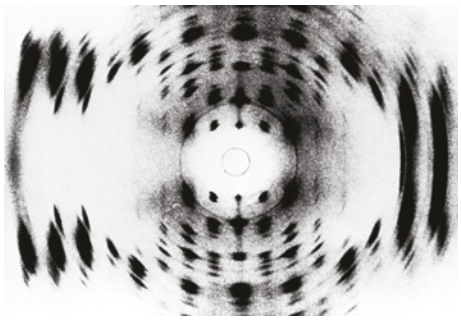


FIGURE 11.4.2 X-ray diffraction image of part of a molecule of DNA. A repeated pattern is seen, which reveals the helical structure of DNA around a core.

For successful analysis, crystals must not have cracks or flaws and they must be small enough to allow photons from X-rays to interact with atoms. Crystals must be secured to prevent vibration of atoms and a general idea of the structure should be known.

The arrangement of atoms within the crystal is what determines the **diffraction pattern**, which appears as a series of spots of varying brightness. The spots indicate where light interacts constructively to magnify the wavelength. The X-ray is shone through the crystal at different angles to produce multiple images. Collectively, the images form a pattern that infers the three-dimensional structure of the molecule. This can be seen in Figure 11.4.3.

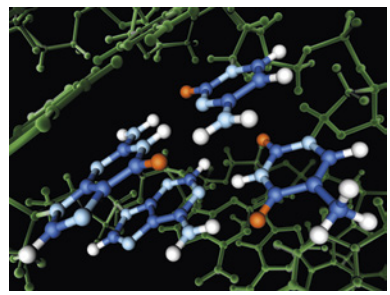


FIGURE 11.4.3 Computer-generated electron density map for a structure of DNA (C-T-C-T-C-G-A-G-A-G). The base pairs guanine and cytosine can be identified.

The Protein Data Bank (PDB) houses an international repository of the structural data of proteins. The information is accessed and contributed to by scientists worldwide. The function of a protein is closely linked to its structure.

The electron density map (Figure 11.4.4) represents the electron cloud size through circular/elliptical shapes that are 'layered' to represent how much **electron density** there is. Darker dots represent more diffraction, which means a higher electron density. The higher the atomic number the larger the electron cloud. The electron density map can be used to determine the structure of organic molecules. This map is interpreted in terms of where the atoms or molecules are. Each atom can be assigned a specific element name according to the size of electron densities.

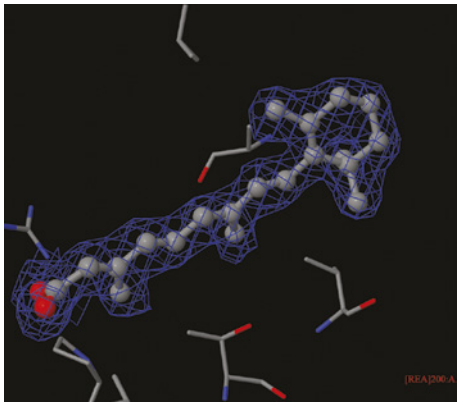
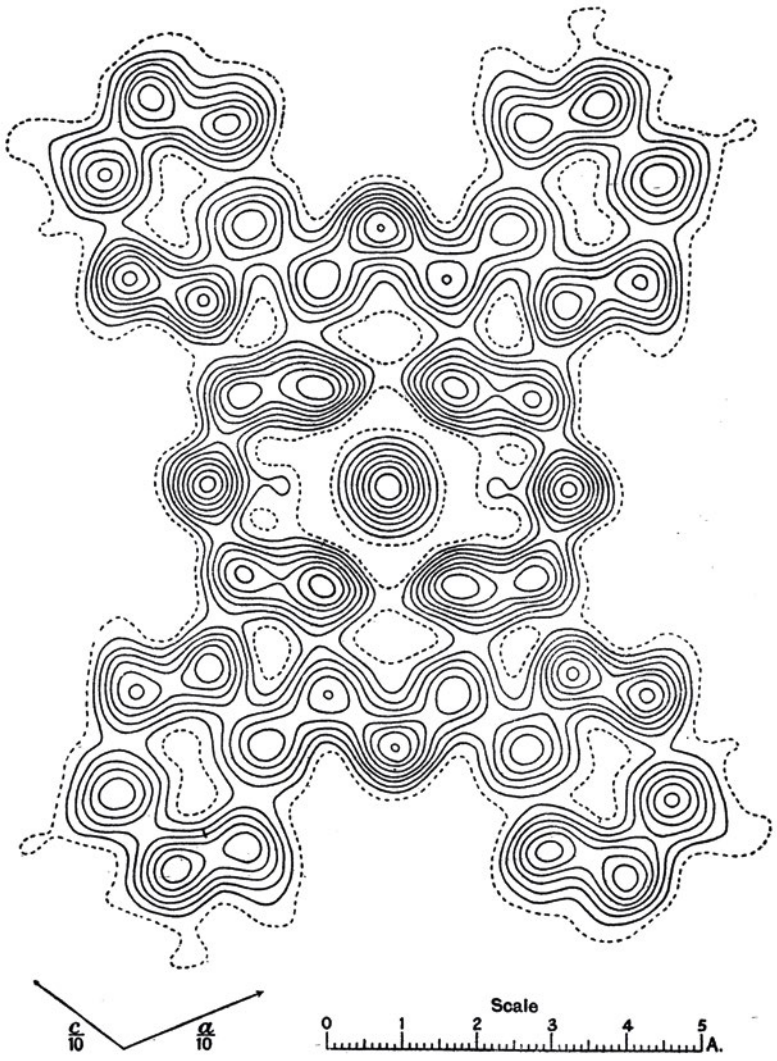


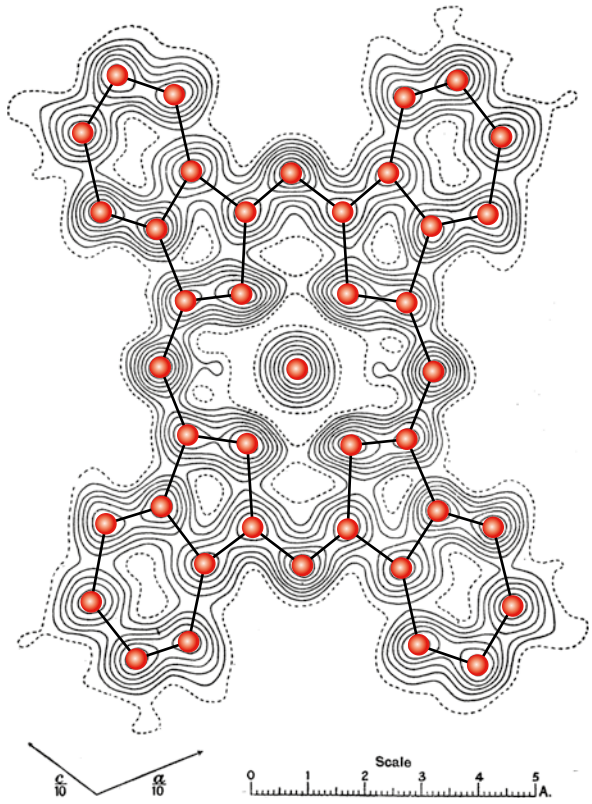
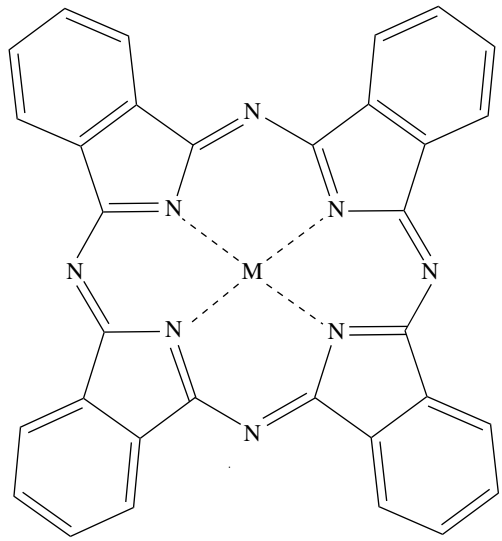
FIGURE 11.4.4 Computer-generated electron density map for retinoic acid

Worked example 11.4.1

DETERMINING THE STRUCTURE OF AN ORGANIC MOLECULE FROM ITS ELECTRON DENSITY MAP

The following is an electron density map of the blue dye metal phthalocyanine ($C_{32}H_{16}N_8$) crystal. Determine the structure of the organic molecule.

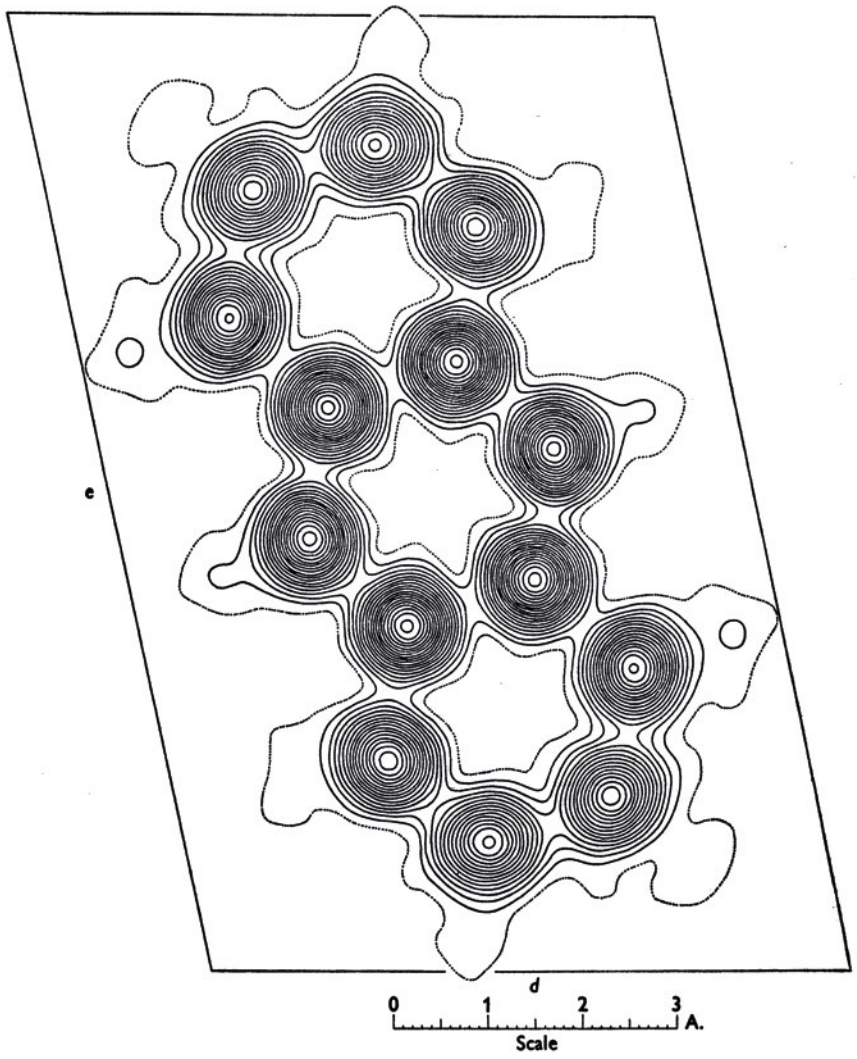


Thinking	Working
Identify the general formula for the crystal and state the atoms it is made of.	The general formula for metal phthalocyanine is $C_{32}H_{16}N_8$. It contains carbon, hydrogen, nitrogen and a metal.
Identify the atoms on the electron density map.	
Determine the structure of the organic molecule.	Hydrogen's electron density is too small to be seen, therefore the electron density map shows the position of the carbon, nitrogen and metal. The metal has more electrons and will scatter X-rays more effectively and is thus the atom in the middle of the figure. Nitrogen has one more electron than carbon and will therefore scatter X-rays more. 

➤ Try yourself 11.4.1

DETERMINING THE STRUCTURE OF AN ORGANIC MOLECULE FROM ITS ELECTRON DENSITY MAP

The following is an electron density map of the anthracene ($C_{14}H_{10}$) crystal. Determine the structure of the organic molecule.



Electron density maps provide the location of atoms relative to each other, including determination of bond angles and lengths.

11.4 Review

SUMMARY

- X-ray crystallography is the study of crystal structures.
- X-rays are used to bombard the crystalline lattice and the characteristic diffraction pattern is used to determine the molecules' structure.
- The diffraction pattern obtained from X-ray scattering off the ordered structure of molecules or atoms in crystals is used to reconstruct the electron density.
- The atoms and molecules are built into the electron density map and the result is an accurate molecular structure.

KEY QUESTIONS

Retrieval

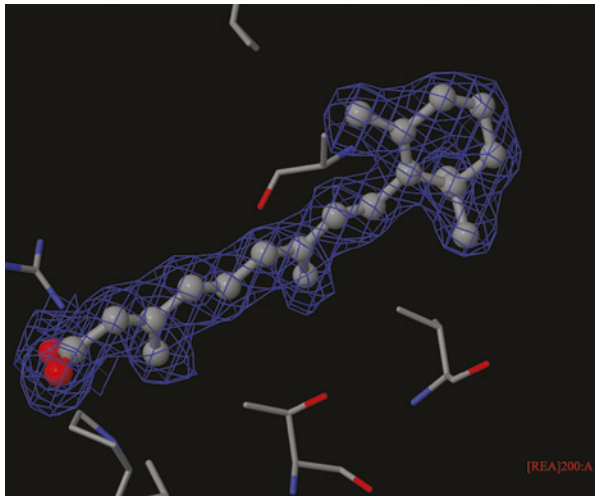
1 Describe the importance of crystal formation in the production of an X-ray diffraction pattern.

2 Recall why X-rays are used to bombard the crystals.

Comprehension

3 Explain the role of electrons in X-ray crystallography.

4 The following figure shows an electron density map for retinoic acid ($C_{20}H_{28}O_2$).



Use the electron density map to determine the organic structural formula of retinoic acid.

Analysis

5 Organise the following steps in X-ray crystallography in the correct order.

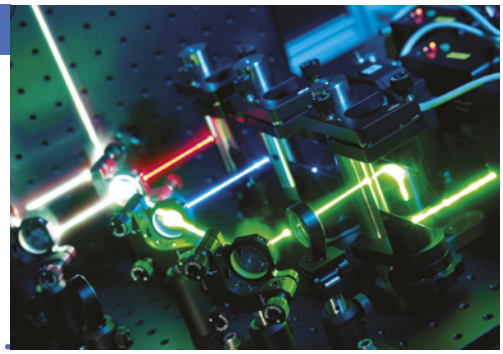
electron density map, diffraction pattern, identification of organic structure, grow perfect crystals

6 Assess why X-ray crystallography is used as an analytical technique.

11.5 Infrared spectroscopy

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- explain that atoms and molecules have different types of energies
- explain how infrared (IR) radiation influences the vibrational energy in atoms and molecules
- use IR spectroscopy to determine bond types and functional groups in organic and inorganic molecules
- use IR absorption data to identify common functional groups in organic compounds.



All types of spectroscopy use electromagnetic radiation to give information about materials found around you. Electromagnetic radiation interacts with atoms and molecules. The nature of this interaction depends upon the energy of the radiation. Different types of spectroscopy utilise the effects electromagnetic radiation has on atoms and molecules to learn about their structure.

The **electromagnetic spectrum** represented in Figure 11.5.1 is divided into different regions of radiation, with different frequencies, wavelengths and energies. Ultraviolet light has short wavelengths with high frequency and energy, while radio waves have long wavelengths and low frequency and energy.

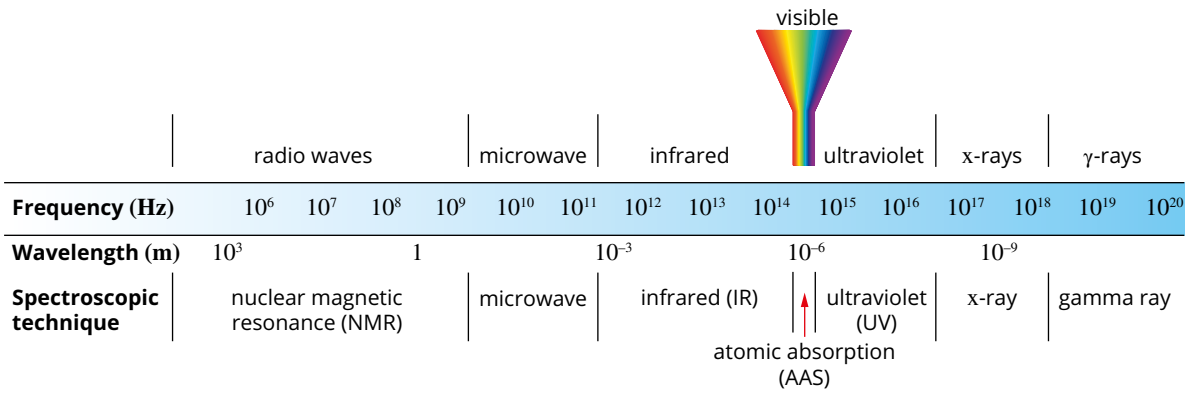


FIGURE 11.5.1 The electromagnetic spectrum showing the frequency and wavelength of different regions and their applications to spectroscopy

Atoms and molecules have different types of energy. The water molecule in Figure 11.5.2 shows four different types of energy in order of increasing energy.

When you studied atomic absorbance spectroscopy you learnt how electrons in an atom can absorb fixed amounts of energy and move to higher energy levels.

These spectroscopic techniques use the facts that:

- atoms and molecules absorb and emit electromagnetic radiation of specific energies
- atoms and molecules undergo a change when they absorb electromagnetic radiation
- different parts of the electromagnetic spectrum affect atoms or molecules in different ways.

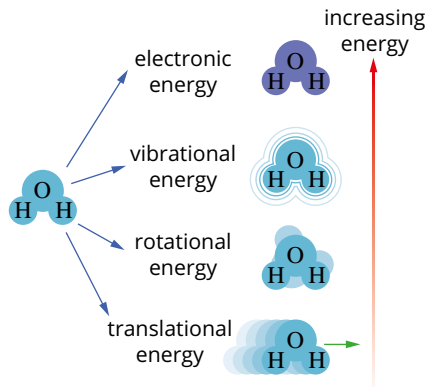


FIGURE 11.5.2 A water molecule has different types of energy.

PRINCIPLES OF INFRARED SPECTROSCOPY



FIGURE 11.5.3 A food chemist uses an infrared spectrometer to evaluate the quality of raisins.

Infrared (IR) spectroscopy is a powerful analytical tool that can be applied to the analysis of many organic and inorganic compounds.

IR spectroscopy can be used to analyse solids, liquids and gases. IR spectroscopy is used as a quality control tool in the pharmaceutical industry, agriculture, food processing (Figure 11.5.3), paint, paper and other industries (Figure 11.5.4).

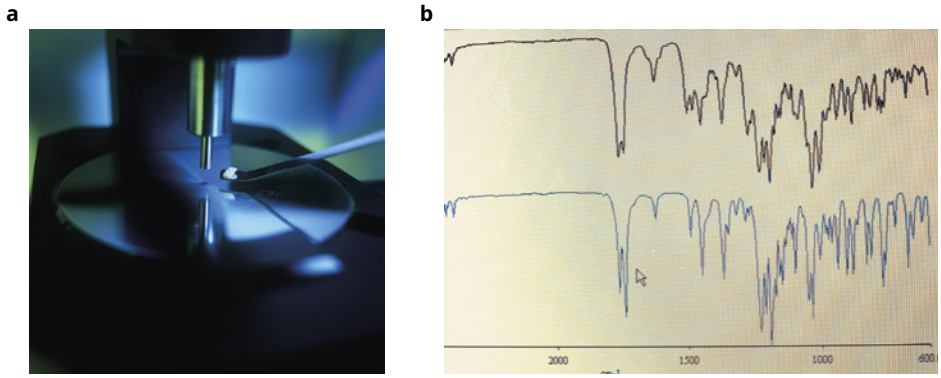


FIGURE 11.5.4 (a) Obtaining the infrared spectrum of a suspected illegal drug. (b) The spectrum of the substance (black) closely matches that of a heroin sample (blue), indicating that the substance contains the illegal drug.

Researchers combine IR spectroscopy with other techniques to study biological molecules. The technique is used to analyse blood and urine samples and is also used to determine the level of atmospheric pollutants.

IR spectroscopy is particularly useful because it can give you information about the functional groups present in an organic molecule. This information helps to clarify its structure.

The C–C bond absorbs infrared radiation of a lower frequency and is thus weaker than the C≡C bond. The absorption band seen on the IR spectrum will have a lower **wavenumber** (cm^{-1}), or waves per unit distance (Table 11.5.1).

TABLE 11.5.1 Bond energy, representing strength of the bond, compared to the frequency of infrared light absorbed

Bond	Bond energy ($kJ\,mol^{-1}$)	Infrared absorption frequency (cm^{-1})
C≡C	839	2100–2260
C=C	614	1620–1680
C–C	346	880

The mass of the atoms attached to a bond also affects the frequency of the IR radiation that will be absorbed. Since the hydrogen atom is lighter than the carbon atom the wavenumber of the absorption band is higher, thus atoms with higher masses absorb lower frequency radiation. Table 11.5.2 compares the energy absorbed when atoms of different masses are bonded to carbon with a single bond.

TABLE 11.5.2 Atomic mass affects the frequency of infrared light absorbed.

Bond	Typical absorption frequency (cm^{-1})
C–H	2720–3100
C–O	1050–1410
C–Cl	600–800
C–Br	500–600

Instrumentation

Figure 11.5.5 shows the main components of a simple infrared spectrophotometer. These include:

- a source of infrared radiation (electrically heated filament)
- a sample and reference cell
- a wavelength selector (monochromator)
- an infrared detector.

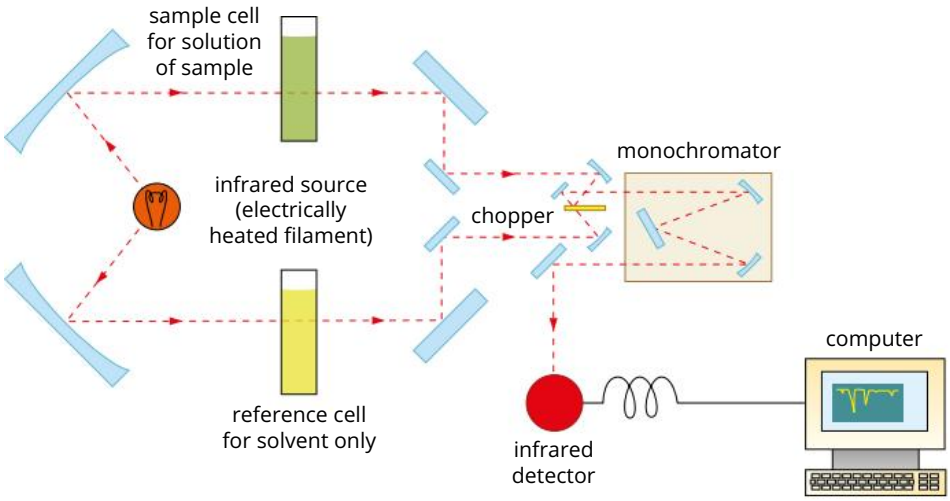


FIGURE 11.5.5 Essential features of a simple IR spectrophotometer

The IR radiation from the source is split into two beams and passed separately through the sample cell and a reference cell. The reference cell is used to discount the effect of the material of the sample cell, the solvent, and any interference from water or carbon dioxide in the atmosphere.

The difference in **transmittance**, or transmitted radiation, between the sample and reference cell is due to the absorption of certain frequencies by the molecules of the sample. These absorptions result in changes in the **vibrational energy levels** in the molecule under examination.

INTERPRETATION OF INFRARED SPECTRA

Features of an infrared spectrum

The frequency of the electromagnetic radiation in IR spectroscopy is usually expressed in wavenumbers (cm^{-1}). The wavenumber is the number of waves per centimetre and is inversely proportional to wavelength. A bond that vibrates at a higher frequency absorbs IR radiation with a higher wavenumber and greater energy than a bond that vibrates at a lower frequency.

The horizontal axis of an IR spectrum shows the wavenumber and the highest wavenumber is usually shown on the left. This axis often has two scales to ensure all features are visible. In the infrared spectrum of 2-methylpropan-2-ol, shown in Figure 11.5.6 on page 452, you can see that the scale starts with intervals of 1000 cm^{-1} and then changes to intervals of 500 cm^{-1} in the region below 2000 cm^{-1}.

The vertical axis (*y*-axis) of an IR spectrum shows the percentage transmittance on a scale of 0 to 100. The 'baseline' of the spectrum is where all of the light, 100%, is passed through the sample. Where the molecule absorbs IR radiation, the spectrum dips down to a lower transmittance. These **absorption bands** appear as inverted peaks in the spectrum.



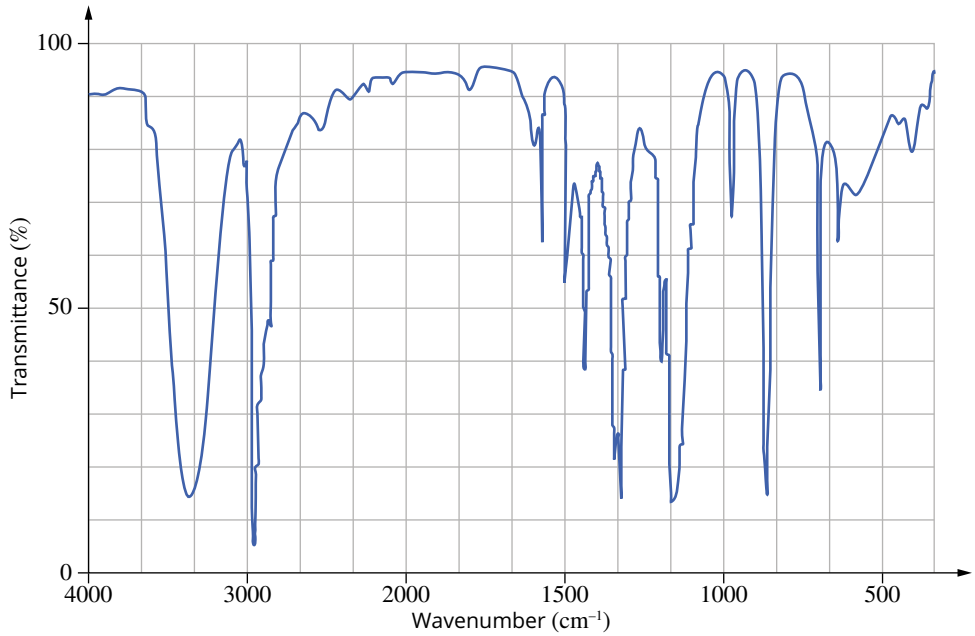


FIGURE 11.5.6 The infrared spectrum of 2-methylpropan-2-ol

Different terms can be used to describe absorption bands in IR spectra. Narrow absorption bands span only a few wavenumbers. This usually means that the peak corresponds to one specific type of molecular vibration. Broader bands may be the result of a number of related vibrational changes that have similar energies or hydrogen bonding. Absorption bands are also described as 'strong', 'medium' or 'weak' (Figure 11.5.7) depending on whether they absorb a large, moderate or small amount of radiation.

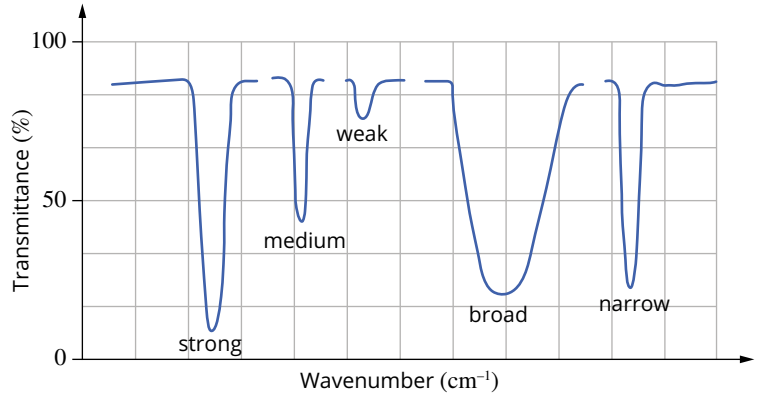


FIGURE 11.5.7 Descriptions used for different shapes and strengths of infrared absorption bands

Absorption bands above about 1400 cm^{-1} are used to identify **functional groups** (discussed in Chapter 8) because this region coincides with the energy associated with the characteristic stretching vibrations of the atoms in these groups. The region below 1400 cm^{-1} is called the **fingerprint region** as absorption bands of this frequency tend to be unique to each compound. If a known compound and an unknown compound have the same absorption spectrum below 1400 cm^{-1}, they are almost certainly the same.

Interpreting infrared spectra

Each type of bond absorbs IR radiation over a typical range of wavenumbers. For example, it takes energy in the 2720–3100 cm^{-1} region to stretch a C–H bond, and energy in the 750–1100 cm^{-1} region to stretch a C–C bond. The characteristic regions of absorption for different bonds in an IR spectrum are shown in Figure 11.5.8.

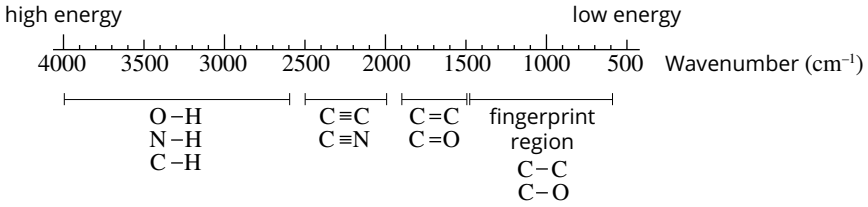


FIGURE 11.5.8 Typical regions for absorption bands from different bonds in the infrared spectrum

When chemists look at the IR spectrum of an unidentified organic compound, they often refer to tables and charts showing the wavenumbers at which the main functional groups absorb. This can give broad clues to the bond types and functional groups present in the molecule. For positive identification, the entire spectrum of an unidentified compound can be compared to a computer library of spectra, often containing tens of thousands of spectra of known compounds.

The characteristic range for IR absorptions of common functional groups are summarised in Table 11.5.3.

IR spectroscopy can be useful for distinguishing between very similar compounds. Consider the molecules propanoic acid and methyl ethanoate. These two compounds are isomers with the molecular formula $C_3H_6O_2$.

Using the data in Table 11.5.3, you can identify the bonds that are likely to be present in an unidentified compound from their characteristic absorption bands.

The infrared spectra of these compounds, shown in Figure 11.5.9, have some features in common and some differences. Both spectra have an absorption band at about 1700 cm^{-1} due to the stretching of the carbonyl (C=O) bond. Both esters and carboxylic acids have a carbonyl (C=O) bond.

TABLE 11.5.3 Infrared absorption data for some common functional groups

Bond	Wavenumber (cm^{-1})
C–Cl	600–800
C–C	750–1100
C–O (alcohol, ester)	1050–1410
C=C (alkenes)	1610–1680
C=O (aldehydes, acids, esters, ketones)	1700–1750
O–H (acids)	2500–3000
C–H (alkanes, alkenes, alkynes, aldehydes, amides)	2720–3100
O–H (alcohols)	3200–3600
N–H (primary amines)	3300–3500

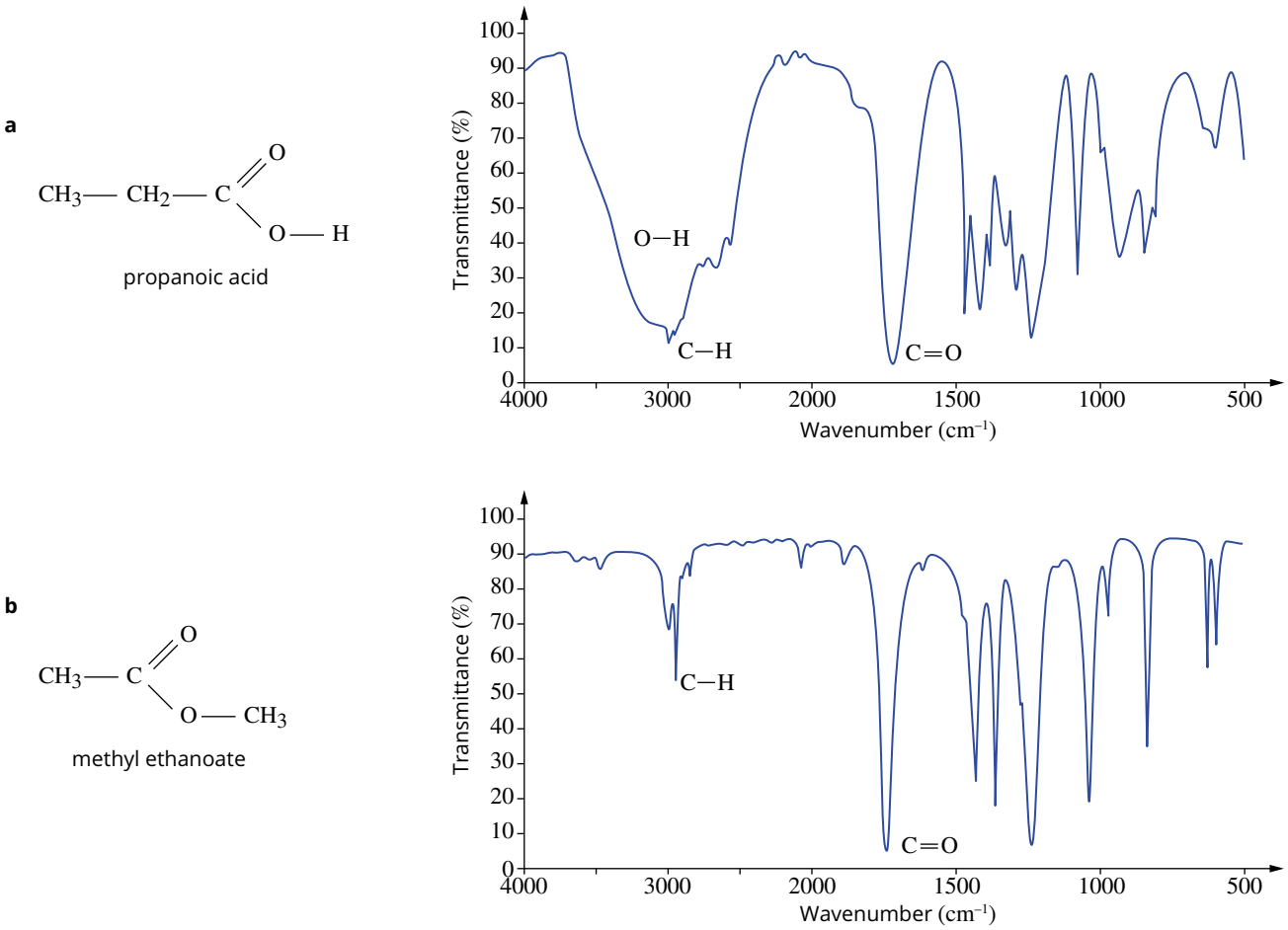


FIGURE 11.5.9 Infrared spectra of (a) propanoic acid and (b) methyl ethanoate

Different types of covalent bonds absorb IR radiation within a characteristic range of frequencies (wavenumbers), allowing the functional groups in an organic compound to be identified.

In methyl ethanoate, the narrow absorption band at around 3000 cm^{-1} is due to the C–H bonds in the two methyl groups as seen in the structural formula.

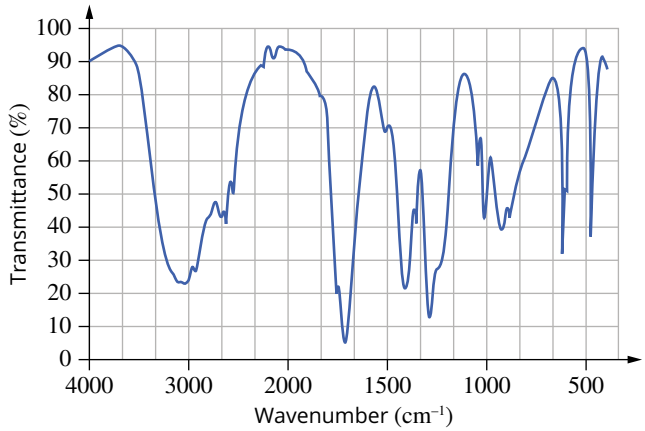
In propanoic acid, the broad absorption band from 2700 cm^{-1} to 3600 cm^{-1} is due to the O–H bond found in a carboxylic acid. This broad absorption band partly masks the absorption due to C–H bonds that are also present in this spectrum.

This information allows you to determine which of the main functional groups are present. The IR spectrum may also be used to prove that a functional group is not present, helping you to narrow down the possible structure of the compound.

Worked example 11.5.1

INTERPRETING THE IR SPECTRUM OF AN UNIDENTIFIED COMPOUND IN SOLUTION

Use the infrared spectrum of an unidentified compound to identify the functional groups present. The molecular formula of the compound is $C_2H_4O_2$. You will need to refer to the IR absorption data in Table 11.5.3 on page 453.

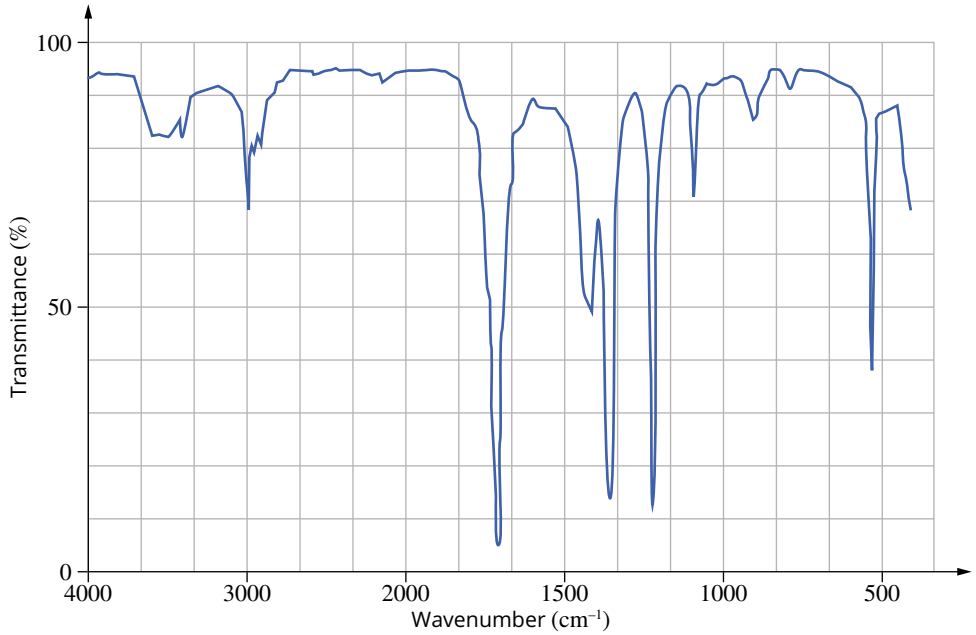


Thinking	Working
Identify the absorption bands that correspond to the absorption bands of bonds in the IR absorption data table.	There is a strong, narrow band at approximately 1700 cm^{-1}, which corresponds to the absorption by a carbonyl, C=O, group. The broad band centred at about 3000 cm^{-1} corresponds to the absorption by the O–H bond of a carboxylic acid.
Identify the functional group or groups that are present.	The spectrum shows absorption bands corresponding to the presence of C=O and carboxylic acid O–H bonds. This suggests the presence of a carboxyl functional group, –COOH. This means that CO_2H is used from the unidentified compound $C_2H_4O_2$, which leaves CH_3. From the formula and IR spectrum, it can be concluded that the compound is ethanoic acid (CH_3COOH).

➤ Try yourself 11.5.1

INTERPRETING THE IR SPECTRUM OF AN UNIDENTIFIED COMPOUND IN SOLUTION

Use the infrared spectrum of an unidentified compound to identify the functional groups present. The molecular formula of the compound is C_3H_6O. You will need to refer to the IR absorption data in Table 11.5.3 on page 453.



IR spectroscopy and quantitative analysis

In Unit 2 you learnt that UV-visible spectroscopy can be used to determine the concentration of a solution by comparing its **absorbance** at a specific wavelength to the absorbance of solutions of known concentrations. In a similar way, the amount of light absorbed by a particular bond in an IR spectrum is directly related to the amount of the compound being tested. This means IR spectroscopy can be used for quantitative analysis. Measurements of the concentrations of toxic gases in the atmosphere, such as sulfur dioxide and hydrogen cyanide, are often carried out by infrared spectroscopy.

In practice, a molecule can be analysed in this way if its spectrum contains a strong, sharp peak. As with chromatography and other spectroscopic techniques, a calibration curve is constructed by using standards of known concentration. The concentration of the sample is found by comparison with the calibration curve. Unfortunately, the correlation of absorbance to concentration is not always reliable because the calibration curves obtained from IR absorbances are often significantly curved rather than linear.

11.5 Review

SUMMARY

- Matter interacts with electromagnetic radiation in different ways depending on the energy of the radiation.
- Molecules have discrete vibrational energy levels. The absorption of IR radiation causes molecules to move to higher vibrational energy levels.
- Different types of covalent bonds absorb IR radiation within a characteristic range of frequencies (wavenumbers), allowing the functional groups in an organic compound to be identified.
- Each compound has a unique absorbance pattern in the fingerprint region of the IR spectrum and this can be used to identify the compound.
- IR spectroscopy can also be used in quantitative analysis.

KEY QUESTIONS

Retrieval

1 Identify which absorption bands would you expect to see from the following functional groups.

a alcohol
b amide
c amine
d carboxyl
e ester
f ketone

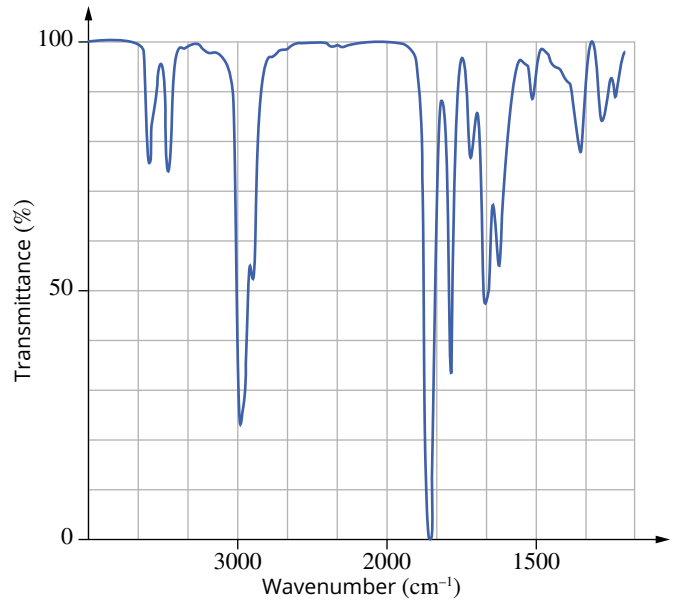
2 State the importance of absorption bands and the fingerprint region.

Comprehension

3 Determine which of the following compounds would show or not show a broad peak at around $3000\,cm^{-1}$.
1-propanol, 2-propanol, ethane, ethanol, ethanoic acid, methanoic acid, ethyl ethanoate, butanoic acid, 1-chloroethane and 1-methylamine.

4 Explain why the absorption bands due to C–O and C–C bonds are often of little help when determining the structure of an unidentified compound but are valuable in the confirmation of the identity of a known compound.

5 Use the following infrared spectrum of an unidentified compound to identify the functional groups present. The molecular formula of the compound is C_3H_5NO.



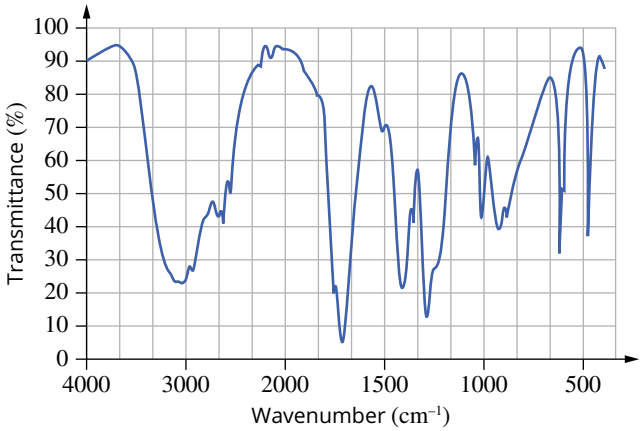
Analysis

6 If a roadside breath test shows that a driver is over the legally allowed blood alcohol limit, the driver is required to undertake a second test in a 'booze bus'. The driver has to breathe into the cell of an IR spectrometer and the ethanol concentration is determined. Breathalysers detect the change in colour as the ethanol is oxidised to ethanoic acid in the presence of acidified potassium dichromate.



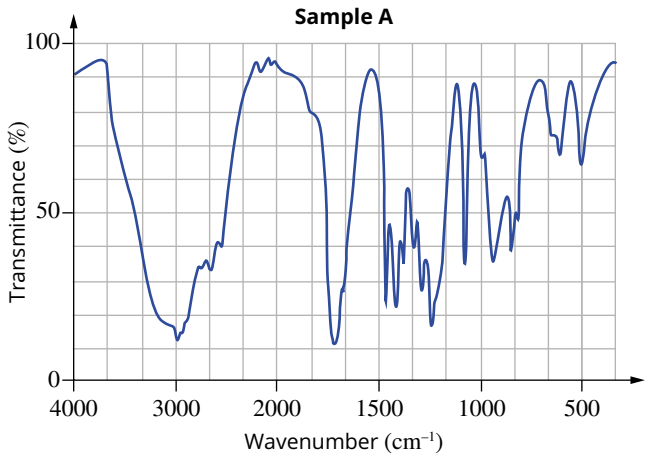
a Identify the expected absorption bands in the breath test.

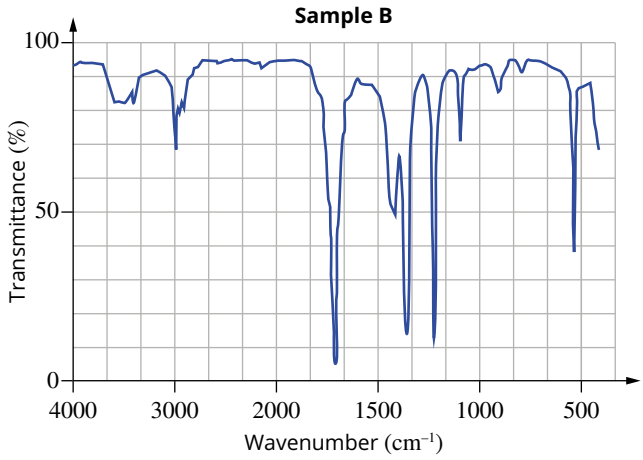
b The following IR spectrum was obtained from the driver's breath test. Deduce whether the driver was drinking and how the police can more accurately determine the ethanol concentration.



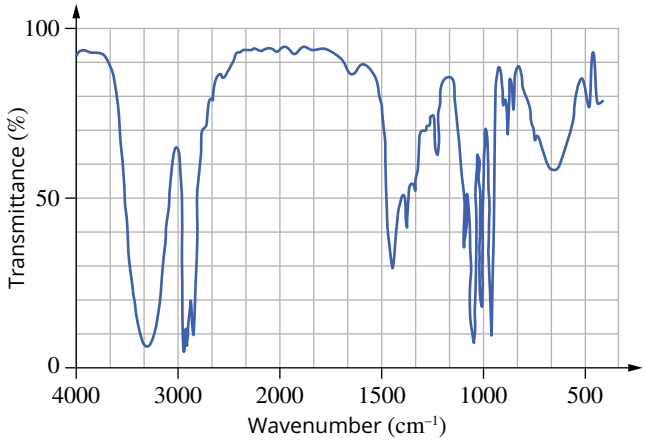
7 A careless laboratory assistant placed solutions of propanoic acid and propanone in unmarked containers. The laboratory assistant decided to analyse small samples of the unknown solutions using IR spectroscopy, and labelled the unknown solutions sample A and sample B.

Identify the two unknown solutions using chemical formulas and the following IR spectra.

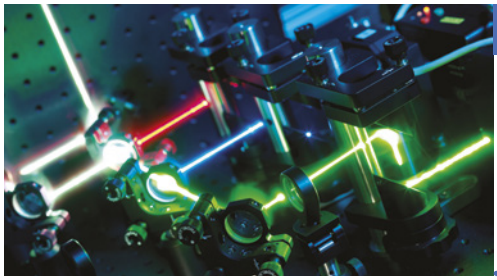




8 Champagne and wine are made by the fermentation of glucose ($C_6H_{12}O_6$) obtained from grapes. During glucose fermentation, ethanol and carbon dioxide are produced. The aqueous solution formed was analysed by IR spectroscopy and the following IR spectrum was obtained. Identify the product in solution.



11.6 Spectral analysis of organic compounds



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- determine the molecular structure of an unidentified compound by using spectral analysis
- state the importance of employing a range of analytical techniques
- combine mass spectrometry and IR spectroscopy to identify components of a solution.

Chemists determine the structure and identity of unknown compounds by employing a range of analytical techniques. Each technique provides a different piece of information about the compound's structure, which, when considered together (along with educated guesses), can identify the substance. The process can be compared to putting together the pieces of a jigsaw puzzle.

The structures of organic compounds are often determined using a combination of IR spectroscopy and mass spectrometry. Chemical and physical properties can also provide clues about the identity of a compound.

In this module you will investigate how the structure of an unidentified compound can be determined.

As you read through and complete the questions in this section, you will need to refer to Tables 11.5.1, 11.5.2 and 11.5.3 on pages 450–453.

COMBINING ANALYTICAL TECHNIQUES

Ethanol (C_2H_5OH) will be used as an example of how the results of different types of analysis can be used to identify an unknown organic compound. Ethanol has a molar mass of 46 g mol L^{-1}. The structural formula of ethanol is shown in Figure 11.6.1.

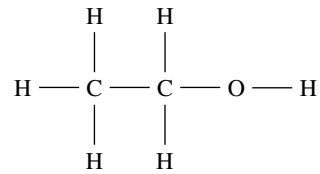


FIGURE 11.6.1 Structural formula for ethanol

The mass spectrum for ethanol can be seen in Figure 11.6.2. Using this spectrum, the following can be determined.

- There is a molecular ion peak at m/z = 46, which corresponds to a relative molecular mass of 46.
- The fragment ion peaks are identified on the spectrum and are consistent with the fragmentation of a molecule with the formula C_2H_6O.

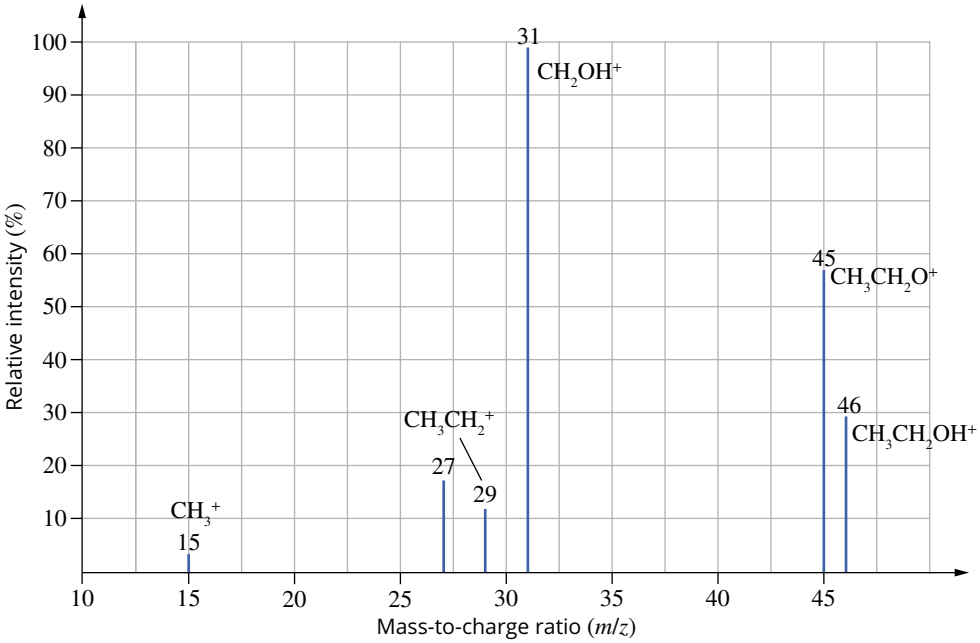


FIGURE 11.6.2 Mass spectrum of ethanol

The infrared spectrum of ethanol shown in Figure 11.6.3 provides the following information.

- The most prominent feature is the broad stretch at 3400 cm^{-1} due to the O–H bond and confirms the presence of an alcohol hydroxyl group.
- The absorption bands due to the C–H and C–O bonds are also shown.

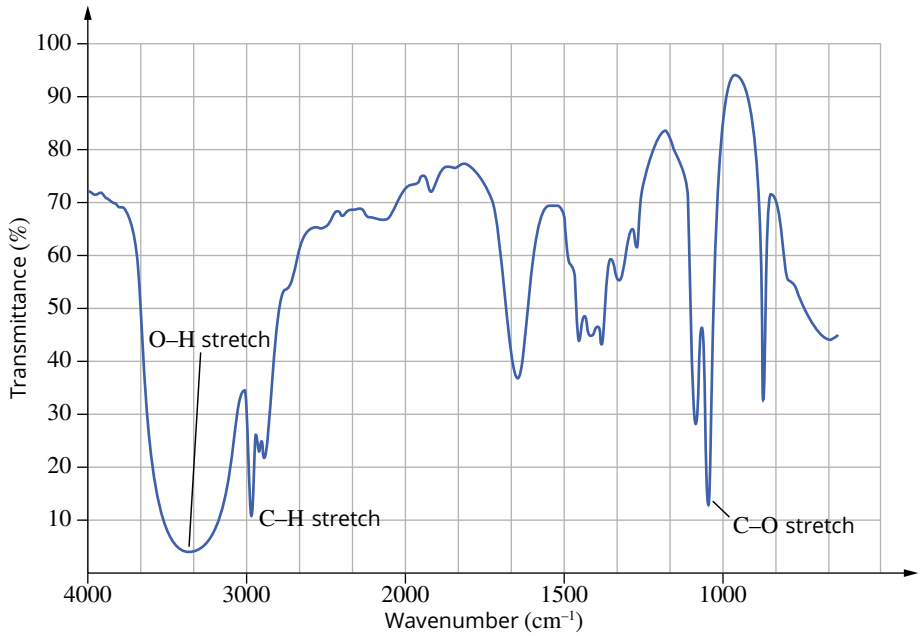


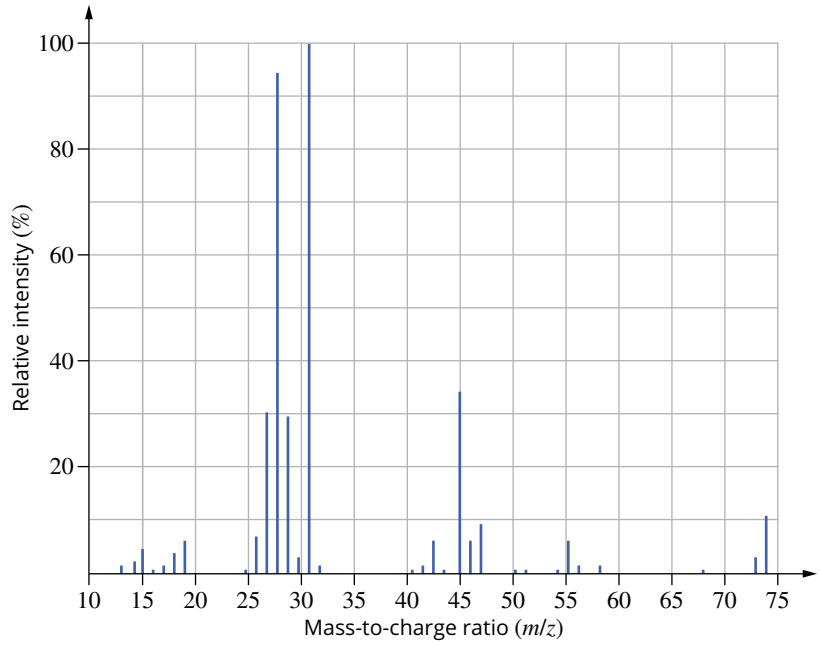
FIGURE 11.6.3 IR spectrum of liquid ethanol

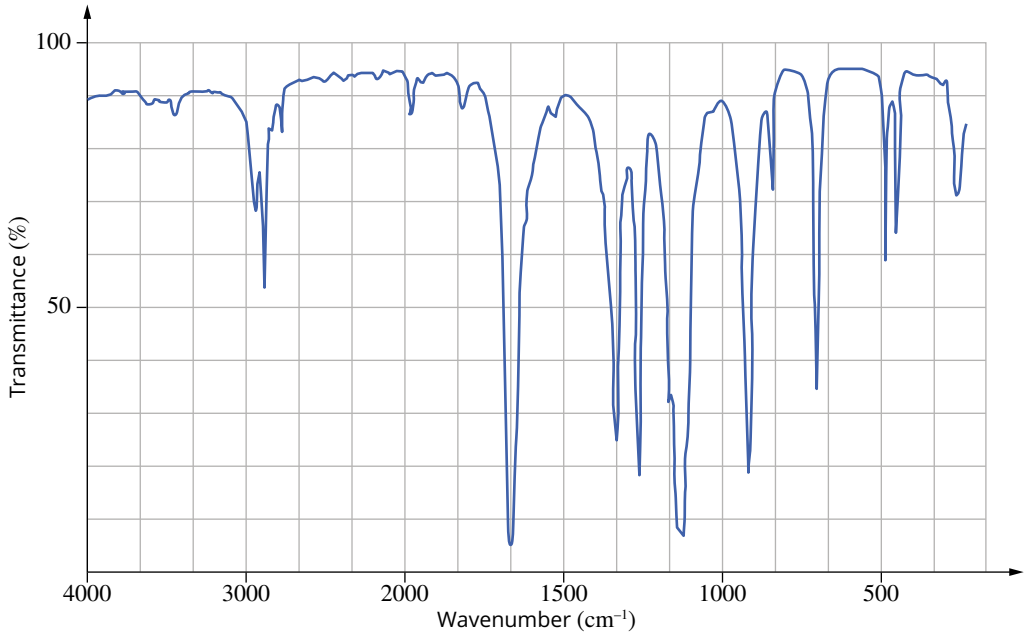
When each piece of evidence from analysing the different spectra is put together, you can see that the structure must be CH_3CH_2OH. Each of the spectra contains the peaks expected of ethanol, and none of the spectra contains information that is inconsistent with ethanol.

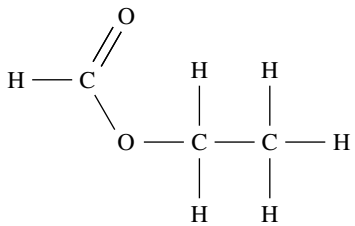
Worked example 11.6.1

DETERMINING MOLECULAR STRUCTURE FROM SPECTRAL ANALYSIS

A sweet-smelling liquid has an empirical formula of $C_3H_6O_2$. Chemical tests show that the compound is not an aldehyde or a ketone. Use this information and the mass and IR spectra provided to deduce the structure and name of the compound.



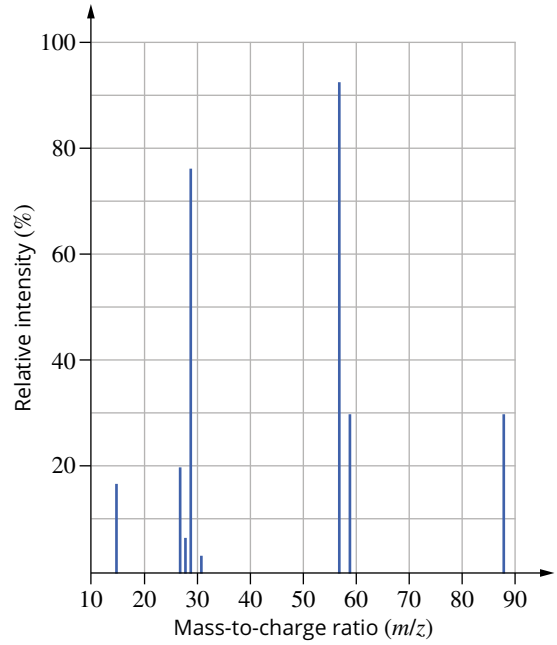


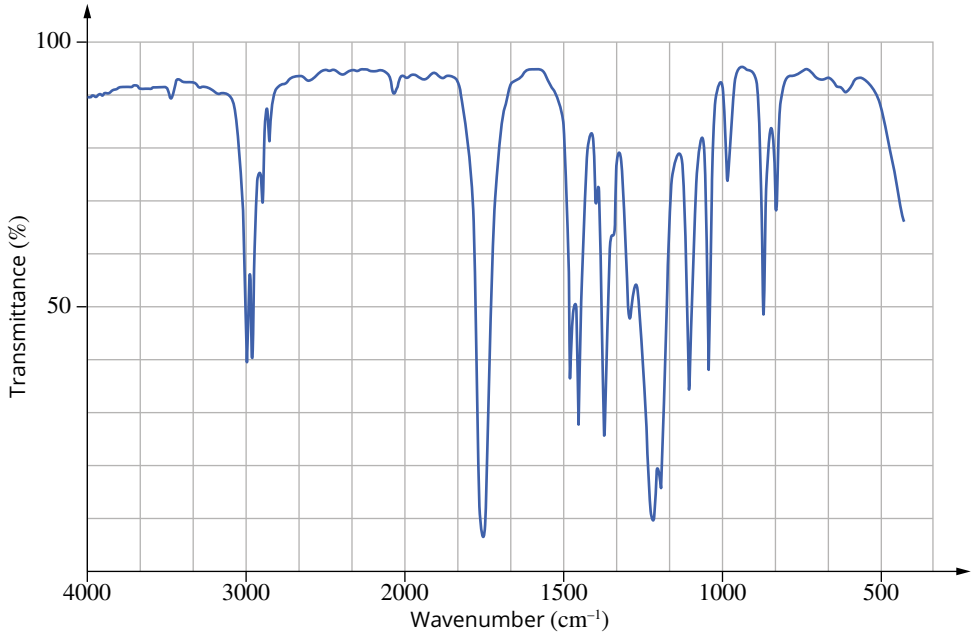
Thinking	Working
Use the mass spectrum to identify the molecular ion and relative molecular mass.	The peak with the largest mass-to-charge ratio is at $m/z = 74$, so the relative molecular mass is 74. This mass is consistent with the molecular formula of $C_3H_6O_2$. According to Table 11.3.1 on page 437, the peaks can be interpreted as follows: $m/z = 45$ correlates to $CH_3CH_2O^+$ or $COOH^+$ $m/z = 28$ correlates to CO^+
Use the IR spectrum to identify functional groups present in the compound. (Refer to Table 11.5.3 on page 453.)	The IR spectrum shows a strong absorption band at 1700 cm^{-1}, suggesting the presence of a C=O bond, and hence a carbonyl group. The IR spectrum does not contain a strong, broad absorption in the range of 2500–3300 cm^{-1}, indicating there is no O–H bond in the molecule.
Use the data from the spectra to deduce the structure of the compound.	The data provided by the spectra shows that: • the molecular formula of the compound is $C_3H_6O_2$ • the mass spectrum also shows peaks correlating to the following possible fragments: $CH_3CH_2O^+$ or $COOH^+$ and CO^+ • the IR spectrum shows the presence of a C=O, carbonyl group but no hydroxyl group, therefore the compound must be an ester with a methyl group attached. A structure consistent with this data is: 
Name the compound.	The compound must be ethyl methanoate.

➤ Try yourself 11.6.1

DETERMINING MOLECULAR STRUCTURE FROM SPECTRAL ANALYSIS

A sweet-smelling liquid has an empirical formula of C_2H_4O. Chemical tests show that the compound is not an aldehyde or ketone. Use this information and the mass and IR spectra provided to deduce the structure and name of the compound.





11.6 Review

SUMMARY

- A combination of information derived from mass spectrometry and infrared spectroscopy can be used to determine the molecular structure of organic compounds.
- The molecular formula of a molecule can be determined from its mass spectrum if its empirical formula is known.
- The infrared spectrum of a compound provides evidence about functional groups present in a molecule.

KEY QUESTIONS

Retrieval

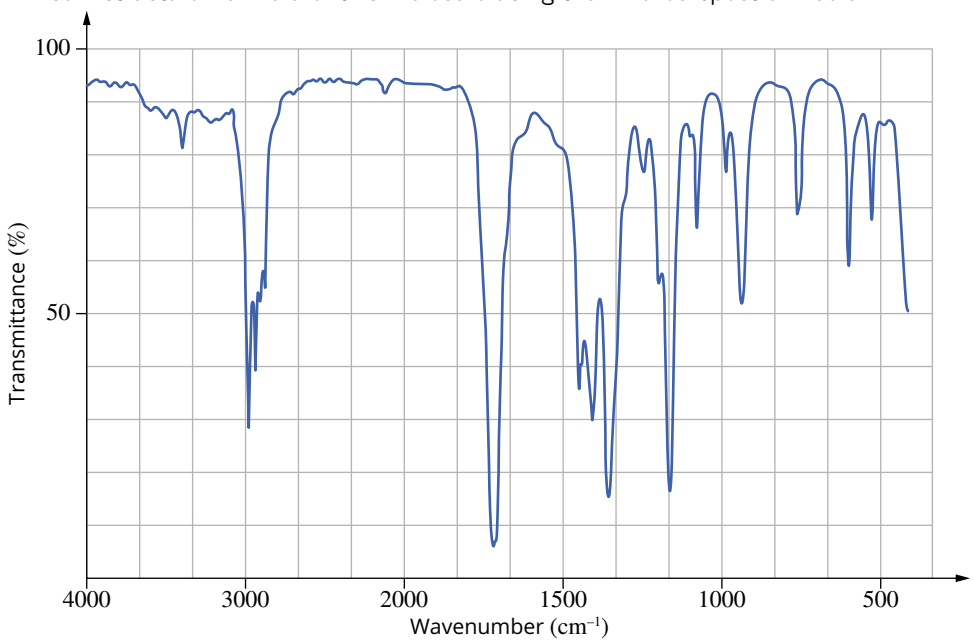
1 State which technique would be used to determine the functional groups in a sample.

Comprehension

2 Explain the advantage of combining different analysis techniques.

Analysis

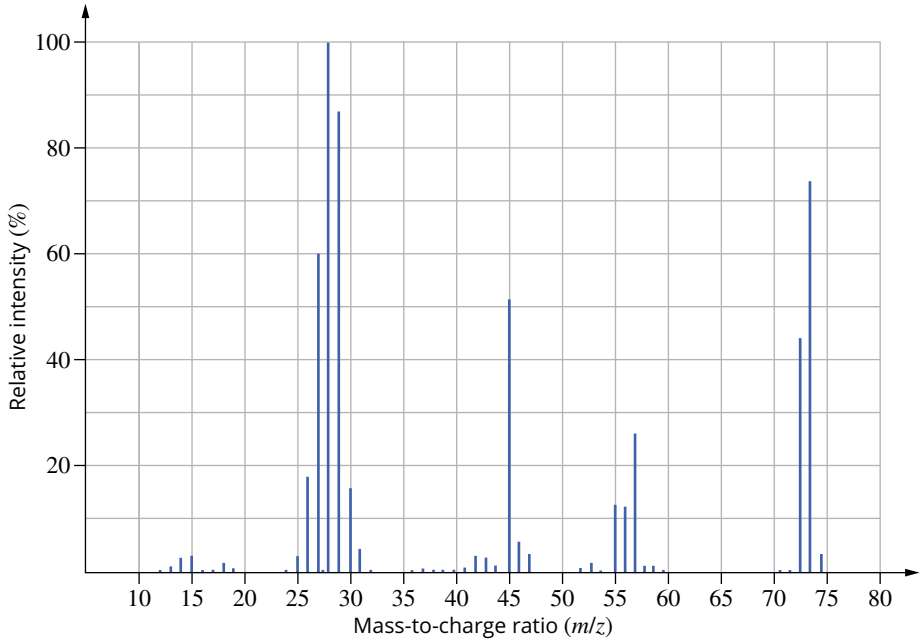
3 An industrial solvent has the molecular formula C_4H_8O. Determine the semistructural formula of this molecule using the infrared spectrum below.

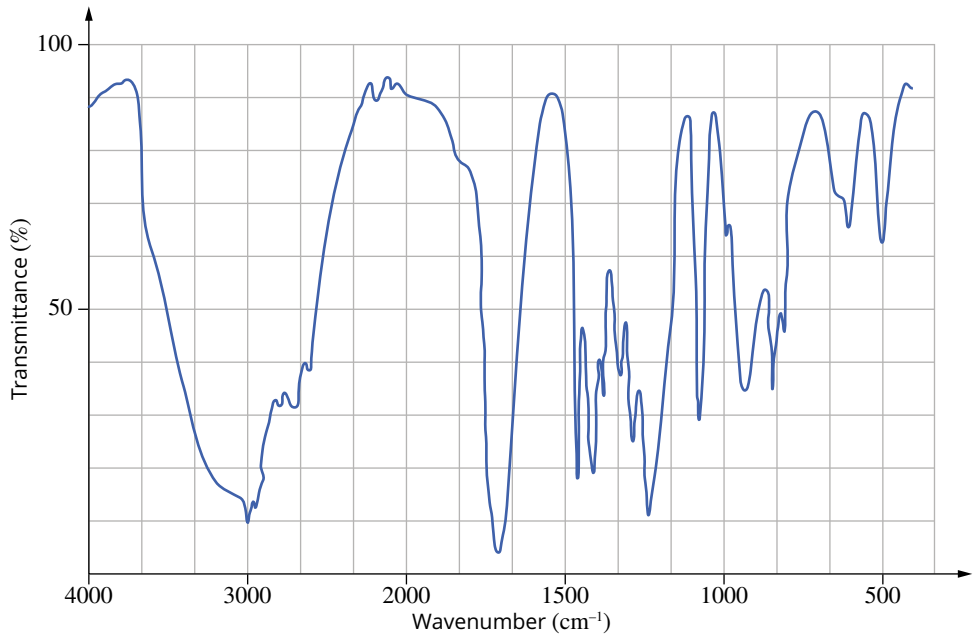


continued over page

11.6 Review *continued*

4 An unidentified organic compound has a structural formula of $C_3H_6O_2$. Determine the name of the compound using this information and the mass and IR spectra below.





Chapter review

11

KEY TERMS

absorbance
absorption bands
adsorption
agarose
amphoteric
base peak
calibration curve
chromatogram
chromatography
column chromatography
components
Coomassie blue dye
crystals
Dalton
denature
desorption
diffraction
diffraction pattern
electromagnetic spectrum
electron density
electron density map
eluent
fragmentation
fingerprint region
gel electrophoresis
high-performance liquid chromatography (HPLC)
infrared (IR) spectroscopy
isotope
mass spectrometer
mass spectrometry
mass spectrum
mobile phase
molecular ion
molecular ion peak
origin
paper chromatography
polyacrylamide gels (PAGE)
Protein Data Bank (PDB)
proteomes
qualitative analysis
relative intensity
retardation factor (R_f)
retention time (R_t)
reversed-phase HPLC
sodium dodecyl sulfate
solvent front
spiking
stationary phase
thin-layer chromatography (TLC)
transmittance
vibrational energy levels
wavenumber
X-ray crystallography

KEY QUESTIONS

Retrieval

1 In the mass spectrum of an organic compound, the signal produced by the unfragmented molecular ion and the signal produced by the most abundant particle correspond respectively to the:
- **A** main ion peak and base peak
- **B** parent (molecular) ion peak and base peak
- **C** base peak and parent (molecular) ion peak
- **D** parent (molecular) ion peak and main ion peak.

2 Proteins can be seen directly in gels by:
- **A** staining them with a dye
- **B** using an electron microscope only
- **C** measuring their molecular weight
- **D** none of the options provided in this list.

3 Consider the following changes that could be made to an analysis to be performed by HPLC. Select the change that is most likely to increase the retention time of a component.
- **A** reducing the length of the column
- **B** using a less tightly packed column
- **C** reducing the pressure of the mobile phase
- **D** increasing the amount of sample injected into the instrument

4 Define each of the following terms.
- **a** adsorption
- **b** chromatography
- **c** desorption
- **d** eluent
- **e** mobile phase
- **f** stationary phase
- **g** retention time

5 State the absorption bands in an infrared spectrum that are used to indicate the presence of:
- **a** a hydroxyl group
- **b** an amide group
- **c** an aldehyde
- **d** a chloroalkane.

6 Crystal quality in X-ray crystallography is very important. State the factors that need to be taken into consideration when using crystals for X-ray crystallography.

7 Identify the analysis technique that would be preferred when:
- **a** determining the molar mass of a compound
- **b** differentiating between compounds with different functional groups
- **c** differentiating between compounds with the same functional group but different molecular masses.

8 The following table shows the steps in gel electrophoresis. Number the steps in the correct order.

Step	Number
As time progresses during the experiment, smaller fragments move faster and further through the gel than larger fragments. This sorts the fragments by size.	
Each protein sample is loaded separately into one of the wells within the gel. A standard protein mixture (called a protein ladder) is also run on the gel for comparison with the samples.	
A buffer solution is added to the electrophoresis chamber, covering the gel uniformly.	
A power source is attached to the electrophoresis bath and switched on. The electrical current causes the negatively charged DNA fragments to migrate through the gel towards the positive terminal of the chamber.	
The protein fragments are detected by applying Coomassie blue dye that binds to protein.	
The gel is placed into a gel electrophoresis chamber, with the wells situated at the negative terminal of the chamber.	
An electrophoresis gel is prepared. It has a jelly-like texture and is usually composed of polyacrylamide gels. The gel is rectangular in shape and contains small wells (holes) at one end.	

Comprehension

9 A sample containing compounds A, B and C is mixed with ethanol and applied to the top of an HPLC instrument that uses ethanol as the solvent and alumina as the stationary phase. The three compounds have the following properties.

- Solubility in ethanol: C is much more soluble than A and B. A and B are equally soluble.
- Adsorption to alumina: B is more strongly absorbed than A. C is least strongly adsorbed.

Identify which of the following lists shows the retention times of the components, from lowest to highest.

A A, B, C
B B, A, C
C C, A, B
D C, B, A

10 The concentration of a substance is most accurately determined in high-performance liquid chromatography (HPLC) by measuring:

A R_f value
B peak area
C peak height
D retention time.

11 More energy is required to vibrate:

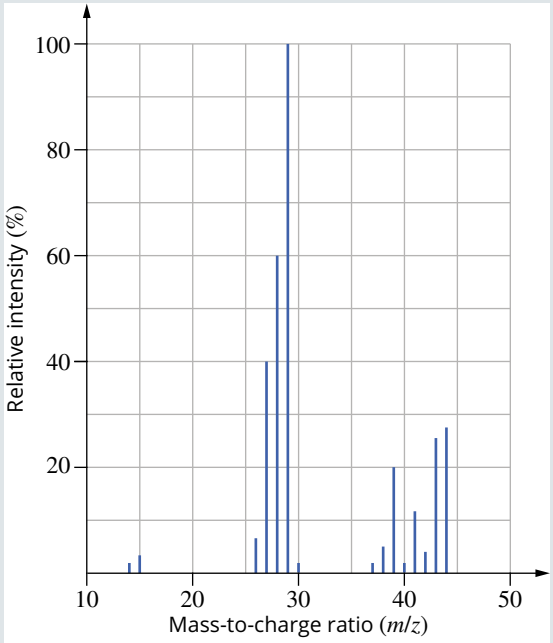
A C–C compared to C=C
B C–O compared to C–H
C C=C compared to C≡C
D C–Cl compared to C–Br.

12 Select from the following list the correct role of sodium dodecyl sulfate (SDS) in SDS-PAGE.

A impart equal mass to all proteins
B impart overall negative charge to all proteins
C denature proteins and impart net positive charge
D denature proteins and impart net negative charge

13 List the bonds in 2-bromoethan-1-ol in order from the bond that will absorb the lowest energy infrared radiation to the bond that will absorb the highest energy infrared radiation.

14 The mass spectrum of an alkane is shown in the following figure. Identify the formula of molecular and base ions.



15 Automatic detectors that use mass spectrometry are often employed by security guards and police officers to search for explosives and illicit drugs. They are powered by a computer that can tell if an illegal substance is present and identify what it is. Explain what the computer should look for in the mass spectrum.

Analysis

16 Explain how each of the techniques of IR spectroscopy, mass spectrometry, gel electrophoresis and X-ray crystallography can be used in the identification of an organic molecule.

17 An unknown compound has a molecular formula of C_3H_6O. Its IR spectrum has a strong, sharp absorption at 1750 cm^{-1}. Identify the possible compounds that could give this absorption band.

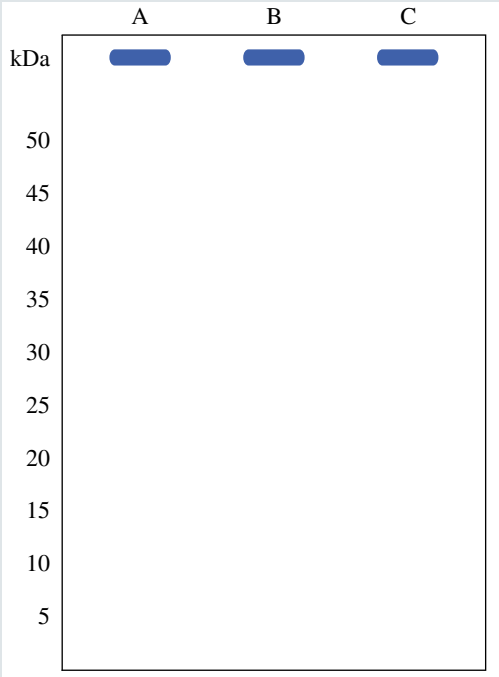
18 **a** The average molecular mass of an amino acid is 120 Dalton. Use the following calculation to determine individual polypeptides in each of samples **i**, **ii** and **iii**: amount of amino acids in polypeptide × average molecular mass of amino acid ÷ 1000 = average mass in kilo Dalton (kDA)

i well A was loaded with a sample composed of four different types of polypeptides (100 amino acids, 175 amino acids, 250 amino acids and 300 amino acids)

ii well B was loaded with a sample composed of three types of polypeptides (200 amino acids, 250 amino acids and 350 amino acids)

iii well C was loaded with a sample composed of five different types of polypeptides (100 amino acids, 150 amino acids, 175 amino acids, 250 amino acids and 300 amnio acids)

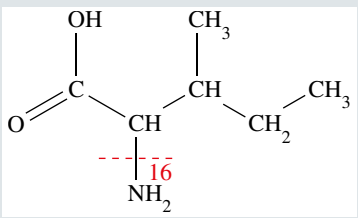
b On the following diagram, use your calculations to draw the predicted gel electrophoresis results.



c Each lane in the diagram represents the proteins from different types of drugs. Identify which two drugs would be most closely related.

d Some of the proteins have the same molecular mass. Explain whether they are the same protein.

19 The following diagram shows the structure of the amino acid isoleucine.



a State its molecular formula.

b Calculate its molecular mass.

c Identify the chiral centres by marking them with an asterisk (*).

d The mass spectrum of isoleucine includes a signal at $m/z = 16$. The dotted line shows how cleavage might occur to produce the $[NH_2]^+$ fragment that would account for this signal.

For each of the following m/z values from the spectrum of isoleucine, write the formula of the fragment ion likely to be responsible and add a dotted line to your diagram to show a simple bond cleavage that could produce this fragment ion.

i $m/z = 15$

ii $m/z = 29$

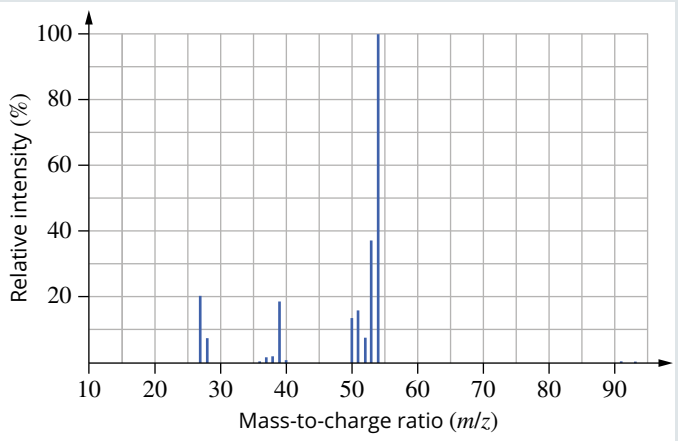
iii $m/z = 57$

e The base peak in the mass spectrum is at $m/z = 86$.

i Explain what is meant by the 'base peak' in a mass spectrum.

ii Suggest the fragment that has been lost from the molecular ion to produce the ion responsible for the base peak.

20 Using the mass spectrum of an alkyne shown below, determine the molecular formula of the alkyne.



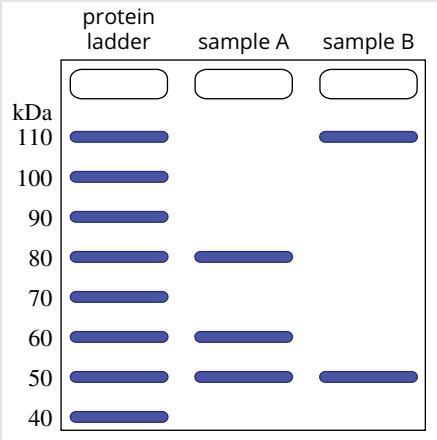
21 Identify the advantages of HPLC for the analysis of drugs compared to an analysis technique based on column chromatography.

22 Australian wines are routinely tested for ethanol content. A quick and reliable method for testing is gas-liquid chromatography (GLC). The peak areas produced by a sample of wine and a number of standard solutions of ethanol are shown in the following table.

	Ethanol content (%)	Relative ethanol peak area
wine	?	82 400
standard 1	4.00	31 200
standard 2	8.00	62 900
standard 3	12.00	94 200
standard 4	16.00	125 700

a Plot a calibration curve of concentration of ethanol against peak area.
b Determine the percentage of ethanol in the wine sample.
c Describe why it is not necessary to measure the peak areas produced by a number of standards.

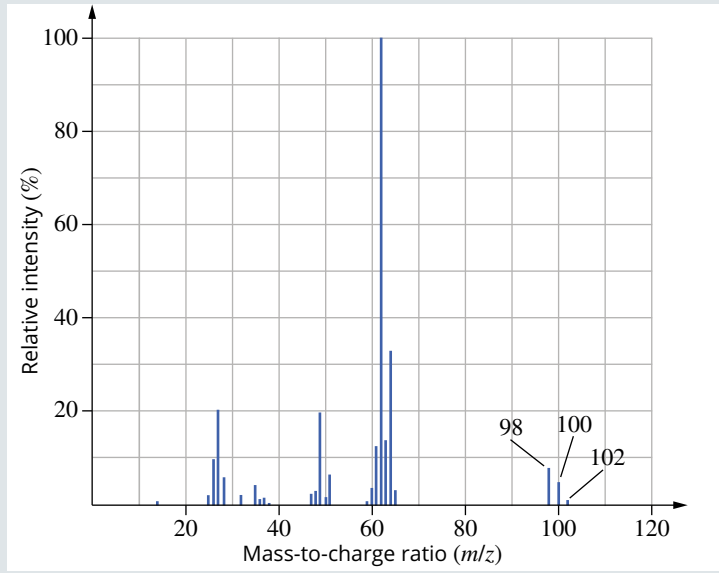
23 A urine protein electrophoresis is a test used by medical practitioners to determine if there is protein in a patient's urine. Proteins are found in the blood of healthy people but should not be detected in urine. The presence of beta globulin (50 kDa) indicates an iron deficiency, albumin (80 kDA) indicates dehydration, and the alpha globulins (110 kDa) indicate kidney disease. The following figure shows a protein ladder and urine samples from two patients.



a Using the information already provided, interpret the results on the urine protein electrophoresis.
b Determine whether any other proteins can be identified.

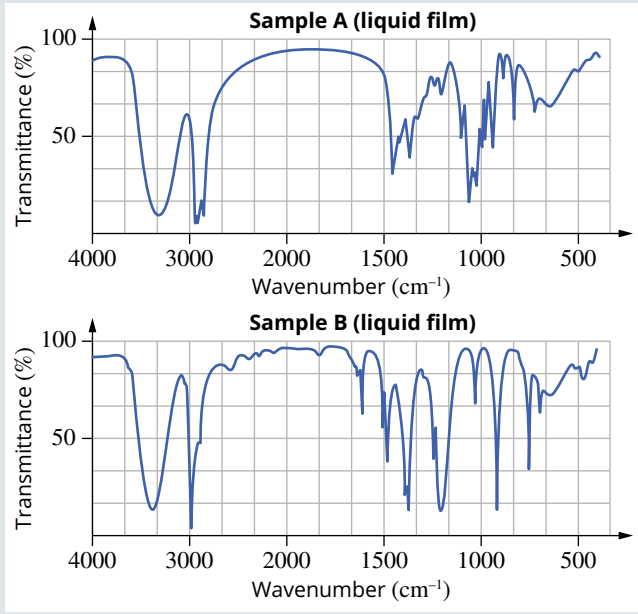
24 A number of compounds with different structures may form molecular ions with the same *m/z* ratio. Give the molecular formula of a hydrocarbon that would give an *m/z* value of 58 if the molecule:
a is an alkane
b contains one oxygen atom
c contains two amine groups.

25 The mass spectrum of dichloroethane is shown below.



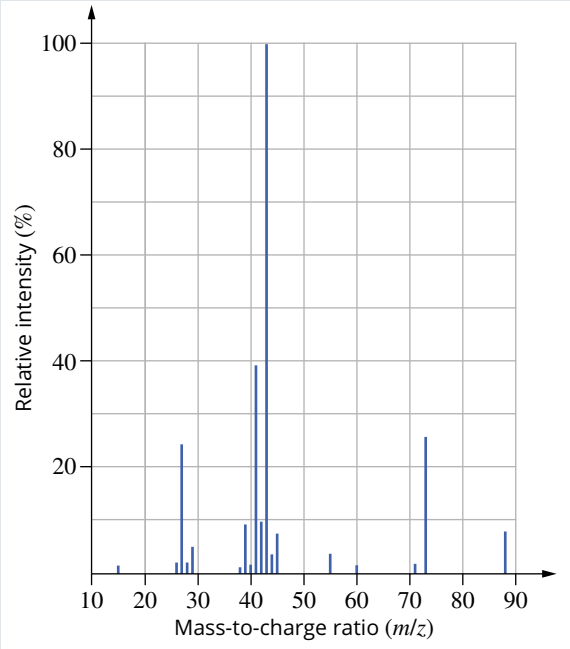
a Explain why the mass spectrum has the peaks with the following *m/z* values.
i 98
ii 100
iii 102
b Explain why the peak with *m/z* = 98 is the largest of these three peaks.
c Write a possible formula for the ion responsible for the base peak.

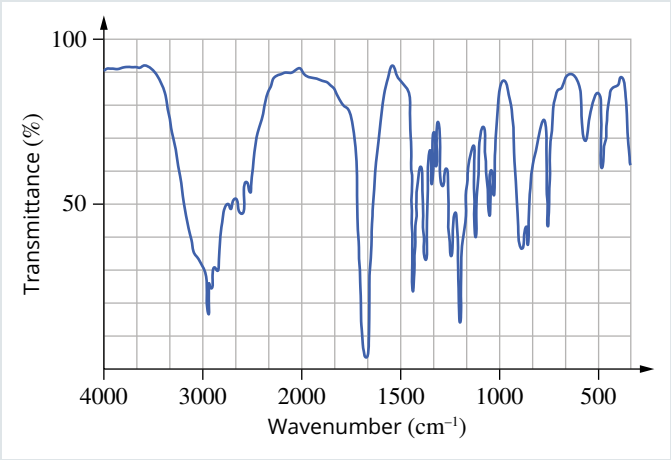
26 The IR spectra of two liquid samples, A and B, are provided below.



a Explain how these two spectra confirm that both samples are alcohols.
b Explain whether these two spectra are of the same compound.

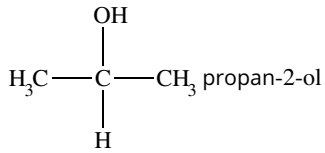
27 A combination of different instrumental techniques was used to analyse a compound that had an empirical formula of C_2H_4O. The mass and IR spectra of this compound are provided below.

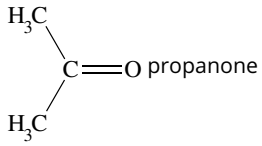




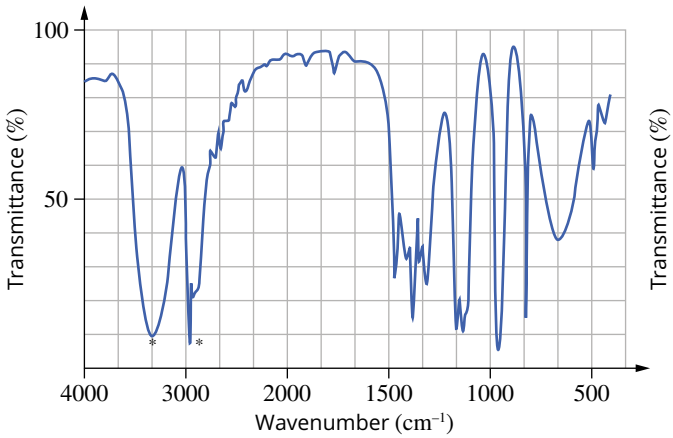
Consider the information about the compound from each of these spectra and determine the possible semistructural formula and name of the compound.

28 The structures of propan-2-ol and propanone are shown below. The infrared spectra of these compounds are labelled IR spectrum A and IR spectrum B.

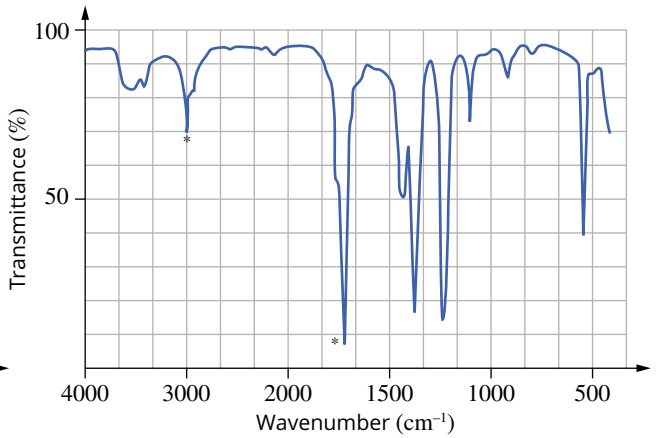




IR spectrum A



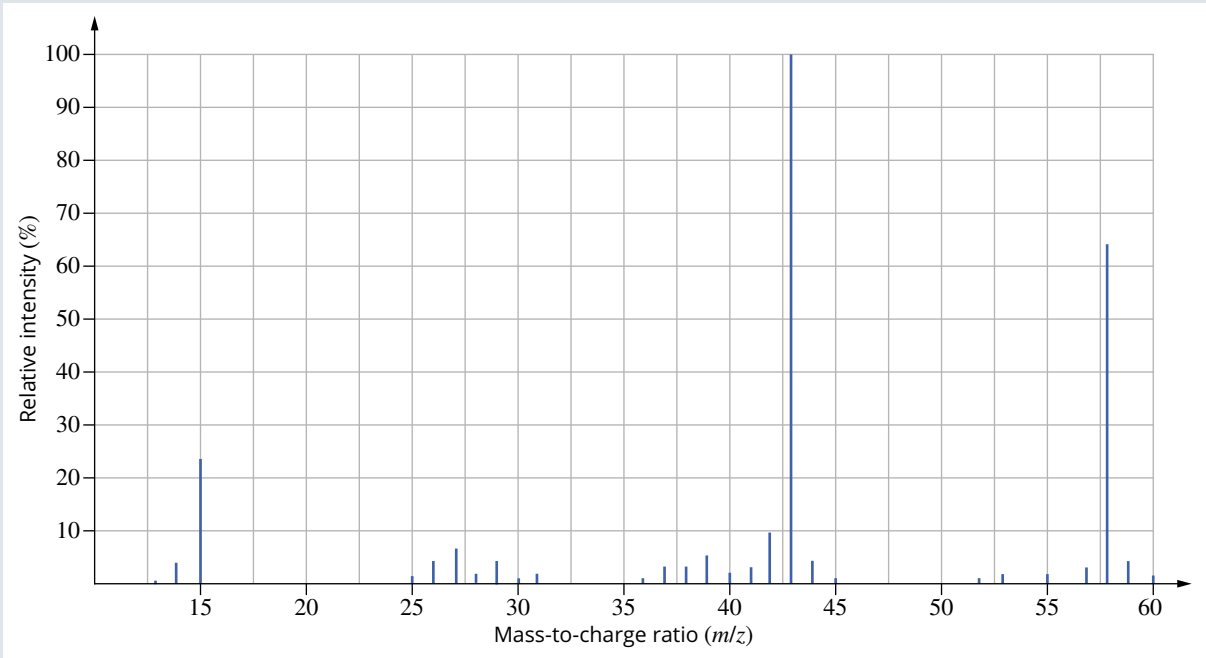
IR spectrum B



a Identify the bonds that produced the IR absorption bands marked with an asterisk (*) in each spectrum.

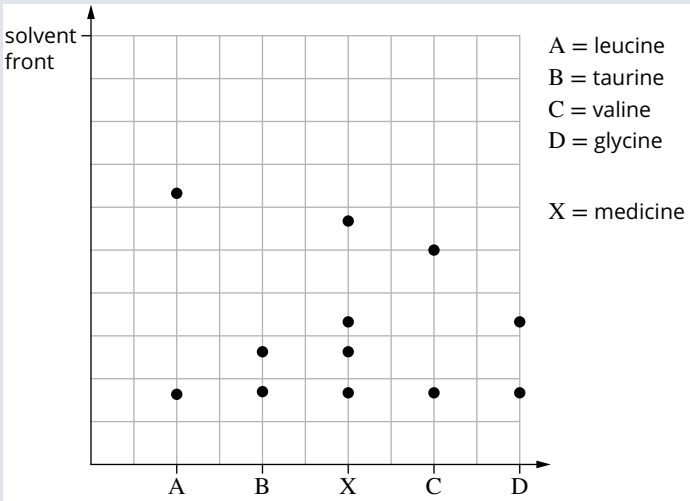
b Determine which spectrum represents which molecule.

29 The mass spectrum of propanone is shown below.



a Identify the mass of the molecular ion.
b Explain what information this provides about the molecule.
c Propose a formula for the molecular fragment that produces the peak at $m/z = 43$.

30 The following figure shows a thin-layer chromatogram of amino acids in a medicine.

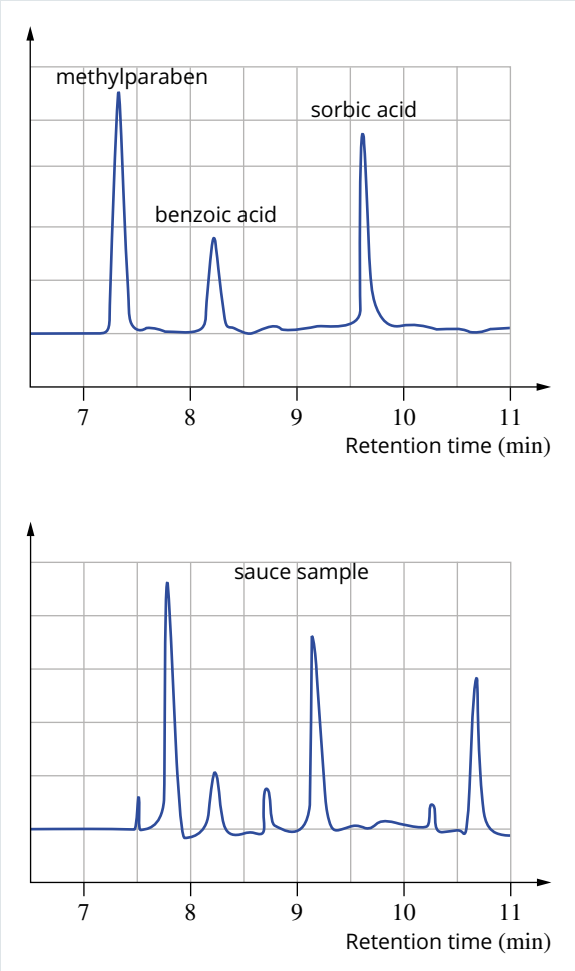


a Identify the amino acids in the medicine.
b Amino acids are colourless. State a technique that could be used to visualise the amino acid spots.
c Calculate the R_f value of taurine.
d Identify the amino acid that is bonded least strongly to the mobile phase.

31 Crystals for X-ray crystallography can be prepared under different conditions. Discuss whether the crystals would have the same shape if prepared under different conditions.

32 A chemist tried to make ethyl methanoate by reacting two compounds, A and B, with sulfuric acid.
a Identify the distinguishing features that the chemist will see in an infrared spectrum for ethyl methanoate.
b Describe how the infrared spectrum for compounds A and B would differ.
c State and explain how the purity of the made methyl ethanoate can be tested.

33 A mixture of three common food preservatives was analysed using high-performance liquid chromatography (HPLC). A sample of tomato sauce was prepared by dissolving 1.50 g of the sauce in a total of 10.0 mL of distilled water in a volumetric flask. This tomato sauce solution was then analysed using the same mobile and stationary phases under the same conditions. The resultant chromatograms are shown below.

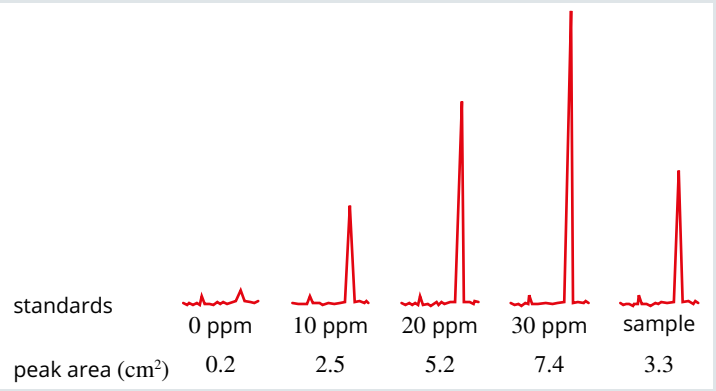


a Given that they are all equally soluble in the mobile phase, identify and explain which of the three preservatives adsorbs most strongly on the stationary phase.

b Explain which of the preservatives appear to be present in the sauce sample.

34 An empty drum of an insecticide was found close to a major reservoir. The Environment Protection Authority analysed the water in the resevoir to determine whether it was contaminated and therefore a threat to human health. (Concentrations of insecticide above 10 ppm are a threat to human health.)

Standard solutions of the insecticide in water at concentrations of 0 ppm, 10 ppm, 20 ppm and 30 ppm were prepared and analysed using high-performance liquid chromatography (HPLC).
A sample of the reservoir water was also analysed under the same conditions.



a Construct a calibration graph for the analysis of the insecticide. Use your graph to determine the concentration of the insecticide in the water sample.

b State and explain whether the reservoir water is safe to drink.

c Explain why a small peak is observed with the 0 ppm standard of insecticide.

35 Explain how X-ray crystallography works and how it is used to determine the structure of compounds.

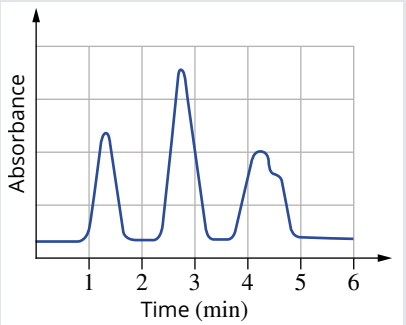
36 Explain what features in an IR spectra could distinguish between the following pairs of compounds.

a propanol and propanoic acid

b propanol and ethanol

c propane and propene

37 A herbal tea extract was analysed using high-performance liquid chromatography (HPLC). The following chromatogram was obtained.



a Explain what information chemists can obtain from this chromatogram.

b Identify how many components are evident.

c Briefly explain how the components are separated by HPLC.



CHAPTER

12 Chemical synthesis



In this chapter, you will see how chemical concepts and reactions are relevant within industrial applications. The industrial production of many chemicals such as paint, plastics, pharmaceuticals and foods may involve organic reactions.

You have identified that some reactions are reversible and that Le Châtelier's principle can be applied to understand how the position of a chemical equilibrium can be changed. The fact that many reactions do not proceed to completion has serious consequences on the efficiency of chemical manufacturing industries. You will learn how reaction conditions for industrial process are adjusted to ensure optimum efficiency by considering both the rate of the reaction and the equilibrium yield.

In addition, you will explore how fuel cells use the chemical energy of hydrogen or other fuels to cleanly and efficiently generate electricity for use as a source of power for transport and for emergency back-up power applications.

Syllabus subject matter

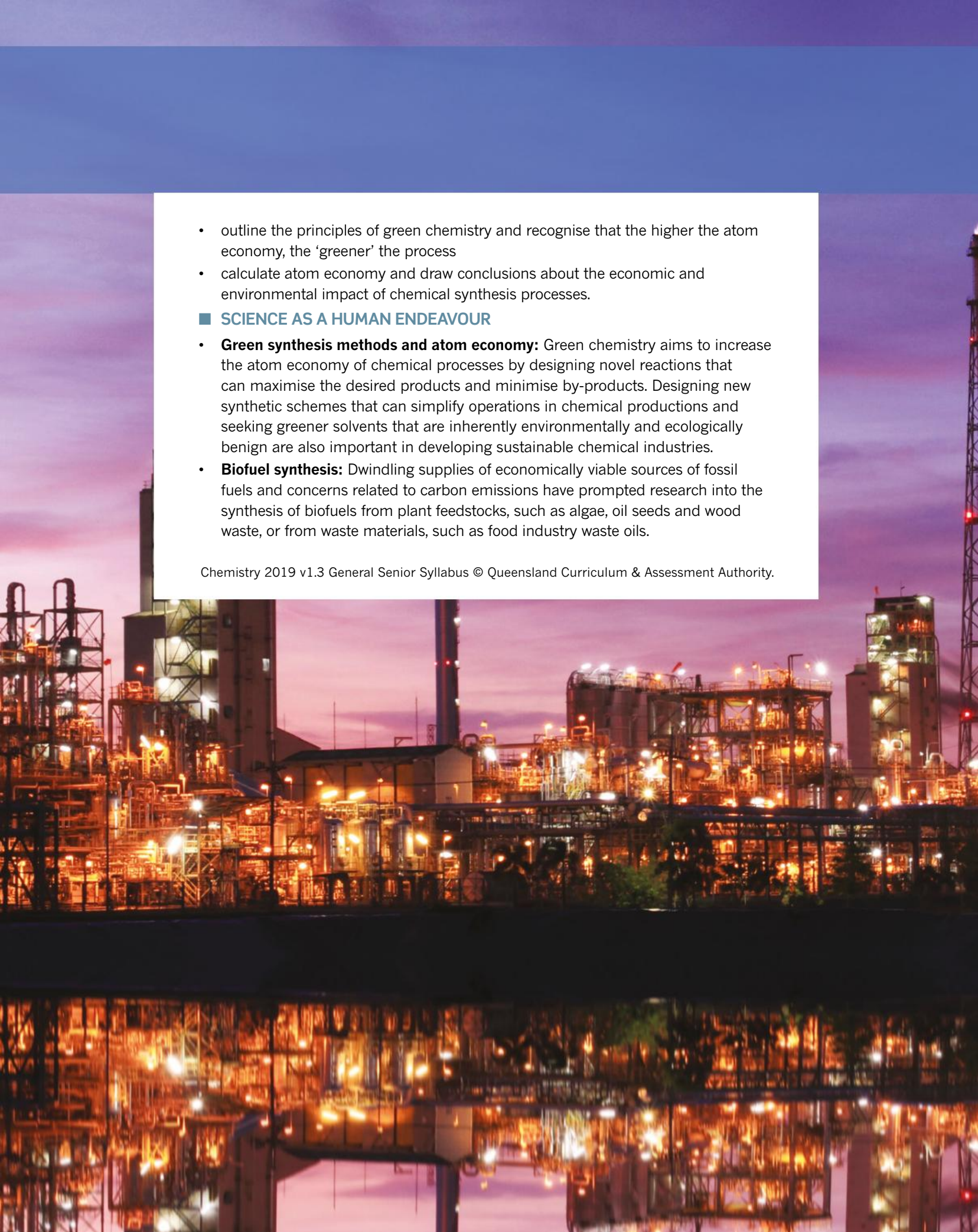
Topic 2 • Chemical synthesis and design

CHEMICAL SYNTHESIS

- appreciate that chemical synthesis involves the selection of particular reagents to form a product with specific properties
- understand that reagents and reaction conditions are chosen to optimise the yield and rate for chemical synthesis processes, including the production of ammonia (Haber process), sulfuric acid (contact process) and biodiesel (base-catalysed and lipase-catalysed methods)
- understand that fuels, including biodiesel, ethanol and hydrogen, can be synthesised from a range of chemical reactions including addition, oxidation and esterification
- understand that enzymes can be used on an industrial scale for chemical synthesis to achieve an economically viable rate, including fermentation to produce ethanol and lipase-catalysed transesterification to produce biodiesel
- describe, using equations, the production of ethanol from fermentation and the hydration of ethene
- describe, using equations, the transesterification of triglycerides to produce biodiesel
- discuss, using diagrams and relevant half-equations, the operation of a hydrogen fuel cell under acidic and alkaline conditions
- calculate the yield of chemical synthesis reactions by comparing stoichiometric quantities with actual quantities and by determining limiting reagents.

GREEN CHEMISTRY

- appreciate that green chemistry principles include the design of chemical synthesis processes that use renewable raw materials, limit the use of potentially harmful solvents and minimise the amount of unwanted products



- outline the principles of green chemistry and recognise that the higher the atom economy, the 'greener' the process
- calculate atom economy and draw conclusions about the economic and environmental impact of chemical synthesis processes.

SCIENCE AS A HUMAN ENDEAVOUR

- **Green synthesis methods and atom economy:** Green chemistry aims to increase the atom economy of chemical processes by designing novel reactions that can maximise the desired products and minimise by-products. Designing new synthetic schemes that can simplify operations in chemical productions and seeking greener solvents that are inherently environmentally and ecologically benign are also important in developing sustainable chemical industries.
- **Biofuel synthesis:** Dwindling supplies of economically viable sources of fossil fuels and concerns related to carbon emissions have prompted research into the synthesis of biofuels from plant feedstocks, such as algae, oil seeds and wood waste, or from waste materials, such as food industry waste oils.

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12.1 Reaction pathways

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- appreciate that chemical synthesis involves the selection of particular reagents to form a product with specific properties
- describe the retrosynthetic approach to chemical synthesis
- explain the benefits of retrosynthetic analysis
- appreciate how other considerations, including the rate of the reaction and cost factors, influence the conditions of an industrial scale reaction.



Organic chemists are highly skilled at developing compounds, such as new pharmaceuticals, polymers or nanomaterials, with the right properties for a purpose. Once the desired compound has been identified, chemists must devise a way to make it. This necessitates that chemists design an efficient reaction pathway to convert readily available starting materials into the more complex product required.

In Chapter 9 you identified that alternate pathways exist to synthesise many chemical products either from the same starting reactant or from a different reactant. In planning a synthetic pathway, chemists find it easier to start the planning from the target molecule and work backwards to simpler molecules. This is known as a **retrosynthetic pathway** and is used to identify possible pathways to successively simpler compounds until a suitable starting reagent can be identified. This module will outline the key features of a retrosynthetic pathway and the considerations of a synthetic chemist when planning the manufacture of a compound.

GETTING FROM REACTANTS TO PRODUCTS

One of the essential features of the retrosynthetic process is recognition of the bond disconnections that allow the molecule to be broken down into key intermediate compounds. Since no reaction generally has a 100% **percentage yield**, the most effective pathway should consider a **convergent synthesis** to reduce the number of steps in the pathway. In this way, the overall yield can be improved. In addition, modern chemists are also concerned with devising the most environmentally friendly synthetic route that minimises waste, uses 'greener' solvents, requires less energy, and helps to conserve the world's resources.

Retrosynthesis

In Chapter 9 the esterification reaction between an alcohol and acids was drawn as shown in Figure 12.1.1.

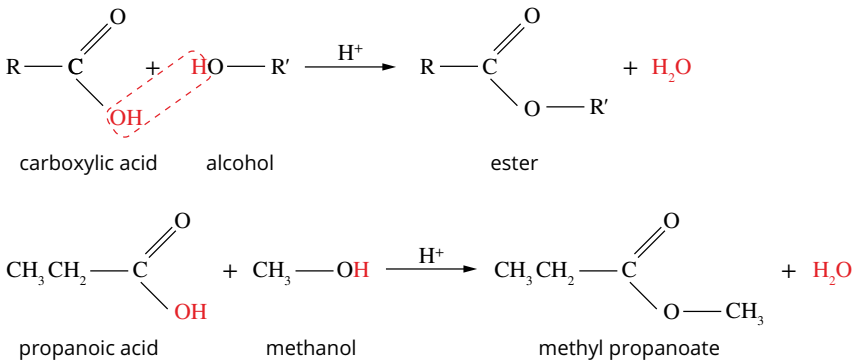


FIGURE 12.1.1 Esterification reaction between propanoic acid and methanol, forming methyl propanoate

When designing a retrosynthetic pathway, the reverse chemical step is represented by an arrow, as shown in Figure 12.1.2a. This enables chemists to identify possible precursors along a multistep pathway. The retrosynthetic representation of the esterification reaction that was shown in Figure 12.1.1 is shown in Figure 12.1.2b.

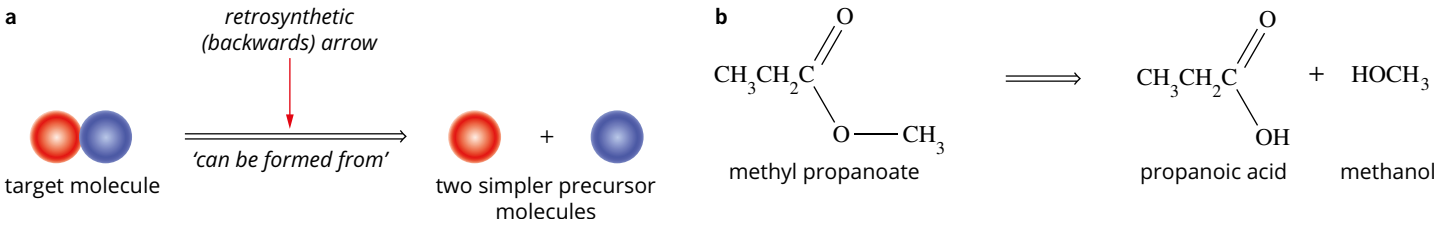


FIGURE 12.1.2 (a) Representation of a retrosynthetic pathway; (b) retrosynthetic step from methyl propanoate to methanol and propanoic acid

Figure 12.1.3 illustrates two pathways to form ibuprofen, one more efficient than the other. In this module, you will learn how to devise reaction pathways for the synthesis of some simple organic compounds by utilising the reactions covered in Chapter 9.

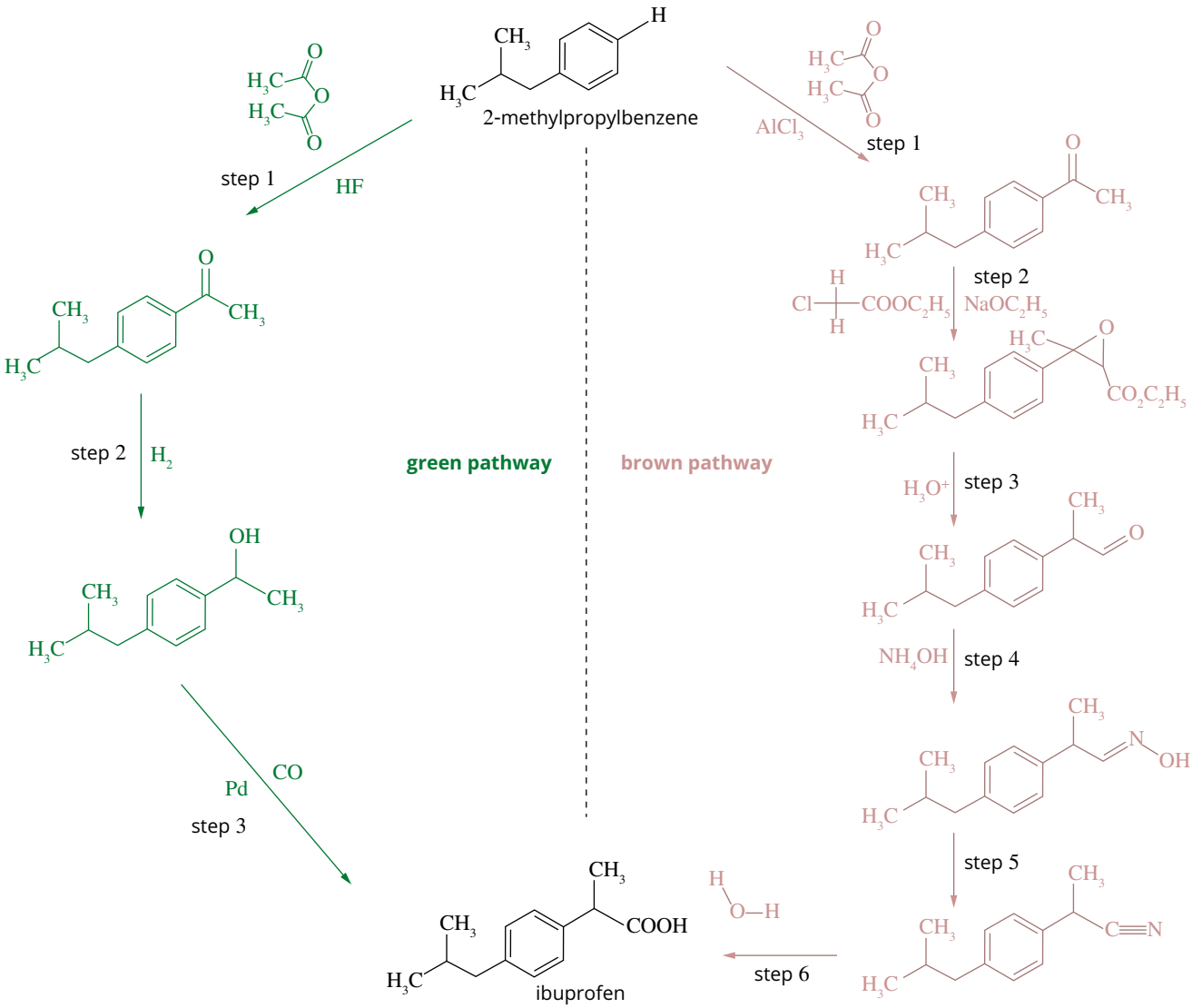


FIGURE 12.1.3 Two alternative reaction pathways for the production of ibuprofen. The green pathway is more efficient than the brown one. In the green pathway, fewer reactants are needed and a higher proportion of atoms in the reactants are present in the final product. This means that there is less waste in the green pathway.

Simple reaction pathways

Reaction pathways of ethane and ethene are shown in Figure 12.1.4. A reaction pathway is a series of one or more steps, or reactions, that can be used to convert a reactant containing certain functional groups to a desired product with different functional groups. Pathways for other alkanes can be constructed using the same overall process with similar inorganic reactants and reaction conditions.

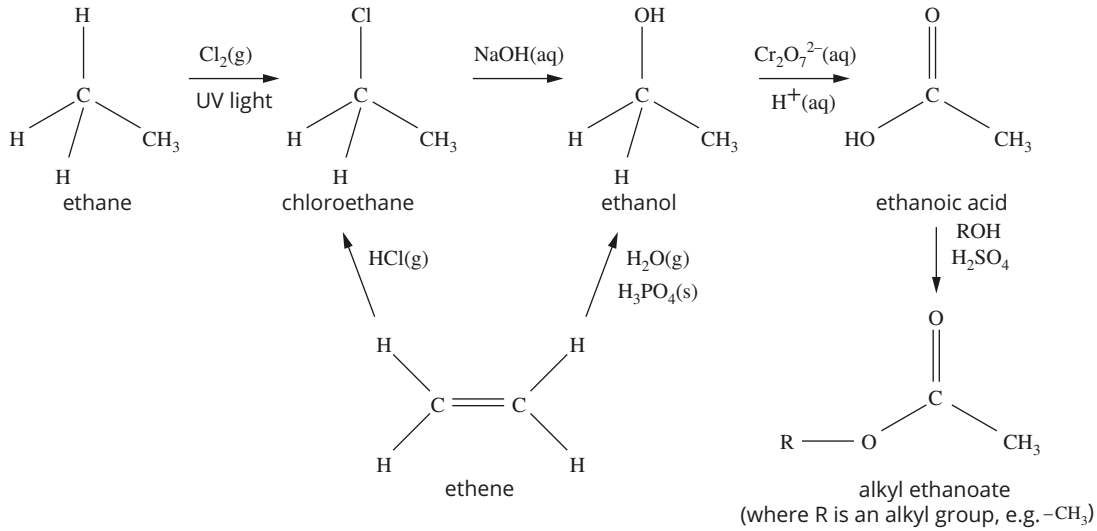


FIGURE 12.1.4 Some reaction pathways based on ethane and ethene. Similar reaction conditions can be used to develop pathways for other members of the alkane and alkene homologous series.

More complex reaction pathways

A close look at the structure of ethyl propanoate, shown in Figure 12.1.5, will show you that it is an ester produced by the condensation reaction between propanoic acid and ethanol.

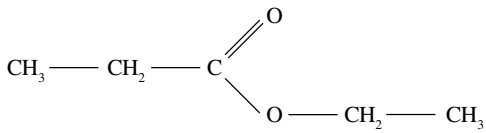


FIGURE 12.1.5 Structure of ethyl propanoate

Suppose you wanted to form ethyl propanoate using only alkanes or alkenes as starting materials. Propanoic acid and ethanol need to be prepared first as described below.

Making ethanol

Ethanol is an alcohol containing two carbon atoms. Ethanol can be synthesised from ethene in two ways: in a single step by the direct addition reaction with water, or in two steps via the intermediate product chloroethane. In this case, the best option is the more direct route, the addition reaction with water. Figure 12.1.6 shows both possible pathways for the production of ethanol from ethene. You can see in each pathway the inorganic reactant is placed above the arrow for each step.

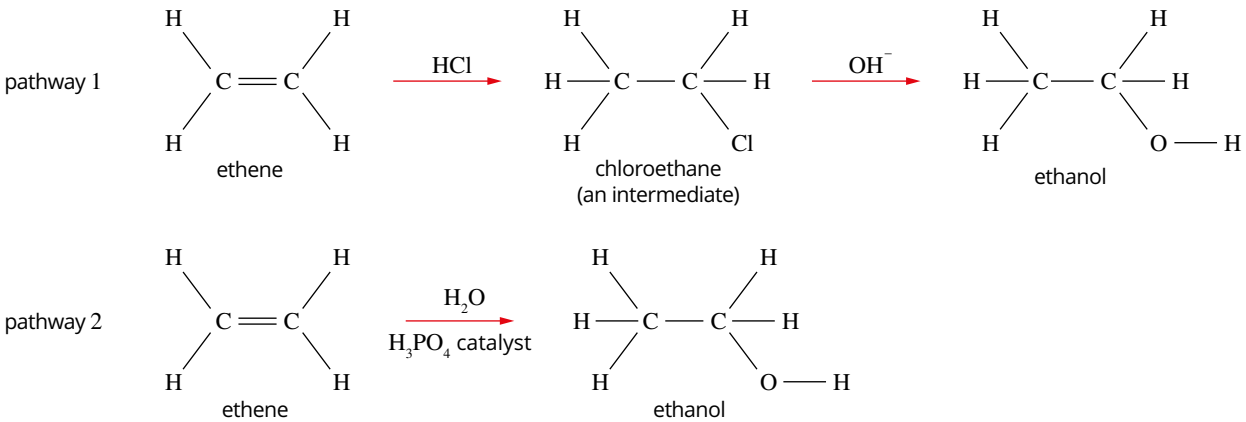


FIGURE 12.1.6 Synthetic pathways for making ethanol from ethene

Making propanoic acid

Propanoic acid is a carboxylic acid containing three carbon atoms. It can be prepared by the pathway shown in Figure 12.1.7. If you work backwards from propanoic acid, you can see that it can be formed from the oxidation of the primary alcohol propan-1-ol. This in turn can be formed by the reaction of 1-chloropropane with sodium hydroxide.

You will recall that 1-chloropropane can be prepared by reacting propane with chlorine. In this way, you can devise the sequence of reactions to reach a particular product. The pathway shown for the preparation of propanoic acid would produce several products, which are separated by fractional distillation.

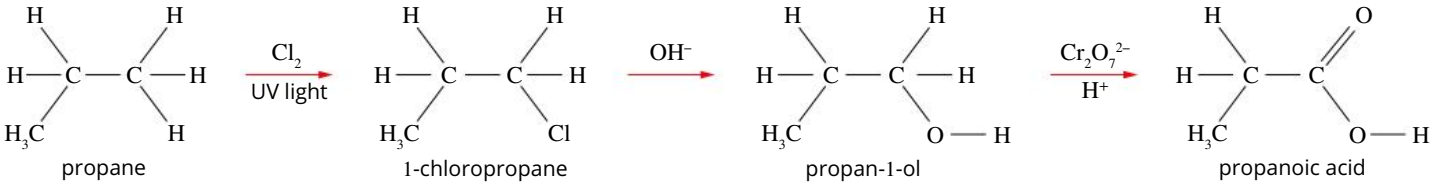


FIGURE 12.1.7 Synthesis of propanoic acid from propene

For the pathway shown in Figure 12.1.7, the substitution reaction of propane is a better choice than an addition reaction of propene. This is because the addition of HCl to propene results in the formation of unwanted 2-chloropropane, as predicted by Markovnikov addition.

Making ethyl propanoate

Having synthesised ethanol and propanoic acid, you can now prepare the ester, ethyl propanoate, using a condensation reaction as shown in Figure 12.1.8.

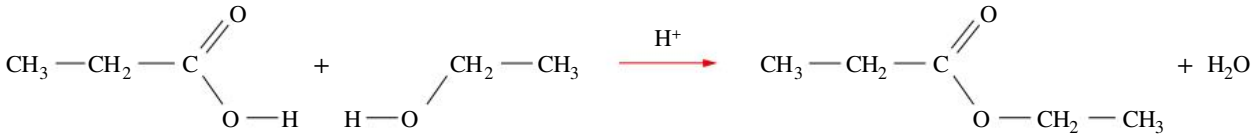


FIGURE 12.1.8 The formation of ethyl propanoate from the condensation reaction of ethanol and propanoic acid

The full reaction pathway for the preparation of ethyl propanoate from ethene and propane via ethanol and propanoic acid is summarised in Figure 12.1.9.

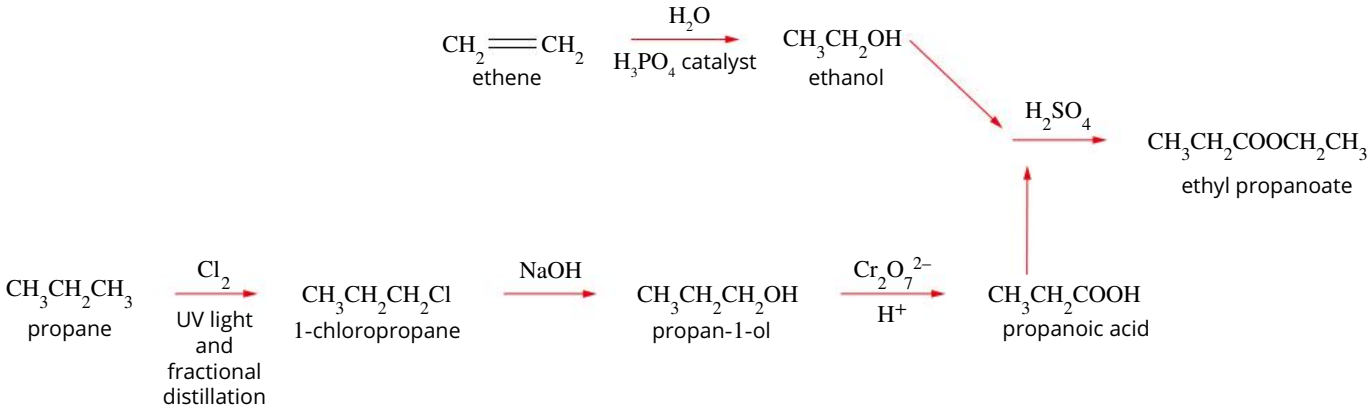


FIGURE 12.1.9 Reaction pathway for the preparation of ethyl propanoate

Other considerations in devising a synthesis

In addition to simply identifying a possible reaction sequence, there are other considerations when planning a reaction pathway, including:

- the equilibrium position of a reaction can have a considerable impact on the overall yield
- scaling up a reaction to an industrial scale
- the principles of **green chemistry** in terms of the solvents required
- the by-products that are formed.

The flow chart in Figure 12.1.10 shows some of the stages in the planning process.

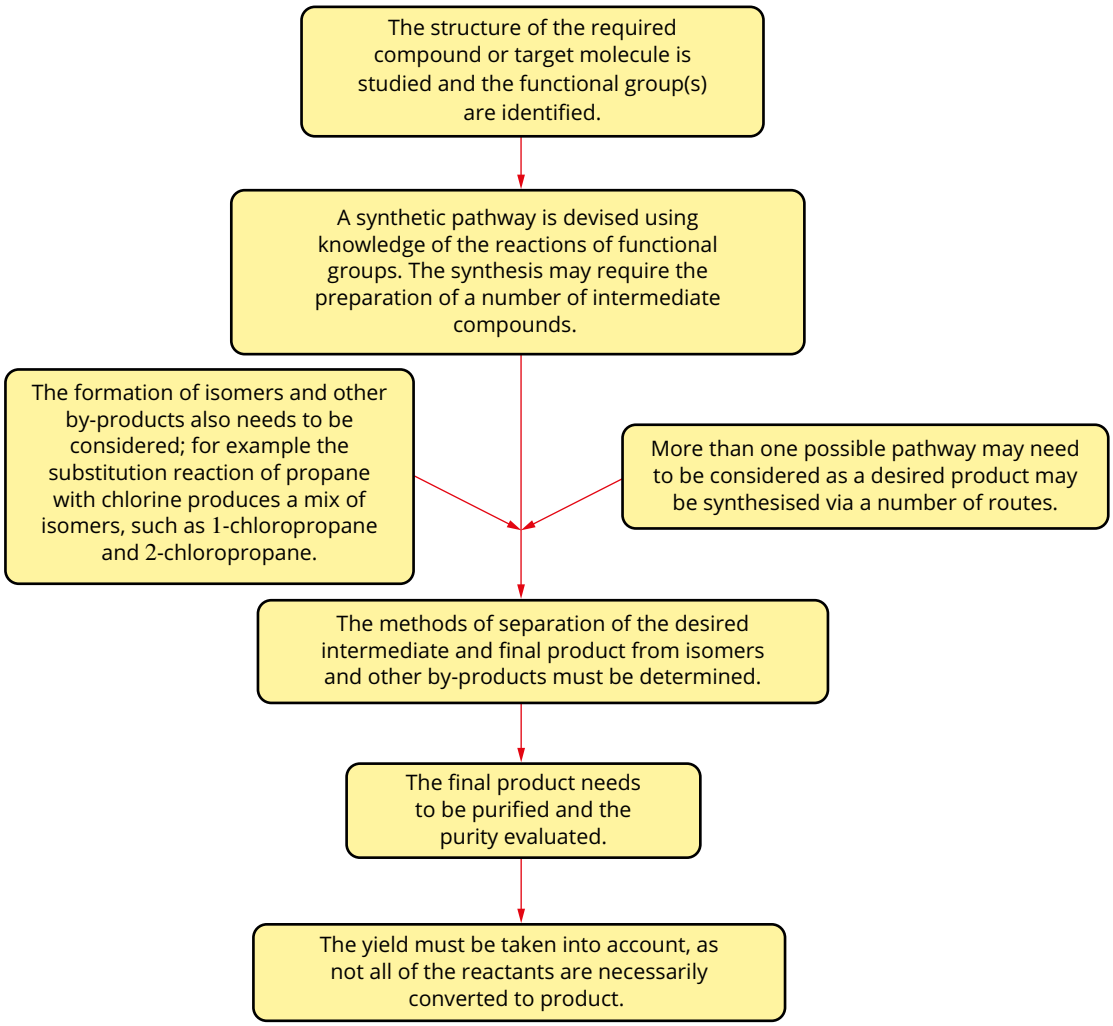


FIGURE 12.1.10 Steps in the design of a synthetic pathway of an organic compound

Thalidomide

The importance of identifying and isolating a product with specific properties came to prominence in the 1950s when thalidomide was prescribed to pregnant women to combat morning sickness. The children of these women were born with serious birth defects, which led to the creation of an independent committee to monitor the safety of new drugs in Europe and the United States.

Enantiomers are optical isomers that are non-superimposable mirror-image structures. The tetrahedral arrangement of the bonds in space results in two enantiomers due to the four non-identical atoms or groups attached to a tetravalent carbon, as indicated by the black dot in Figure 12.1.11.

The drug thalidomide was chiral, which means that the drug was a mixture of two stereoisomers (Figure 12.1.11). Of these mirror images only the form on the right (the R form) was therapeutically active. This is not surprising since the receptors and enzymes in the body have specific three-dimensional shapes. However, the form on the left (the S form) was not only ineffective but was responsible for the birth defects.

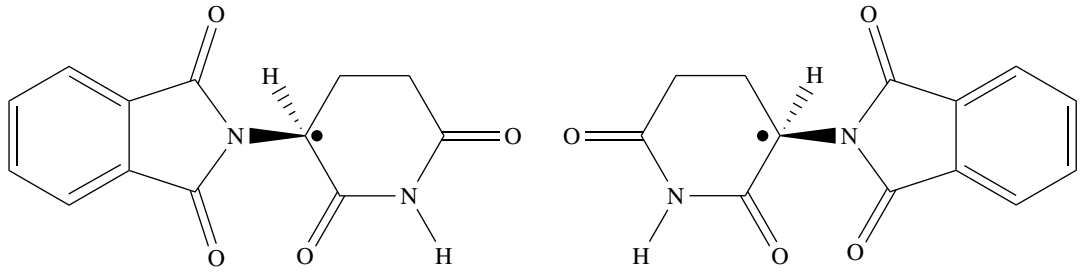


FIGURE 12.1.11 Enantiomers of thalidomide. The black dot indicates the chiral centre, where four non-identical atom groups are bonded to the carbon atom.

Unfortunately, even if the two enantiomers had been separated under biological conditions the two isomers interconvert and the R form would have been changed into the **teratogenic** S form.

Like thalidomide, many pharmaceuticals are chiral and typically only one of the stereoisomers is effective. The wrong isomer could simply be excreted or, like thalidomide, it could be dangerous.

12.1 Review

SUMMARY

- Chemists use a retrosynthetic pathway to design the process to successively simpler compounds from a suitable starting reagent.
- A convergent synthesis will reduce the overall number of steps to convert the reactants into products.
- A retrosynthetic step is represented by an arrow.
- Synthetic pathways often involve the conversion of functional groups.
- Other things to consider when planning a synthetic pathway include:
  - the overall yield of the process and of the individual steps
  - the equilibrium position
  - scaling up to an industrial scale
  - 'green' chemistry principles
  - the by-products formed
  - the chirality of the product
  - cost factors
  - reaction rate.

KEY QUESTIONS

Retrieval

1 Define the term 'retrosynthetic pathway'.

Comprehension

2 Explain why chemists need to make the following considerations when planning a retrosynthetic pathway.
- **a** the total number of steps in the pathway
- **b** purity of the final product
- **c** equilibrium position of a reaction in the pathway

Analysis

3 Identify a retrosynthetic pathway for the preparation of 1-propylamine from:
- **a** propene
- **b** ethane.

4 Determine which of the reaction pathways identified in question **3** would be the preferred synthetic route.

12.2 Modifying chemical properties

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- appreciate that chemical synthesis involves the selection of particular reagents to form a product with specific properties
- describe how the function of a chemical may require the properties of the active ingredient in a pharmaceutical drug to be modified to improve its action
- explain how the solubility of a chemical can be modified by altering the functional groups.



One of the most important processes in chemical synthesis is the design and manufacture of chemicals with particular properties. Once an active compound has been identified, it is important to synthesise a number of **derivatives** with more desirable properties to create the most effective product.

For example, one of the first analgesics was salicylic acid. However, it caused internal bleeding in patients. Scientists synthesised numerous derivatives with a similar chemical structure to find a compound of similar therapeutic properties but without the detrimental side effects. In 1899, a compound was synthesised that possessed the same beneficial properties of salicylic acid but did not pose a health risk to patients. It is still used today marketed under the name of aspirin.

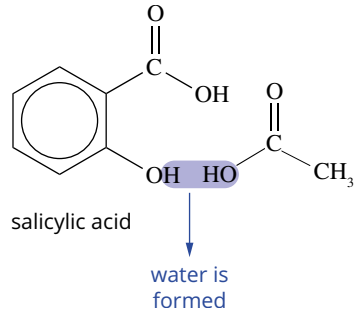


FIGURE 12.2.1 Structure of salicylic acid

ASPIRIN

Salicylic acid, shown in Figure 12.2.1, is a relatively strong acid and was unpleasant to take orally as it damaged the skin lining of the mouth and stomach. Therefore, the drug was modified to reduce its acidic nature while delivering the same analgesic effect.

Aspirin, shown in Figure 12.2.2, does not contain the OH group attached to the benzene ring as it has been replaced by an acetyl group which reduces the acidity to make it non-irritating. Aspirin is known as a **prodrug**.

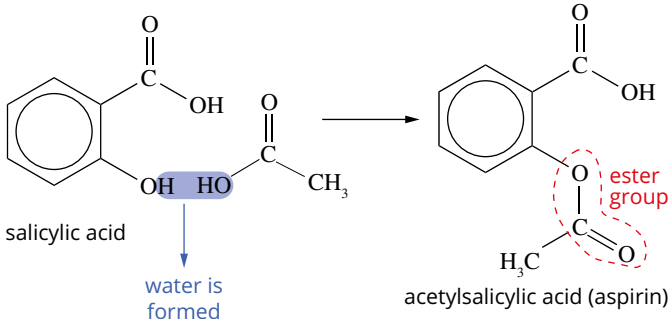


FIGURE 12.2.2 Structure of aspirin (acetylsalicylic acid)

A prodrug is a biologically inactive derivative of a compound that is metabolised (converted in the body) through chemical reactions or enzymes into the active form of the drug. Prodrugs can reduce unwanted side effects, improve chemical stability and reduce toxicity.

Aspirin is hydrolysed slowly by water to form salicylic acid (Figure 2.2.3). The hydrolysis is catalysed by the **alkaline** conditions that exist in the small intestine, from where the salicylic acid is absorbed into the bloodstream.

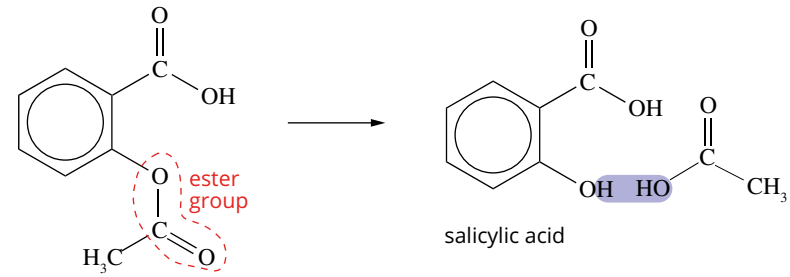


FIGURE 12.2.3 Hydrolysis of aspirin

Most pharmaceutical drugs are formulated into tablets, capsules or liquid. This helps bind the compounds in the tablet, control the rate at which the drug is released (catalysed) into the body and improve the taste of the drug. In order to cross cell membranes and be absorbed within the body, a drug must be in solution. It is vital, therefore, to know the rate at which the drug dissolves. If it is only partially soluble then the pharmacological properties may be reduced.

The **bioavailability** of a drug inside the body is related to how fast the chemical can be absorbed, which is related to the pharmaceutical's solubility.

It is important to be able to modify the structure of a compound to alter its solubility without affecting its therapeutic properties. The solubility of a tablet or capsule depends on the:

- conditions inside the body, such as pH and temperature
- structure of the tablets or capsules
- nature of the packing ingredients in the tablet or capsule.

Aspirin is not very soluble in water, which makes it difficult for some people to take. To increase its solubility in water the sodium salt is made.

Altering the solubility

Solubility is one of the main parameters to formulating drugs that produce the desired pharmacological response without exceeding the $\mathbf{TD_{50}}$. Almost half of new drugs formulated are practically insoluble, so it is a major challenge for scientists.

The solubility of a drug can be improved by creating a derivative. Derivatisation is a technique that transforms a chemical into a product with a similar chemical structure and with the same properties but a different solubility.

Aspirin is a weak acid. In aqueous solution, aspirin will only **partially dissociate**, as shown in the following equation:

$$R-COOH(s)+H_2O(l) \rightleftharpoons H_3O^+(aq)+R-COO^-(aq)$$

In the stomach, where there is a strong acid, aspirin dissociates completely in aqueous solution resulting in an increase in the concentration of hydronium ions. According to Le Châtelier's principle, to counter the increase in the concentration of hydronium ions, the equilibrium shifts to the left and produces aspirin. This will result in fewer ionised molecules of aspirin in solution reducing the solubility of aspirin within the stomach.

When aspirin reaches the alkaline conditions in the small intestine, the hydronium ions will be removed and so the equilibrium will shift to the right and the aspirin will dissolve.

When the anion reaches the stomach it is protonated by the hydronium ions to form aspirin, which will precipitate out until it reaches the alkaline conditions in the small intestine. By creating the sodium salt, the ingestion of the drug is easier and more acceptable to patients.

The sodium salt is ionic and dissolves completely in water making it much easier for patients to ingest:

$$R-COONa(aq) \rightarrow R-COO^-(aq)+Na^+(aq)$$

TD_{50} is the amount (dose) per unit mass required to elicit toxic or negative effects on half a sample group. The lower the TD_{50}, the higher the toxicity of the drug.

DETERGENTS

Detergents are another example of modifying a compound's structure to create a chemical for a particular purpose. Detergents are substances that act with water to clean things. They are compounds with long hydrophobic tails and hydrophilic heads; for example, sodium octadecenoate (Figure 12.2.4).

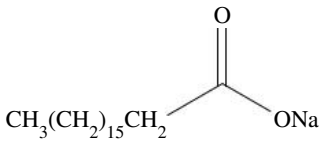


FIGURE 12.2.4 Structure of sodium octadecenoate

The charged COO^- group at the polar end of the molecule enables it to dissolve in water. When it dissolves it forms spherical clusters called micelles. The non-polar tail mixes with oily substances and leaves the grease surrounded by an outer covering of water-soluble COO^- groups (Figure 12.2.5). This means that the oil is lifted up from the surface and dissolves in the water, where it can be removed.

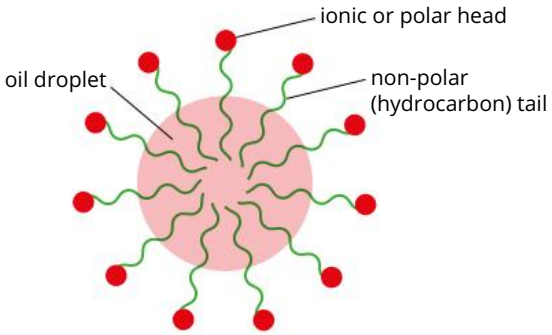


FIGURE 12.2.5 Oil droplet in a detergent solution

A disadvantage of detergent soaps is that in hard water in the presence of calcium ions, Ca^{2+}, an undesirable hard scum forms. The lower solubility of the calcium salts means that the calcium salt formed precipitates out of solution:

$$Ca^{2+}(aq) + 2RCOO^-(aq) \rightarrow (RCOO)_2Ca(s)$$

Therefore, it would be useful to have a compound that has similar grease-removing properties like soap but does not form a scum in hard water.

Soapless detergents, such as the one shown in Figure 12.2.6, have been synthesised with similar grease-removing properties as soap but with the advantage that they do not form a scum in hard water. This is because, unlike the calcium octadecenoate, calcium dodecylbenzenesulfonate is water soluble and therefore does not precipitate out.

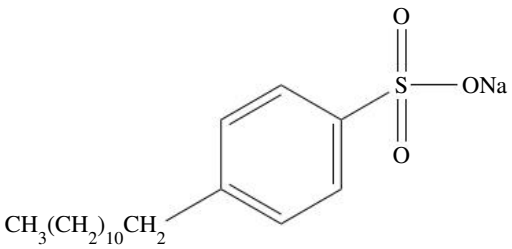


FIGURE 12.2.6 Structure of sodium dodecylbenzenesulfonate

12.2 Review

SUMMARY

- Once a beneficial compound has been synthesised, chemists work to identify other closely related chemicals that have similar properties but might have fewer side effects or improved action.
- A prodrug is a biologically inactive derivative of a chemical that is metabolised in the body, usually by chemical transformation or enzymatic action, to produce the same active chemical as the original drug. It possesses improved properties compared to the parent drug.
- The bioavailability of a drug inside the body is related to how fast the drug can be absorbed, which is related to the drug's solubility.
- The solubility of a tablet or capsule depends on:
  - the conditions inside the body, such as pH and temperature
  - the structure of the tablet or capsule
  - the nature of the packing ingredients in the tablet or capsule.
- Drugs can be made more soluble by making the salt of the active form.

KEY QUESTIONS

Retrieval

1 Define a prodrug.

Comprehension

2 Explain two reasons why the structure of a beneficial chemical might be altered.

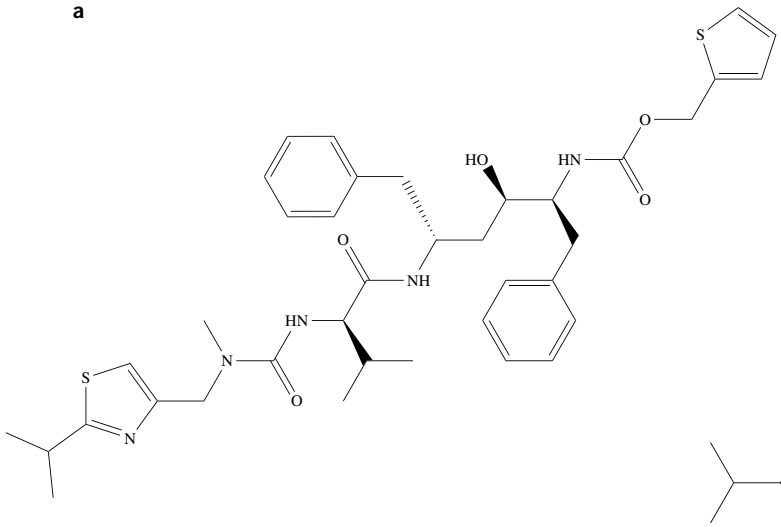
3 Explain how a detergent affects the surface tension of a water droplet.

4 Explain how aspirin is converted back into the active form of the drug in the body.

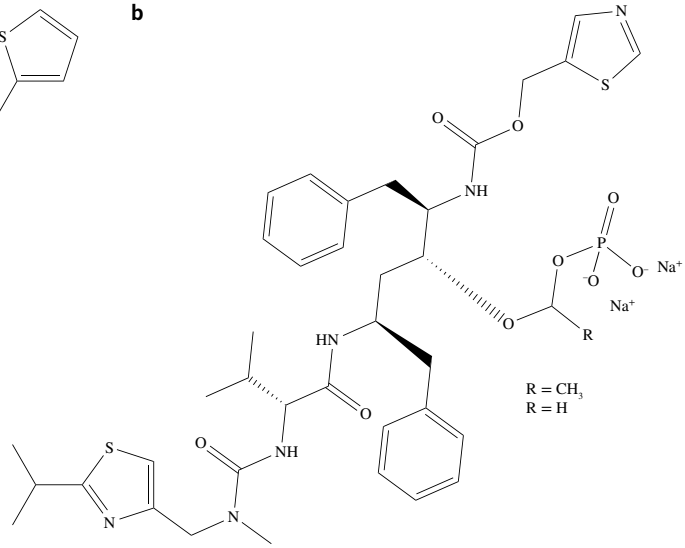
Analysis

5 Compare the structure of the two drugs shown below and explain which of the two would be more soluble.

a



b



12.3 Synthesis of fuels

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- explain how fuels can be synthesised from a range of chemical reactions
- describe, including chemical reactions, how ethanol can be produced by the fermentation and hydration of ethene
- describe, including chemical reactions, how biodiesel is produced by the transesterification of triglycerides.



The fuel shortages in the mid-1970s, together with the desire to reduce pollution since the 1990s, has increased the need to develop alternatives to **non-renewable** petroleum-based fuels. As a result, there is increased interest in the production and use of **biodiesel**, ethanol and hydrogen.

BIODIESEL

Biodiesel is a fuel derived from vegetable oils and fats with similar combustion properties to regular petroleum diesel fuel. Biodiesel can be produced from oil-yielding crops including soybean, canola, corn and sunflower. It is **biodegradable** and non-toxic, and combustion produces significantly fewer **emissions** than petroleum-based diesel. The process used to convert these oils to biodiesel is called **transesterification**, and was discussed in Unit 2.

Biodiesel is a mixture of organic compounds called esters. The structure of a typical biodiesel molecule is shown in Figure 12.3.1. These esters are produced by the transesterification of triglycerides contained in vegetable or animal fats and oils with short-chain alcohols. Typically, ethanol is the most common alcohol used due to its low cost. However, higher yields of up to 98% can be achieved using methanol. The reaction can be catalysed by either acid or bases.

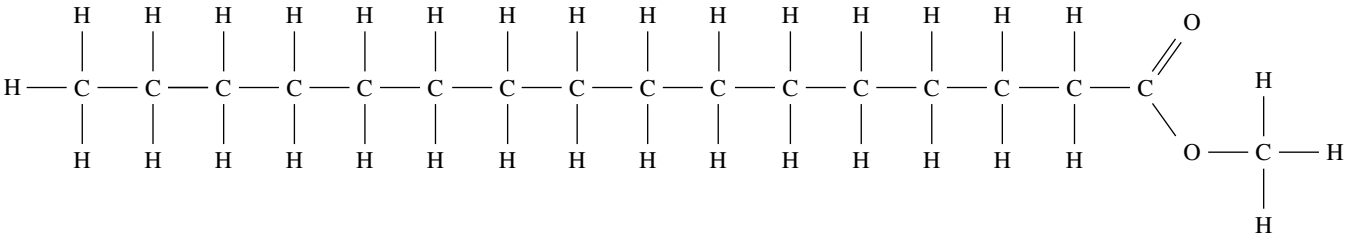


FIGURE 12.3.1 Structural formula of a typical biodiesel molecule

Manufacture from fats and oils

Fats and oils are triglycerides with a molecular structure consisting of three hydrocarbon chains attached by ester functional groups to a glycerol (Figure 12.3.2).

In the transesterification process, shown in Figure 12.3.3 on page 486, the triglyceride, which is an ester composed of a triglyceride structure with three long-chain fatty acids, is reacted with short-chain alcohols to produce a different ester, usually the methyl or ethyl ester (biodiesel) and **glycerol**. The reaction is carried out under low temperature and pressure as it is catalysed using a base which deprotonates the alcohol to increase the rate of the transesterification.

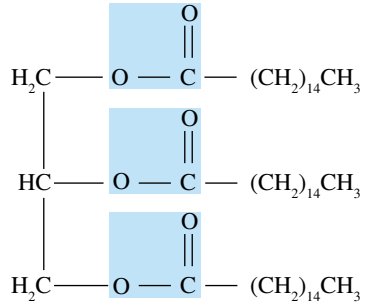


FIGURE 12.3.2 The structure of a triglyceride molecule. There are three ester functional groups in the molecule. The ester groups are shaded.

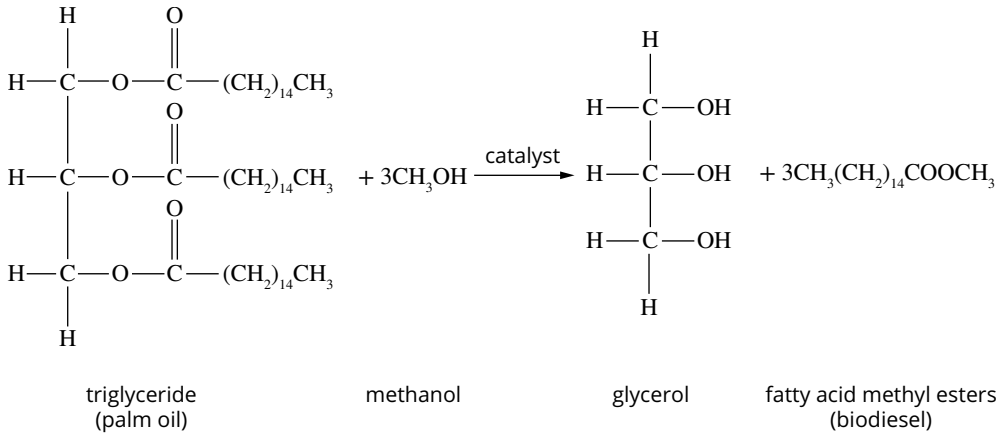


FIGURE 12.3.3 The reaction of a triglyceride with alcohol to form fatty acid esters (biodiesel) and glycerol

Biodiesels are sometimes referred to as fatty acid esters because carboxylic acids with relatively long hydrocarbon chains are referred to as fatty acids.

Like petrodiesel, biodiesel is not a pure substance. The structure of the triglyceride varies depending on the particular plant or animal used as the source. Triglycerides produced by animals, such as tallow, usually form saturated esters that have only carbon–carbon single bonds in the hydrocarbon chain. However, triglycerides produced by plants often form unsaturated esters like the one shown in Figure 12.3.4.

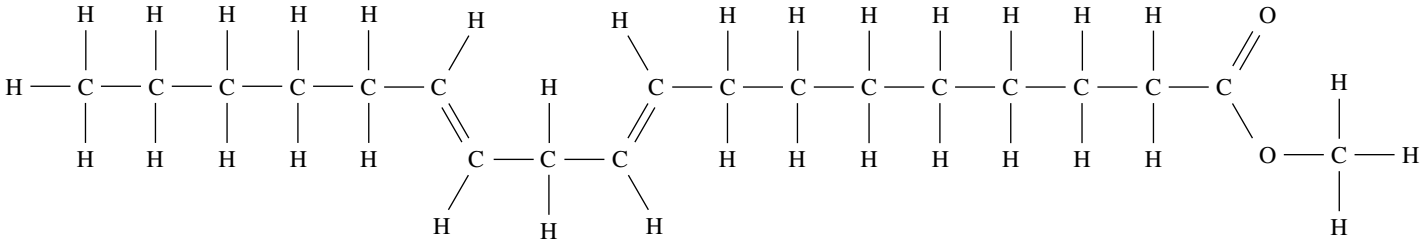


FIGURE 12.3.4 Biodiesel molecules derived from plants often contain carbon–carbon double bonds.

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

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

Comparison of petrodiesel and biodiesel

Properties and performance

Some of the properties of petrodiesel and biodiesel are compared in Table 12.3.1.

TABLE 12.3.1 A comparison of the properties of petrodiesel and biodiesel

Property	Explanation of property	Petrodiesel	Biodiesel
density ($kg\,L^{-1}$)	mass of fuel in a given volume	0.84	0.87
viscosity (cSt)	measure of a fluid's resistance to flow at 40°C	2.5	4.9
cloud point (°C)	lowest temperature at which crystals start to form	–15 to 5	–3 to 12
energy content ($kJ\,g^{-1}$)	energy released per gram of fuel	48	41
energy density ($kJ\,L^{-1}$)	energy released per litre of fuel	40	36

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

Examination of the data in Table 12.3.1 assists in understanding the following key points.

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

Obviously, an engine will not run if the fuel will not flow on a cold day. The differences in viscosity and flow under cold conditions are related to the chemical structures of the two forms of diesel. Petrodiesel consists of smaller, non-polar molecules (see Figure 12.3.5). The only forces present between neighbouring petrodiesel molecules are weak dispersion forces. However, the hydrocarbon chain in biodiesel is often longer and each molecule also contains two highly electronegative oxygen atoms (Figure 12.3.5).

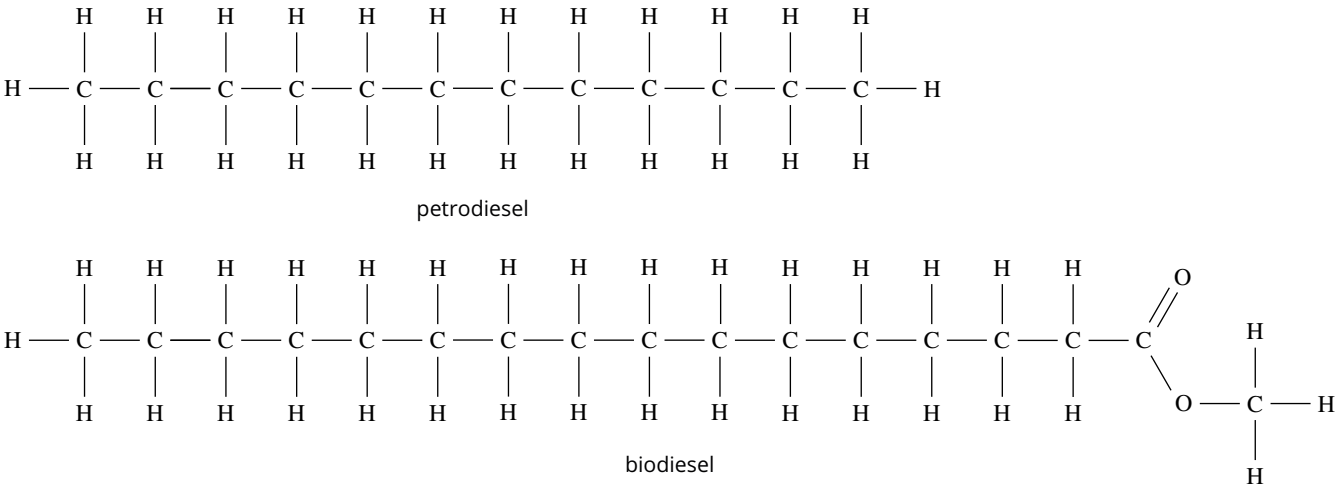


FIGURE 12.3.5 Petrodiesel and biodiesel molecules. Petrodiesel molecules are shorter than biodiesel molecules and are non-polar. Biodiesel molecules are longer and contain polar C–O bonds. As a result, biodiesel is more viscous than petrodiesel.

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

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

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

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

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

Environmental impact

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

Combustion and emissions

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

petrodiesel

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

biodiesel

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

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

As with petrol engines, use of either form of diesel leads to emissions of pollutants such as nitrogen oxides, carbon monoxide and unburnt hydrocarbons. Petrodiesel also produces some sulfur dioxide (SO_2) emissions. Whether biodiesel produces SO_2 depends upon the origins of the triglycerides that it is produced from. For example, soya bean oil does not contain sulfur but canola oil does.

Biodiesel exhaust contains up to 20% less particulate matter than diesel. There is considerable debate about which fuel, diesel or petrol, is the cleanest in terms of emissions. The answer is not clear-cut. While diesel engines produce less carbon dioxide, carbon monoxide and unburnt hydrocarbons, petrol engines produce virtually no particulates and emit less nitrogen oxides.

Fuel production

Both types of diesel impact on the environment from where they are sourced and the environment around the industrial plants where they are refined. Some of these impacts are illustrated in Table 12.3.2.

TABLE 12.3.2 A comparison of the impacts of sourcing and producing petrodiesel and biodiesel

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

In the immediate future, the growth of biodiesel production may depend upon economics. If biodiesel manufacturers cannot produce biodiesel from canola for a price lower than the market price of petrodiesel, then the industry is unlikely to expand.

ETHANOL

Hydration of ethene

In Chapter 9 you learnt that it was possible to form ethanol by either a substitution reaction involving a haloethane, or the acid-catalysed reaction of ethene with water (using a strong acid, such as H_3PO_4, as a catalyst). Since the substitution reaction of the haloalkane involved a slow catalytic reaction with water and competed with the elimination of the halide, ethanol is produced industrially by the addition reaction of steam and ethene. This reaction, shown in Figure 12.3.6, uses solid silicon dioxide coated with a phosphoric acid catalyst at 300°C and 60–70 atm.

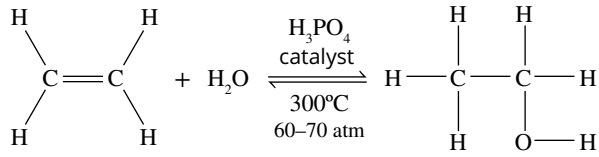


FIGURE 12.3.6 Addition reaction of ethene with steam in the presence of a phosphoric acid catalyst

The reaction is reversible and the forward reaction is slightly exothermic ($\Delta H = -45\,kJ\,mol^{-1}$). Each time the ethene is passed over the catalyst, about 5% is converted to ethanol; however, by repeating the process the overall conversion of ethene is about 95%.

Fermentation of glucose

Alternatively, ethanol can be produced by the **fermentation** of carbohydrates, usually in the form of glucose. This process depends on the presence of enzymes produced by yeasts that catalyse the conversion of glucose to ethanol and carbon dioxide according to the equation:



$$C_6H_{12}O_6 \xrightarrow{\text{enzymes}} 2C_2H_5OH + 2CO_2$$

This is discussed in greater detail in Module 12.6.

Biofuels from algae

The global economy requires hydrocarbons to produce plastics and fertilisers and provide energy for lighting, heating and transportation. Our increasing population and expanding economy means fossil fuel use will increase, putting pressure on non-renewable fossil fuel supplies.

In 2017, the United States alone required 19.9 million barrels of oil per day. To meet US oil demand, estimates suggest that 30 million acres of land will be required for production facilities. In addition, fossil fuel combustion increases atmospheric carbon dioxide concentration, leading to significant greenhouse gas-mediated climate change.

The International Energy Agency predicts that by 2030 biofuels will contribute 6% of total fuel use (Figure 12.3.7). Biofuels are a diverse range of technologies that generate fuel with at least one component based on a biological system. To date, this has mainly focused on converting corn starch and sugar to ethanol, particularly in Brazil.

One major drawback of biofuels is the enormous amount of agricultural land required to replace a fraction of petroleum production. This has generated increased interest in the conversion of cellulose to sugars for fermentation into fuel, and gasification of residual biomass to produce liquid fuels. Although these strategies are currently used to produce fuels, they are still insufficient to meet the global demand.

Recently, researchers from Kobe University in Japan have suggested that microalgae biofuels could relieve the current reliance on fossil fuels since they avoid some of the previous drawbacks associated with crop-based biofuels. While current technology is unsuitable, future progress in the area of microalgae biofuels could contribute to sustainable development in many developing countries.

Microalgae can produce oil without using up large tracts of arable land and water needed for drinking. Because microalgae only need light, water, carbon dioxide and a small amount of minerals to grow, they offer a potentially more stable energy supply. Additionally, their cells divide quickly, meaning that they can be harvested faster than land-based biomasses and can be harvested all year round.

Many species of algae can produce large amounts of oil, but this is the first time that researchers have captured the metabolic changes occurring on a molecular level when lipids are produced in algae cells.

Professor Hasunuma's group at Kobe University found that a green algae called *Chlamydomonas sp.* (JSC4) combines a high growth rate with high levels of lipids. By incubating JSC4 with carbon dioxide they found that just four days after the start of incubation over 55% of cell weight consisted of carbohydrates (mainly starch). They observed that when 1–2% salt water was added to the incubation liquid, the amount of carbohydrates decreased with a corresponding increase in oil formed. Analysis showed that seven days after the start of incubation, over 45% of cell weight had become oil. At the start of the cultivation period, starch particles were observed in the cells, but in salt water these particles vanished and numerous oil droplets could be seen (Figure 12.3.8).

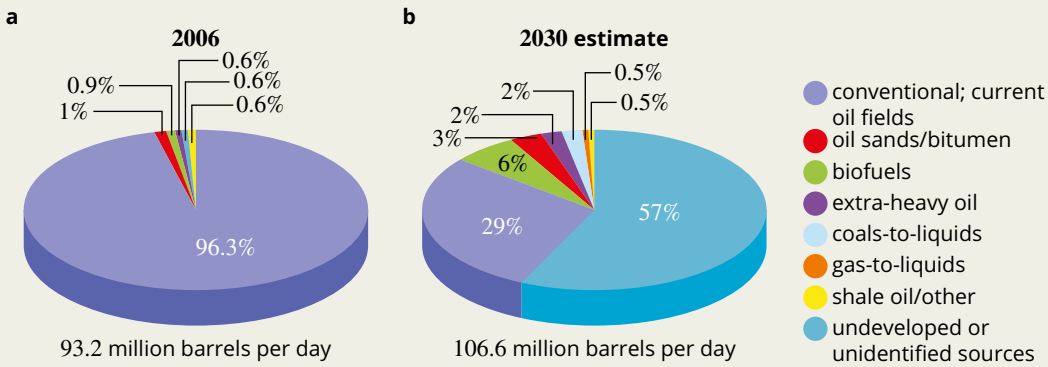
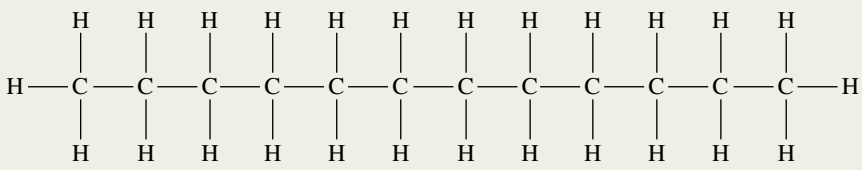


FIGURE 12.3.7 Historical and predicted global biofuel use



dodecane, a component of petrodiesel

FIGURE 12.3.8 Differences in cell contents based on the presence of salt water

Benefits of microalgae biofuels

Microalgae are single-celled organisms that have the potential to offer a variety of solutions for our liquid transportation fuel requirements. Algae grow in a wide range of aquatic environments, from fresh water to saturated saline. Algae efficiently use CO_2 and can rapidly produce biomass (some species doubling every six hours) in the form of long-chain hydrocarbons.

Microalgae have several advantages over terrestrial plants.

- They are single-celled organisms that reproduce by division.
- High-throughput technologies can be used to rapidly evolve strains, reducing the time required to generate sufficient yields to a few months.
- They impact on the environment less than terrestrial sources of biomass used for biofuels.
- They can be grown on land not typically used for traditional agriculture.
- They use nutrients from water more effectively, meaning that not only would production of microalgae biofuels minimise land use compared with biofuels produced from terrestrial plants, but also reduce the amount of waste generated.
- They have the potential to be bioengineered, allowing improvement of specific traits and production of valuable co-products, enabling microalgae biofuels to compete economically with petroleum.

The production of microalgae biofuels may be further enhanced through more efficient algae cultivation methods and genetic engineering.

The study from Kobe University suggests algae cultivation has the potential to produce cost-competitive biofuels; however, significant challenges need to be overcome for microalgae biofuel commercialisation. These challenges include:

- how and where to grow algae
- improved oil extraction and fuel processing
- strain identification and isolation
- improvement of crop protection
- nutrient and resource allocation and use
- the production of co-products to improve the economics of the entire system.

Although there is much excitement about their potential, more work is required to realise the economic viability of algae biofuels.

Review

1 Read the review on possible microalgal biofuel production processes by Michael Kröger and Franziska Müller-Langer that can be found at https://www.tandfonline.com/doi/pdf/10.4155/bfs.12.14. Identify the four main steps in the production of synthetic fuels.

2 As well as the wet hydrothermal and thermochemical dry methods, identify three other approaches scientists use to employ microalgae as fuel.

12.3 Review

SUMMARY

- Petrodiesel is a non-renewable fuel, whereas biodiesel is a renewable fuel.
- Petrodiesel is composed of about 75% alkanes containing 10–15 carbon atoms and 25% aromatic compounds.
- Biodiesel is produced from triglycerides in animal fats or plant oils. The triglycerides react with methanol in a transesterification reaction to form biodiesel.
- Biodiesel molecules can be described as fatty acid esters.
- Biodiesel is derived from oils and fats and has similar combustion properties to petrodiesel but produces fewer emissions.
- Biodiesel is produced by the transesterification of triglycerides using ethanol or methanol catalysed by either an acid or a base.
- Triglycerides from animals usually form saturated esters.
- Triglycerides from plants usually form unsaturated esters (C=C bonds in the hydrocarbon chain).
- The C=C bonds reduce the ability to pack tightly reducing the melting point of biodiesel from plant oil.
- Biodiesel is polar due to the presence of two electronegative oxygen atoms in the ester group.
- Petrodiesel is non-polar.
- On an industrial scale, ethanol is produced by either the:
  - acid-catalytic addition of water to ethene at 300°C and 60–70 atm
  - fermentation of glucose by enzymes from yeast.

KEY QUESTIONS

Retrieval

1 Describe the industrial synthetic route for the formation of ethanol.

Comprehension

2 Draw the structure of a biodiesel.

3 Explain an advantage that biodiesel has compared to petrodiesel.

Analysis

4 Compare the possible laboratory pathways to make ethanol with the industrial-scale process. Explain why one of the pathways is not practical to scale to an industrial size.

12.4 Fuel cells



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- describe the design of a fuel cell
- discuss, using diagrams and relevant half-equations, the operation of a hydrogen fuel cell under acid and alkaline conditions
- understand the production of hydrogen through steam reforming
- discuss how the properties of hydrogen necessitate specific requirements for storage of the hydrogen for the operation of a fuel cell.



FIGURE 12.4.1 A hydrogen fuel cell for an electric bicycle. The hydrogen bicycle operates like a standard electric bicycle, but the battery lasts three times longer.

Around the world, governments, businesses and academic institutions are spending millions of dollars to develop and produce fuel cells. A **fuel cell** is a type of galvanic cell that generates electricity from redox reactions quietly and efficiently and with almost no pollution. Unlike the cells you studied in Chapter 6, fuel cells do not run down or need recharging. A key difference between a fuel cell and a primary or secondary cell is that the reactants are not stored in the fuel cell but must be continuously supplied.

Fuel cells were invented in 1838. The National Aeronautics and Space Administration (NASA) was the first organisation to use fuel cells to generate power for satellites and space capsules. Today, fuel cells provide energy for forklifts, buses and cars (Figure 12.4.1), and act as a source of primary and back-up power for buildings and communities.

Fuel cells are an important component of a vision of the future called the 'hydrogen economy', in which hydrogen will become the major source of energy, replacing fossil fuels. Major technological and cost breakthroughs are needed before a hydrogen economy can become a reality and there is dispute among scientists over its viability.

In this module, you will learn how fuel cells operate. You will also learn about some of the issues associated with the supply, storage and use of hydrogen in fuel cells.

FUEL CELL DESIGN

Figure 12.4.2 shows a simplified diagram of the key parts of a hydrogen–oxygen fuel cell. The fuel cell has two compartments: one for the hydrogen gas and the other for the oxygen gas. The gas compartments are separated from each other by two porous electrodes and an electrolyte solution. The electrode at the hydrogen compartment is the anode; the electrode at the oxygen compartment is the cathode. The electrolyte in a fuel cell carries ions from one electrode to the other.

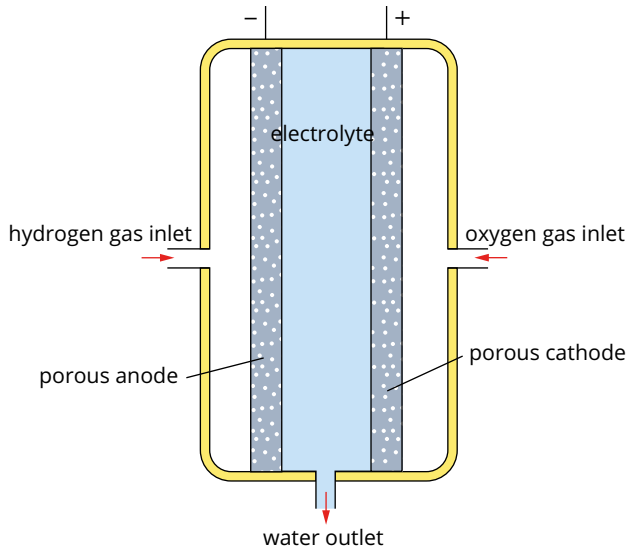


FIGURE 12.4.2 A simplified diagram showing the key parts of a hydrogen–oxygen fuel cell

OPERATION OF FUEL CELLS

Fuel cells can be operated under either acidic or alkaline conditions.

Hydrogen fuel cell under alkaline conditions

The type of fuel cell used in the NASA Apollo program used potassium hydroxide solution as the electrolyte and the cell operated at about 250°C. Because the fuel cell uses potassium hydroxide for the electrolyte, it is commonly referred to as an alkaline fuel cell. Alkaline fuel cells are still used in the space program today.

At the anode (negative electrode), hydrogen gas (the 'fuel') is oxidised by reacting with hydroxide ions from the electrolyte. The catalyst incorporated in the anode increases the rate of oxidation of the hydrogen gas. Platinum metal is commonly used as a catalyst at this electrode.

$$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$$

At the cathode (positive electrode), oxygen gas is reduced. The cathode catalyst, which increases the rate of the reduction half-reaction, can be made from a different material, such as nickel powder or a nanomaterial.

$$O_2(g) + 2H_2O(l) + 4e^- \xrightarrow{\text{catalyst}} 4OH^-(aq)$$

The overall equation for the reaction is:

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

Each cell produces about 1 volt. Higher voltages are obtained by connecting fuel cells in series to form a battery. The only **by-products** are water and heat.

To increase the rate of reaction catalysts are added to the electrolyte. The electrodes must be both conducting and porous to allow the hydrogen and oxygen to come into contact with the ions in the electrolyte so that the redox half-reactions occur at their surface. The size of the current that can be drawn from a fuel cell depends on the surface area of the electrodes.

Hydrogen fuel cell under acidic conditions

The most common type of acid fuel cell is a phosphoric acid fuel cell, as shown in Figure 12.4.3. The hydrogen enters the fuel cell and the atoms are ionised to form H^+ at the anode. The electrons travel through wires to provide a current. The oxygen enters at the cathode and is reduced by gaining electrons and combines with the ionised hydrogen atoms (H^+) to form water (H_2O).

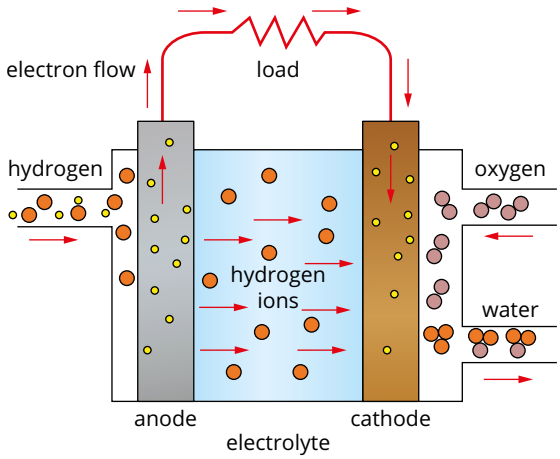


FIGURE 12.4.3 A simplified diagram showing the key parts of a phosphoric acid fuel cell.

The electrolyte plays an essential role as well. It only allows the appropriate ions to pass between the anode and cathode. If other ions were allowed to flow between the anode and cathode, the chemical reactions within the cell would be disrupted.

The reactions involved in the fuel cell under acidic conditions are as follows:

At the anode, hydrogen gas (the 'fuel') is **oxidised**:

$$2H_2(g) \rightarrow 4H^+(aq) + 4e^-$$

At the cathode, oxygen gas is **reduced**:

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

The overall equation for the reaction is:

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

Efficiency of fuel cells

Fuel cells transform chemical energy directly into electrical energy, enabling efficient use of the energy released by spontaneous redox reactions. They are a useful source of continuous electricity and could be used to provide energy for vehicles, buildings and even cities. Energy losses such as those that occur in coal-fired power stations and combustion engines are avoided, with a consequential reduction in the volume of greenhouse gases produced.

Fuel cells are generally quoted as being 40–60% efficient, compared with efficiencies of 30–40% for thermal power stations and 25–30% for car engines, which involve a series of different energy transformations.

In addition, modern fuel cells use the waste heat that they produce to make steam. This steam can be used for heating or to operate a turbine, thus raising the efficiency of the cells up to 85%.

Fuel cells have a much higher efficiency than thermal power stations because chemical energy is converted directly into electrical energy.

Hydrogen production

A fuel cell using hydrogen can be described as a 'zero-emission' device because water is almost the only product apart from electricity and heat. However, unless the hydrogen fuel is produced using renewable energy, the production of hydrogen can result in significant levels of greenhouse gases and other pollutants. To some extent, this negates the benefits of the use of fuel cells.

At present, almost 95% of hydrogen is produced from fossil fuels, such as natural gas, oil and coal through the process of **steam reforming**. In this process, steam reacts with the fossil fuel at high temperatures in the presence of a nickel catalyst.

The reaction for methane is represented by:

$$CH_4(g) + H_2O(g) \xrightarrow{Ni} CO(g) + 3H_2(g)$$

The carbon monoxide generated can be used to generate further hydrogen, using a copper or iron catalyst:

$$CO(g) + H_2O(g) \xrightarrow{Cu \text{ or } Fe} CO_2(g) + H_2(g)$$

The hydrogen produced by steam reforming has a lower **energy content** than the original fuel, as some of the original chemical energy is lost as waste heat during production. Furthermore, steam reforming leads to carbon dioxide emissions, in the same way as the use of the fossil fuel in a power station or car engine would do.

It is argued that hydrogen generated in this way would still be cleaner overall than fossil fuels due to the higher efficiency of fuel cells. Advocates of the use of steam reforming for generating hydrogen for fuel cells also suggest that because the carbon dioxide is produced at the site of the steam reforming process it could be possible to capture the greenhouse gas at its source and store it, preventing its release into the atmosphere.

Hydrogen storage

Widespread adoption of hydrogen as the primary fuel for powering vehicles and providing electricity for industrial and domestic applications would require massive expenditure on infrastructure. Changes to pipelines and filling stations, as well as improvements in hydrogen storage methods, would be required. Figure 12.4.4 shows a vision for the future use of hydrogen.

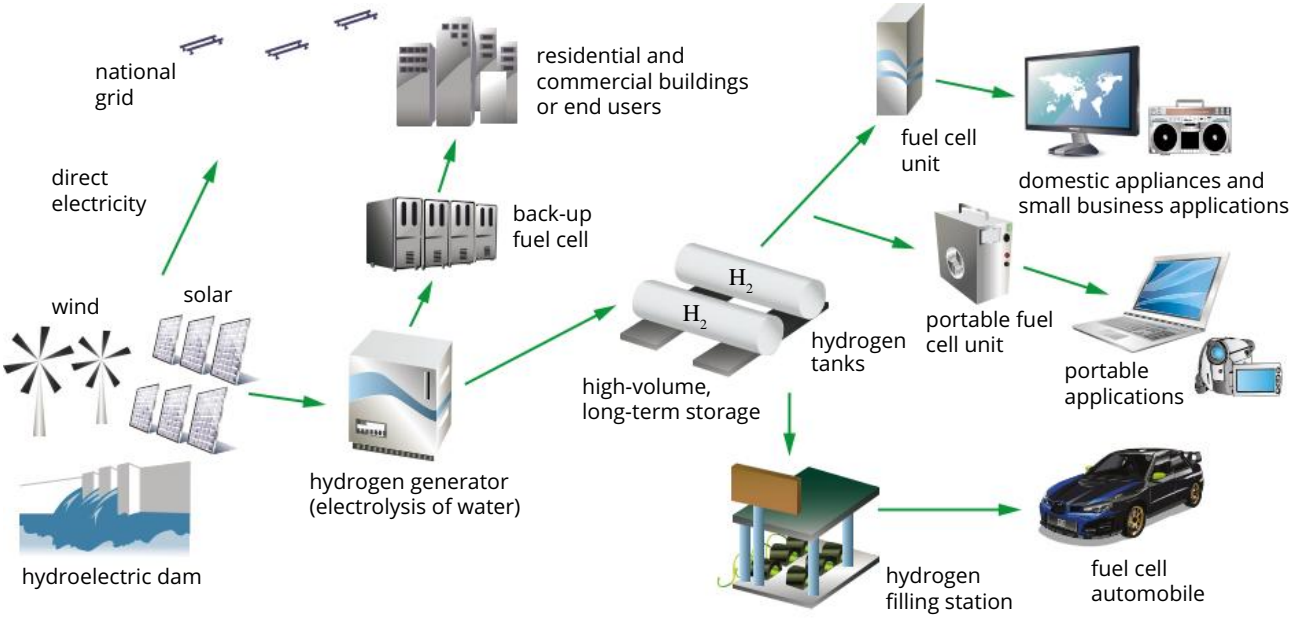


FIGURE 12.4.4 A view of future energy production based on the use of hydrogen

Although hydrogen has a very high energy content by mass ($143\,kJ\,g^{-1}$) compared with fuels such as petrol ($44\,kJ\,g^{-1}$), there are issues with storage, particularly within vehicles. This is because hydrogen is a gas at room temperature.

The established methods of hydrogen storage in cars, trucks and buses are as liquid hydrogen or compressed hydrogen.

Liquid hydrogen boils at the extremely low temperature of –252°C and a considerable quantity of energy is needed to liquefy it. The tanks used to store liquid hydrogen must be well insulated. The energy available per litre of liquid hydrogen ($8\,MJ\,L^{-1}$) is about four times less than for a liquid hydrocarbon fuel such as petrol ($32\,MJ\,L^{-1}$), so a vehicle using liquid hydrogen requires a much larger fuel tank to achieve the same driving range.

Compressed hydrogen can be stored in high-pressure tanks (up to 690 atm). A high-pressure hydrogen storage tank needs to be larger to store the same amount of energy as a liquid hydrogen tank. In fact, using currently available high-pressure technology, a high-pressure tank would need to be larger than the boot of a typical car to effectively replace a standard hydrocarbon fuel tank.

Scientists are investigating alternative methods of storing hydrogen, known generally as **materials-based storage** (Figure 12.4.5), which offer considerable promise but require further development.

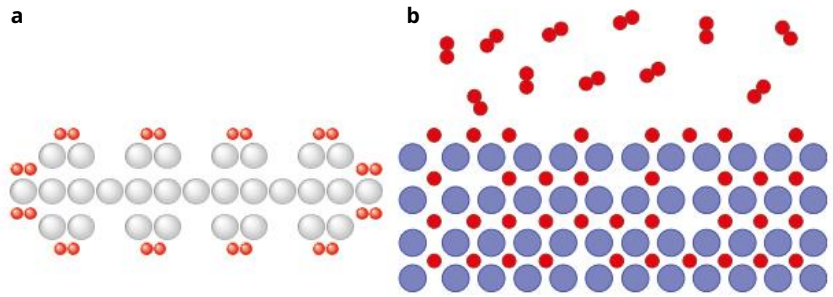


FIGURE 12.4.5 Two materials-based methods of storing hydrogen: (a) surface adsorption of hydrogen molecules and (b) absorption into a solid lattice as hydrogen atoms.

- Hydrogen can adsorb to the surface of materials such as metal hydrides, either as hydrogen molecules or as hydrogen atoms.
- Hydrogen can dissociate and be **absorbed** into the lattice structure of some solid materials.
- Hydrogen can react reversibly with a range of different chemicals.

PA 4.2.3



FIGURE 12.4.6 Technicians with a prototype aircraft powered by a combination of solar cells, which power the on-board electronics, and a hydrogen fuel cell, which powers the electric engine.

Safety issues

Hydrogen is generally regarded as a more dangerous fuel than hydrocarbon fuels such as petrol. Hydrogen burns readily and a flame or spark will ignite almost any combination of hydrogen and air. An explosion, rather than merely a flame, is the likely outcome.

On the other hand, the low density of hydrogen means that if a leak occurs hydrogen rises rapidly and quickly disperses in ventilated areas, often without ignition. In fact, a fire in a hydrogen-powered vehicle can be less damaging than a fire in a petrol-powered vehicle.

The use of hydrogen poses unique safety challenges. Strict codes and standards will be required for its use, including the need for hydrogen sensors to detect leaks. A number of studies have concluded that, while there are different safety concerns, hydrogen is no more dangerous than petrol. Experts predict that in the future hydrogen will be used as a fuel with at least the same level of safety and convenience as today's hydrocarbon fuels.

Applications of fuel cells

Most major vehicle manufacturers are investigating the use of fuel cells as an alternative to the internal combustion engine, given that fuel cells have better fuel efficiency and lower emissions of greenhouse gases and other pollutants. Also, fuel cells do not rely on oil (Figure 12.4.6).

Aside from their use in transport, the use of fuel cells is small at present but growing rapidly.

- A 1.3 MW power plant in Italy is a phosphoric acid fuel cell that uses hydrogen from steam reforming of natural gas as its fuel source (Figure 12.4.7).
- A 59 MW power plant began operation in South Korea in 2014, providing power and heat for local homes.
- One supermarket chain in the United States has ordered fuel cells to power its fleet of 1700 forklifts.
- Silicon Valley technology companies in California, USA, are installing fuel cells as a stable, sustainable source of power.



FIGURE 12.4.7 Interior of the PRODE fuel cell power station in Milan, Italy, which began operating in 1992. The cells use hydrogen as the fuel and phosphoric acid as the electrolyte. The fuel cells can produce up to 1.3 MW of electricity.

12.4 Review

SUMMARY

- Fuel cells are a type of galvanic cell, converting chemical energy directly into electrical energy.
- Unlike batteries, fuel cells do not run out of power or 'go flat' as the reactants are supplied continuously, allowing the constant production of electrical energy.
- The electrodes used in fuel cells allow direct contact between the gases and electrolyte. They have a high surface area and are porous to ensure high cell efficiency. Catalysts are often part of an electrode to increase the rate of reaction.
- The hydrogen–oxygen fuel cell is made up of two compartments separated by porous electrodes and an electrolyte.
- The hydrogen electrode is the anode (negative electrode).
- The oxygen electrode is the cathode (positive electrode).
- Electricity generation using fuel cells is more efficient than if the electricity were generated by the combustion of the same amount of fossil fuel.
- The emissions of greenhouse gases from a fuel cell are much less than if the fuel were burnt in a power station or internal combustion engine.
- The widespread use of hydrogen as a source of energy presents special challenges and issues in terms of its production, distribution, storage and safety.
- Hydrogen is produced through steam reforming of fossil fuels by the reactions:

$$CH_4(g) + H_2O(g) \xrightarrow{Ni} CO(g) + 3H_2(g)$$

$$CO(g) + H_2O(g) \xrightarrow{Cu \text{ or } Fe} CO_2(g) + H_2(g)$$

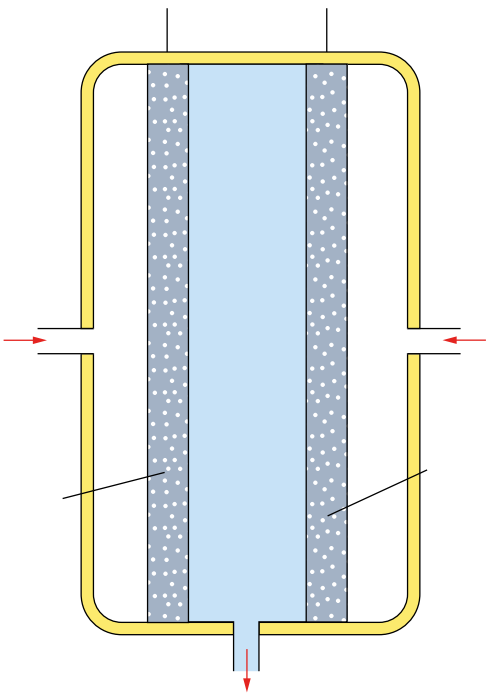
- Hydrogen has a very high energy content by mass ($143\,kJ\,g^{-1}$) compared with hydrocarbon fuels such as petrol ($44\,kJ\,g^{-1}$).
- Storage, particularly within vehicles, is an issue because hydrogen is a gas at room temperature.
- The use of fuel cells is growing particularly for transport but also in the production of electricity for residential and industrial purposes.

KEY QUESTIONS

Retrieval

1 Describe a fuel cell and state how it differs from a battery. Include an example in your answer.

2 Label the following diagram of a fuel cell.



Comprehension

3 Describe the reactions occurring at the anode and cathode in a fuel cell under:

a acidic conditions

b alkaline conditions.

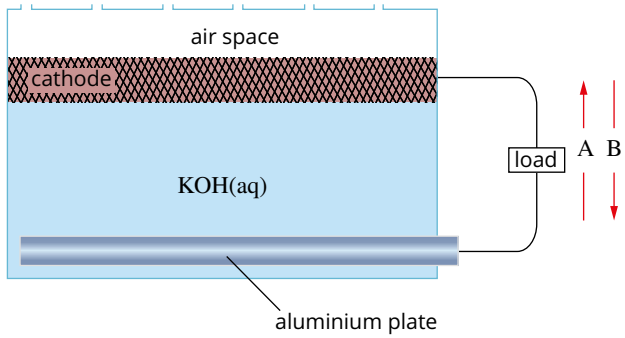
4 Compare the overall balanced equations for both conditions described in question **3**.

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12.4 Review *continued*

Analysis

5 The diagram below shows a version of an alkaline aluminium–air fuel cell being used to power a load, such as an electric motor.



The half-reactions occurring are:

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$$

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

a State whether arrow A or arrow B shows the direction of electron flow through the load.

b Identify which species is the oxidant in this cell.

c Construct a balanced equation for the overall cell reaction.

d Deduce why it is important for the cathode to be porous.

If a zinc plate is used in place of the aluminium plate, the cell would still function. However, if a silver plate is used, the cell would not function.

e Explain this difference by referring to the relative strengths of the oxidants and reductants involved.

f Determine if the potential (voltage) produced by the fuel cell with the zinc plate would be larger or smaller than the fuel cell with the aluminium plate. Explain your answer.

g When the potassium hydroxide electrolyte was replaced with a sulfuric acid solution, the cell with the silver plate began to deliver a current. Deduce why changing the electrolyte had this effect.

12.5 Industrial chemistry

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand how reagents and conditions are chosen to optimise the yield of a reaction
- appreciate how other considerations, including the rate of reaction and cost, influence the conditions of an industrial scale reaction
- describe and explain the choice of conditions for the Haber process and contact process.



HABER PROCESS

Between 1908 and 1914, Fritz Haber developed and industrialised a catalytic process for the production of ammonia from nitrogen and hydrogen according to the equation:

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

The **Haber process** made the production of high nitrogen content fertilisers feasible, which allowed for better crop yields in agriculture. Easy access to reasonably priced fertilisers has reduced starvation and saved lives in many areas across the world. This fact was acknowledged when Haber was awarded the Nobel Prize in Chemistry in 1918, following the end of World War I. However, Haber's involvement in the production of chemical weapons for use by the German army in World War I meant that the award of a Nobel Prize was seen as controversial by many scientists who considered him to be guilty of war crimes.

Ammonia (NH_3) is one of the most commonly produced industrial chemicals. Most of the ammonia produced by industry is used in agriculture as fertiliser. Ammonia is also used in the manufacture of plastics, explosives, textiles, pesticides, dyes and other chemicals.

Ammonia is produced in large industrial plants, such as the one north of Newcastle in New South Wales (Figure 12.5.1), where Orica produces 360 kilotonnes of ammonia annually.



FIGURE 12.5.1 Orica produces ammonia at its Kooragang Island plant in New South Wales. It also produces nitric acid and ammonium nitrate.

Equilibrium considerations

In Chapter 2 you explored Le Châtelier's principle and how the conditions of a reaction could be changed to shift the equilibrium towards the products:

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

Effect of changing the pressure

In the balanced chemical equation, there is a total of four gaseous molecules on the left-hand (reactant) side of the equilibrium, whereas there are only two gaseous molecules on the right-hand (product) side.

Therefore, the equilibrium yield of ammonia can be increased by changing the pressure in the reactor. According to Le Châtelier's principle, increasing the pressure will cause the system to partially oppose this increase in pressure by shifting to the side of the equation with less gaseous particles.

Because the equation for the Haber process has four gaseous reactant molecules and two gaseous product molecules, increasing the pressure will cause a shift to the right and increase the amount of ammonia present at equilibrium.

Effect of changing the temperature

Changing the temperature in the reactor will change the equilibrium constant of the reaction. Because the reaction in the Haber process is exothermic ($\Delta H = -92\,\text{kJ mol}^{-1}$), Le Châtelier's principle predicts a decrease in the temperature will shift the equilibrium to increase the temperature. This means that the exothermic forward reaction will be favoured at low temperatures thereby increasing the equilibrium yield of ammonia.

Effect of a catalyst on the equilibrium

The most common catalyst used in the reaction is finely ground magnetite (Fe_3O_4), which is often fused with other metals oxides. The grinding of the magnetite increases the surface area of the heterogeneous catalyst allowing the gaseous molecules to rapidly absorb and react.

The use of the catalyst increases the reaction rate meaning that the reaction can proceed at a viable rate at a lower temperature than without the catalyst. As explained above, the equilibrium yield of ammonia increases at a lower temperature. So while not directly increasing the amount of ammonia at equilibrium, since the reaction can be performed at a lower temperature the use of the catalyst increases the overall yield of ammonia formed.

The effects of changing temperature and pressure and the use of a catalyst on the equilibrium yield and reaction rate are shown in Table 12.5.1. As pressure is increased, the proportion of ammonia present at equilibrium increases. As the temperature is decreased, the proportion of ammonia present at equilibrium increases. The catalyst does not directly affect the equilibrium yield but does increase the rate of the reaction. Therefore, a high **yield** is obtained at a low temperature and high pressure (Figure 12.5.2).

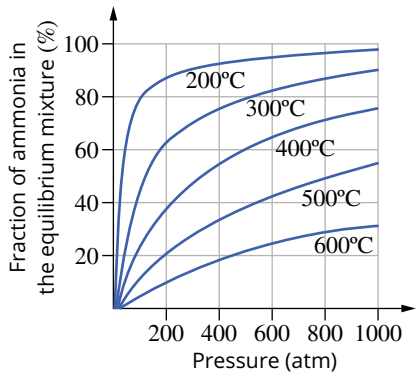


FIGURE 12.5.2 The percentage of ammonia present when a mixture of nitrogen and hydrogen has reached equilibrium.

TABLE 12.5.1 The effects of changing conditions on the reaction rate and the equilibrium yield of the reaction

Condition	Effect on the equilibrium yield	Effect on reaction rate	Actual conditions
catalyst	no effect	increases	Fe_3O_4 catalyst
decreasing temperature	increases	increase	350–550°C
increasing pressure	increases	increases	100–200 atm

Other considerations

In industry, it is essential to balance the reaction conditions for high equilibrium yield and reaction rate for the best economic outcome.

Increasing the pressure of a system, especially on an industrial scale, is a costly and potentially hazardous process. However, in the production of ammonia, a high pressure favours both a high yield and a high reaction rate. In this process, the economic benefits from the increased rate and yield outweigh the cost of maintaining high pressures.

A conflict arises in the choice of temperature: a low temperature is desirable for a high equilibrium yield, whereas a high temperature gives higher reaction rates.

The actual conditions used to overcome the conflict between rate and yield in the production of ammonia are:

- high pressures of 100–250 atm
- moderate temperatures of 350–550°C
- a porous iron/iron oxide (Fe_3O_4) catalyst.

Improving the catalyst for ammonia synthesis

The effectiveness of the catalyst in the converter in the Haber process is critical to its efficiency. Fritz Haber and his colleague Carl Bosch tested nearly 2000 different materials as catalysts when developing their process for ammonia synthesis. Haber used rare elements such as osmium and even suggested uranium as a potential catalyst in his earlier research.

By good fortune, the iron ore that they tested was from Sweden and contained traces of group 1 metal compounds that act as '**promoters**', increasing the efficiency of the catalyst. A promoter creates many small pores in the catalyst, exposing iron crystals and providing a greater surface area and more sites for reaction. The catalyst widely used today is not very different—iron oxide with a potassium hydroxide promoter.

An alternative catalyst is ruthenium metal supported on high-surface-area carbon. This material began to attract considerable interest from industry in the 1990s. While this catalyst is much more expensive, it is 45 times more active per square metre of surface, allowing the use of a lower operating temperature of about 400°C and 40 atm pressure. It has been installed in a number of ammonia plants.

Even more recently, a Danish company has announced the discovery of a new catalyst based on metal nitrides such as $Fe_3Mo_3N_3$ and Co_3Mo_3N. This catalyst is two to three times as effective as commercial iron oxide catalysts but less expensive than the ruthenium-based ones.

A dream for many chemists has been to devise a catalyst with the efficiency of **nitrogenase**, the **enzyme** found in nitrogen-fixing bacteria in legumes such as broad beans (Figure 12.5.3). Nitrogenase enzymes convert atmospheric nitrogen to ammonia without the need for the high pressures and temperatures of the industrial process. Harnessing this process would allow for the efficient production of ammonia at ambient temperatures and atmospheric pressure.

Nitrogenase contains clusters of iron, molybdenum and sulfur. Research is continuing to develop similar artificial clusters that could allow low-cost ammonia synthesis at room temperature and pressure. The area of catalysis for the production of ammonia remains an active field; recent research includes the use of photocatalysts developed from osmium–gold nanoparticles.

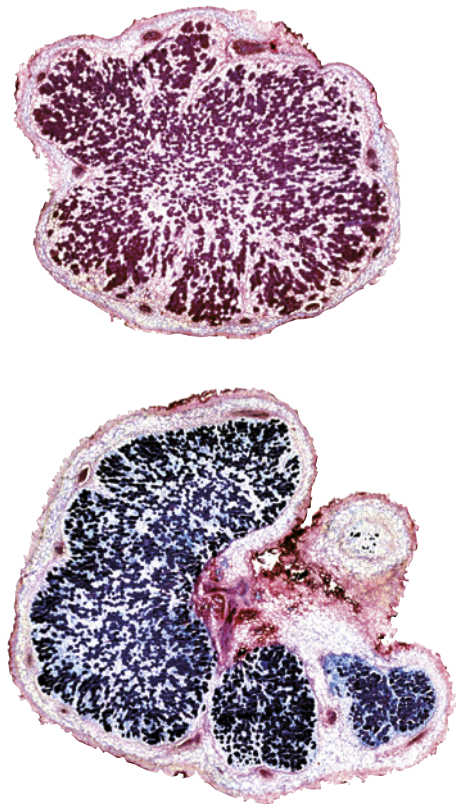


FIGURE 12.5.3 Sections through root nodules from broad beans, stained to show the presence of nitrogen-fixing bacteria. Chemists developing new catalysts for the production of ammonia at atmospheric temperature and pressure hope to mimic the pathways used by bacteria.

CONTACT PROCESS

The **contact process** is the industrial manufacture of sulfuric acid from either sulfur, as shown in the chemical reaction below, or iron sulfide.

$$2S(s) + 3O_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(l)$$

The contact process comprises three main steps:

- the production of sulfur dioxide
- a **reversible reaction** that converts the sulfur dioxide into sulfur trioxide
- the conversion of the sulfur trioxide into concentrated sulfuric acid.

Only the conversion from sulfur dioxide to sulfur trioxide is reversible; the other two processes are irreversible.

Making sulfur dioxide

Sulfur dioxide is produced by burning sulfur in an excess of air:

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

Sulfur dioxide can also be produced by the combustion of sulfide **ores**, like pyrite, in an excess of air:

$$4FeS_2(s) + 11O_2(g) \rightarrow 8SO_2(g) + 2Fe_2O_3(s)$$

Using an excess of air means that the sulfur dioxide is already mixed with oxygen for the next stage.

Converting sulfur dioxide into sulfur trioxide

The conversion of sulfur dioxide into sulfur trioxide is a reversible reaction with the formation of sulfur trioxide being exothermic:

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

Optimising the yield

According to Le Châtelier's principle, excess oxygen shifts the equilibrium to the right-hand (product) side to partially reduce the concentration of oxygen.

As highlighted above, the forward reaction to produce sulfur trioxide is exothermic ($\Delta H = -196\,\text{kJ mol}^{-1}$). Therefore, according to Le Châtelier's principle the forward reaction will be favoured by a lower temperature as the equilibrium will shift to counter this by producing more heat through the exothermic reaction.

In the industrial process, the temperature is between 400 and 450°C, which is not very low. This is because as the temperature is reduced, the rate of the reaction decreases. To produce a sufficient amount of sulfur trioxide per day a compromise must be reached.

On the left-hand (reactant) side of the equilibrium there are three gaseous molecules compared to two gaseous molecules on the right-hand (product) side. Therefore, according to Le Châtelier's principle, increasing the pressure will shift the equilibrium to the right as the reaction will respond by partially reducing the pressure, i.e. favour the side of the reaction with fewer gaseous molecules.

As with the Haber process, increasing the pressure also has the advantage of increasing the reaction rate; however, the industrial process takes place between 1 and 2 atm. Even at this pressure the conversion to sulfur trioxide is almost 100%; therefore, there is no substantial economic advantage that can be achieved by increasing the yield compared to the expense incurred producing such high pressures.

The use of a vanadium catalyst does not shift the equilibrium, as the rates of both the forward and reverse reactions are increased. Thus, the purpose of the catalyst is simply to increase the rate of formation of sulfur trioxide. Without the catalyst the rate of the reaction is so slow that virtually no sulfur trioxide is produced within a reasonable time. The effects of changing the conditions on the equilibrium yield and reaction rate, as well as the actual conditions, are shown in Table 12.5.2.

TABLE 12.5.2 The effects of changing conditions on the reaction rate and the equilibrium yield of the reaction

Condition	Effect on the equilibrium yield	Effect on reaction rate	Actual conditions
catalyst	no effect	increases	vanadium pentoxide
decreasing temperature	increases	increases	400–450°C
increasing pressure	increases	increases	1–2 atm
increase oxygen concentration	increases	increases (up to a point then decreases)	1:1

Converting sulfur trioxide to concentrated sulfuric acid

Because the reaction of sulfur trioxide with water is so uncontrollable, the sulfur trioxide must first be dissolved in concentrated sulfuric acid to form **oleum**:

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$

The oleum is then reacted in a much safer way to produce concentrated sulfuric acid:

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

12.5 Review

SUMMARY

- The Haber process is the catalytic production of ammonia from nitrogen and hydrogen.
- The position of the equilibrium in the formation of ammonia can be predicted from Le Châtelier's principle.
- Since there are fewer product molecules, increasing the pressure of the reaction favours the product and increases the rate of the reaction.
- Since the forward reaction is exothermic, decreasing the temperature favours the product but slows down the reaction rate.
- An iron oxide catalyst does not change the equilibrium position but does increase the rate of ammonia formation.
- The contact process is a three-step process for the manufacture of sulfuric acid from either sulfur or iron sulfide.
- Only the conversion of sulfur dioxide to sulfur trioxide is reversible.
- The equilibrium is favoured by increased pressure and low temperatures; however, due to other considerations conditions are adjusted.
- Because the reaction of sulfur trioxide is uncontrollable, sulfur trioxide is first dissolved in sulfuric acid before reacting with water to produce sulfuric acid.

KEY QUESTIONS

Retrieval

1 Define Le Châtelier's principle.

2 Describe the three steps involved in the contact process to produce sulfuric acid from sulfur. Use balanced chemical equations in your answer.

Comprehension

3 Explain how Le Châtelier's principle can increase the yield of ammonia based on the following equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -ve$$

4 Explain why the use of a catalyst does not affect the position of the equilibrium.

Analysis

5 During the Haber process, as a gas passes through the catalyst in the converter its temperature increases. Determine why the temperature of the gas rises.

6 During the process for sulfuric acid manufacture, sulfur dioxide is converted to sulfur trioxide at temperatures of 400–450°C:

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

a Determine and explain the effect of increasing the pressure on:
- **i** reaction rate
- **ii** equilibrium yield.

b In practice, this step is usually performed at atmospheric pressure. Explain why.

c During the process, sulfur trioxide is removed from the reaction mixture by converting it to sulfuric acid. The remaining gases are then recycled to the reaction vessel. Explain the reason for recycling the gases.

d Identify factors that would have influenced the choice of the reaction temperature.

7 The reaction used to manufacture ammonia is represented by:

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

The equilibrium constant for the reaction is $0.052\ mol^2\ dm^{-6}$ at 400°C.

Each of the following gas mixtures is contained in a 1.0 L vessel at 400°C. Determine if each mixture is in equilibrium. If not, predict the direction the reaction will shift in order to reach equilibrium.

a 0.20 mol of N_2, 0.20 mol of H_2, 0.20 mol of NH_3

b 0.050 mol of N_2 and 0.50 mol of H_2

8 The gases leaving the converter are cooled and liquid ammonia is removed before unreacted nitrogen and hydrogen are pumped back into the converter. Explain why this gas mixture is cooled before re-entry into the reaction.

9 At 200°C, nearly twice as much ammonia forms when a 3:1 hydrogen/nitrogen mixture under 250 atm pressure reaches equilibrium as is formed at 400°C. Deduce why temperatures above 400°C are used to manufacture ammonia.

12.6 Use of enzymes in industry



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand that enzymes can be used on an industrial scale for chemical synthesis to achieve an economically viable rate, including fermentation to produce ethanol and lipase-catalysed transesterification to produce biodiesel.

Thousands of chemical reactions are involved in sustaining life. These reactions occur in a highly organised, sequential fashion. The biological catalysts that accelerate the rate of chemical reactions in cells are a particular type of protein called enzymes. Enzymes are highly efficient catalysts that can increase reaction rates by as much as a factor of 10^{10}. This is like taking one second to complete a task that would normally take 300 years!

In this module, you will look at how enzymes may be useful to industrial production processes, which could reduce our impact on the environment.

ACTION OF ENZYMES

In Chapter 10 you learnt that enzymes are protein molecules that catalyse biological reactions in your body. Enzymes are essential for the normal operation of reactions in our body and without them we would die. Enzymes share features with all catalysts, including that they:

- are only needed in relatively small amounts
- are not used up or changed at the end of the reaction
- do not alter a reaction's equilibrium position
- provide an alternative reaction pathway that lowers the activation energy for a reaction (Figure 12.6.1).

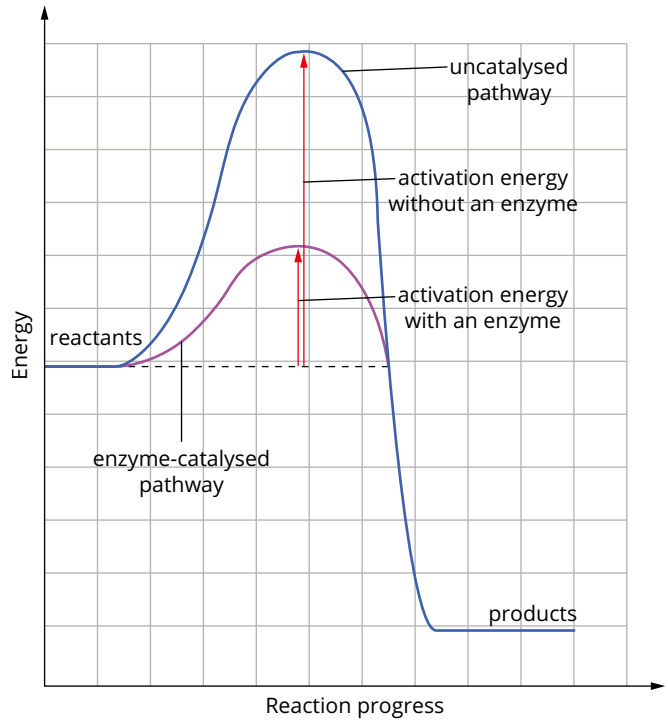


FIGURE 12.6.1 Both inorganic catalysts and enzymes lower the activation energy of a reaction by providing an alternative pathway by which the reaction can occur.

Enzymes share many characteristics with inorganic catalysts. Both enzymes and inorganic catalysts increase reaction rate by lowering a reaction's activation energy barrier without altering the equilibrium position or being changed themselves in the process. Despite these similarities, enzymes only catalyse one specific or a small group of reactions, and this is markedly different from the versatility displayed by many inorganic catalysts.

Generally, enzymes only catalyse one specific reaction or small group of reactions that involve a particular chemical bond or functional group. This characteristic is often referred to as the 'specificity of enzymes'. For example, the hydrolysis of the disaccharides sucrose and lactose to their constituent monosaccharides are catalysed by different enzymes. The models of enzyme action, discussed in Unit 2, account for this key difference.

Furthermore, since the activity of enzymes is connected to their three-dimensional structure, they are also more sensitive than inorganic catalysts to changes in reaction conditions, such as temperature and pH. Changing conditions can disrupt the **intermolecular forces** that create the α-helix and β-pleated sheet folding as well as the tertiary structure within the enzyme, described in Module 10.3.

The disruption of the enzyme's tertiary structure changes the shape of the enzyme's active site and so the **enzyme activity** decreases. Extremely high or low pH values generally cause complete loss of activity for most enzymes.

INDUSTRIAL USE OF ENZYMES

Every day we use biocatalysts around the home without ever realising it. From biological detergents or contact lens cleaners to cooking ham with pineapple, a proteinase enzyme is hydrolysing a protein substrate. However, research into biocatalysts is becoming increasingly interesting from an industrial perspective.

Industrially produced enzymes are used to produce a wide range of products including paper, leather, textiles, detergent, food and drinks, animal feed, pharmaceuticals and biodiesel. This module will focus on the use of enzymes in industrial processes, in particular the enzyme-catalysed fermentation of ethanol and the lipase-catalysed production of biodiesel.

Biocatalyst is the term for a biologically produced industrial catalyst, which includes, but is not limited to, enzymes. The use of enzymes can allow manufacturers to produce the same, or sometimes even higher, quality products with fewer raw materials and/or energy consumption and with less waste than traditional processes.

Benefits of biocatalysis

Some of the benefits of biocatalysis include:

- fewer by-products
- reduced energy use
- greener production by reducing environmental pollution
- reduced toxicity when the biocatalyst reaches the environment after use.

While plants or animals have been used to isolate the enzymes, most industrial enzymes are mass produced by microorganisms in large fermentation vats.

Enzymatic catalysis has a number of benefits over traditional chemical catalysis because enzymes:

- have a high catalytic power
- work under mild conditions of temperature, pH and pressure
- display high specificity for the substrate (frequently differentiating between molecules with similar structure)
- perform well in organic solvents.

However, the enzymes may not be sufficiently stable for commercial applications. They may also be unavailable for reuse because it can be difficult to separate them from the aqueous reaction mixture.

To make it easier to collect the enzymes after use, scientists can immobilise the enzymes by adsorbing them onto a support, such as charcoal, glass beads or clay, through hydrophobic interactions and ionic bonds.

Enzymes can be immobilised in a number of ways. Some enzymes may be trapped in gel-like beads packed into a container. The solution of the substrate flows over the beads thereby converting the substrate into product in the process. While this facilitates their reuse, immobilised enzymes often cannot mix freely with the substrate and so the reaction rate may be slower than with free enzymes.

LIPASE-CATALYSED PRODUCTION OF BIODIESEL

The reduced availability of fossil fuels as well as the associated environmental issues as a result of increasing industrialisation and motorisation have increased the demand of petroleum-based fuels from limited reserves. These finite reserves are concentrated in certain areas in the world meaning that countries without these resources have to import crude petroleum.

This has increased the impetus to find alternative fuels produced from locally available resources such as alcohol, vegetable oils and animal fats. One such alternative fuel is biodiesel produced from a lipid feedstock and an alcohol. As you learnt in Module 12.3, biodiesel is a non-petroleum-based diesel fuel consisting of short chain alkyl (methyl or ethyl) esters, typically produced by transesterification of vegetable oils and animal fats using an alkali catalyst. This is carried out at elevated temperatures and consumes heat and chemicals such as NaOH (catalyst) and sulfuric acid (neutralising agent) and is therefore quite expensive.

One alternative approach is the enzymatic hydrolysis of the triglyceride by lipases to catalyse the transesterification. In this way, it may be possible to produce a highly pure biodiesel that can be easily separated from the by-product, glycerol. While the cost of the enzyme is high and still an issue for its industrial implementation, the enzyme can be reused by immobilising it on a suitable biomass support.

Lipases

All living organisms contain lipases and can be produced in high yields from microorganisms such as bacteria and fungi. The precise lipase required depends on oil or fat being transesterified.

The advantages of using a lipase catalyst as opposed to the acid or base catalysts, described in Chapter 10 (Module 10.6), include:

- no soap formation
- being able to esterify both fatty acids and the triglycerides in a single step
- the production of a higher quality glycerol
- the ability to transesterify triglycerides of different quality
- working under milder conditions resulting in lower energy consumption.

However, enzymatic transesterification has several disadvantages including:

- a longer reaction time
- higher catalyst concentrations to achieve a commercially viable reaction rate
- high production costs
- the reduction in effectiveness after 100 days of application.

Lipases hydrolyse the ester bonds enabling them to hydrolyse fats; however, many lipases are limited because they are fatty acid chain length specific, substrate specific and **regioselective**.

Lipases are useful in biodiesel production since they:

- are able to work in different media, including both hydrophilic or hydrophobic solvents
- can be produced in bulk
- show considerable catalytic ability to transesterify long or branched chained alcohols, which are difficult to convert using conventional alkaline catalysts
- facilitate the downstream separation of the products and by-products
- can be reused after removal from the reaction mixture by immobilisation onto a support
- have higher **thermostability** and short-chain alcohol-tolerance.

The limitations of using lipases in biodiesel production include:

- significant cost
- the reduction in activity if the glycerol covers the lipase reducing its contact with the substrate
- reduced activity due to the volume of the oil molecule.

The enzymatic production of biodiesel works at lower temperatures, reducing energy costs and the amounts of chemicals used and avoiding soap formation. Therefore, it appears that there are considerable economic and environmental advantages to lipase-catalysed production of biodiesel. However, more research is needed in order to be able to produce modified lipase on an industrial scale.

ENZYME-CATALYSED PRODUCTION OF ETHANOL

Ethanol is produced by the fermentation of either corn or sugar cane. Whichever starting ingredient is chosen, both processes involve the conversion of polysaccharide sugars to glucose and then the fermentation of glucose to ethanol.

It is important that oxygen is excluded because, as you have learnt in Chapter 9 (Module 9.3), primary alcohols can be oxidised to the corresponding carboxylic acid. Thus, if oxygen was present the ethanol could be oxidised to ethanoic acid.

When corn or sugar cane are ground up and mixed with water and α-amylase, the glycosidic bonds between individual glucose molecules in starch are hydrolysed to produce maltose. A second enzyme is added to convert the disaccharide, maltose, to glucose:

$$\text{starch} + \text{amylase} \rightarrow \text{maltose}$$

$$\text{maltose} + \text{enzyme} \rightarrow \text{glucose}$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{enzymes}} 2C_6H_{12}O_6$$

The glucose is then fermented by **zymase** within yeast to produce ethanol and carbon dioxide. Nutrients such as phosphoric acid and urea are added to the mixture to enable the yeast to reproduce. Only about 15% ethanol can be produced through fermentation as at higher concentrations the ethanol poisons the yeast. At this stage, the ethanol is removed from the mixture by **distillation** and then the mixture is left to ferment again.



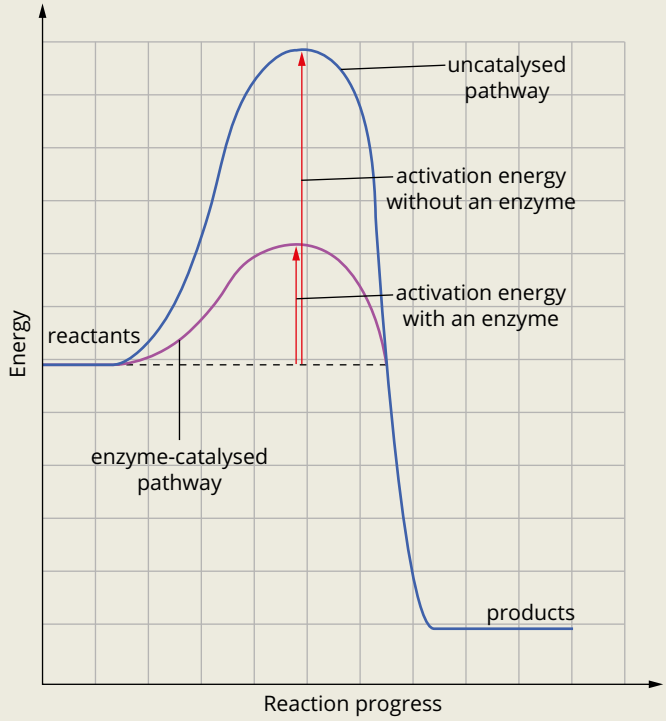
The overall fermentation reaction is:

$$C_6H_{12}O_6 \xrightarrow{\text{enzymes}} 2C_2H_5OH + 2CO_2$$

12.6 Review

SUMMARY

- Enzymes are biological catalysts that speed up the rate of chemical reactions in cells.
- Enzymes share similar features to inorganic catalysts, in that they work by providing an alternative reaction pathway that has a lower activation energy, they are not used up or changed in the reaction so only small amounts are required, and they do not alter the equilibrium position of a reaction.



- Unlike inorganic catalysts, enzymes are often specific for a particular reaction and operate within very narrow conditions outside which they either do not work or the enzyme itself is destroyed.
- Benefits of biocatalysts include:
  - fewer by-products
  - reduced energy use
  - greener production by reducing environmental pollution
  - readily biodegradable.
- Enzymatic catalysis has a number of benefits over traditional chemical catalysis because enzymes:
  - have a high catalytic power
  - work under mild conditions of temperature, pH and pressure
  - display high specificity for the substrate (frequently differentiating between molecules with similar structure)
  - perform well in organic solvents.
- Enzymes have several industrial applications including the lipase-catalysed fermentation of biodiesel and the production of ethanol from corn or cane sugar.

KEY QUESTIONS

Retrieval

1 Define a catalyst.

2 Name the general reaction that converts vegetable oils into biodiesel.

3 Describe the advantages of using a lipase catalyst as opposed to the conventional acid or base catalysts.

Comprehension

4 Enzymes are protein molecules. Explain briefly how this affects their ability to operate outside certain conditions.

5 Explain how the ability to produce biodiesel at lower temperatures is an advantage for enzymes.

6 Explain why it is important that oxygen is excluded from the fermentation of sugars to ethanol.

Analysis

7 Compare and contrast an enzyme with an inorganic catalyst.

12.7 Yield and the chemical industry

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- calculate percentage yields of reactions by identifying limiting reagents and comparing stoichiometric quantities with actual quantities in balanced chemical reactions
- calculate the percentage yields in multistep syntheses
- evaluate the efficacy of different reaction pathways based on the percentage yields.



A major consideration in industrial chemistry is the amount of product that can be produced from a given amount of reactants in a given time. Many industrial processes involve a number of steps in order to make the final product. At each step, the conversion from reactants to products is usually less than complete. For every step in a reaction pathway, the amount of final product diminishes.

YIELD AND THE CHEMICAL INDUSTRY

Industrial chemists must consider the efficiency of a **synthetic pathway** and the wastes that are produced (Figure 12.7.1).

In this module, you will calculate the efficiency of chemical reactions and help in the development of strategies to minimise waste. While the focus in this chapter is on reactions involving organic chemicals, the principles discussed apply to all chemical industries and research.



FIGURE 12.7.1 Most chemical reactions carried out in industrial processes are not 100% efficient and so waste chemicals are produced. The reduction or elimination of waste chemicals is a major concern for industrial chemists.

Theoretical and actual yields

The theoretical yield represents the mass of product that can be formed if all reactants produce products according to the reaction equation. The **theoretical yield** is calculated using the **stoichiometric** mole ratios of the limiting reagent and assumes 100% conversion of the reactants. However, when reactants are mixed together in the correct mole ratio, the amount of products will not always be exactly as predicted from stoichiometric calculations.

A number of factors can influence the amount of product that will be produced for a given reaction.

- When a reaction reaches equilibrium rather than continuing on to completion, the **actual yield** will be less than the theoretical yield.
- If the reaction rate is slow, the reaction may not proceed to completion in the time available. This will reduce the actual yield so that the theoretical yield is not obtained.
- Loss of reactants and products during transfers between reaction vessels and in separation and purification stages, such as filtration, will result in smaller amounts of the product being obtained than expected.

Percentage yield

The percentage yield compares the actual yield to the theoretical yield. It is a measure of the efficiency of a production process, for the particular conditions and method used for the synthesis. The higher the value of the percentage yield, the greater the degree of conversion from reactants to products for the reaction.

Percentage yield can be calculated using the formula:

$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

Worked example 12.7.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

30.0 g of propan-2-ol was oxidised to propanone using an acidified solution of potassium dichromate ($K_2Cr_2O_7$). The propanone that was distilled from the reaction mixture had a mass of 20.0 g. Calculate the percentage yield of this oxidation reaction.

Thinking	Working
Write an equation for the reaction.	$CH_3CH(OH)CH_3 \xrightarrow{K_2Cr_2O_7/H^+} CH_3COCH_3$ Note that in this case it is not necessary to write a full equation. Because a molecule of the organic product has the same number of carbon atoms as the organic reactant, the number of moles of the product is equal to the number of moles of the reactant.
Use the formula $n = \frac{m}{M}$ to determine the number of moles of the reactant.	$n(CH_3CH(OH)CH_3) = \frac{m}{M}$ $= \frac{30.0}{60.11}$ $= 0.500$ mol
Use the mole ratio for the reaction to determine the number of moles of the product that would be made if all of the reactant reacted.	mole ratio $= \frac{n(CH_3COCH_3)}{n(CH_3CH(OH)CH_3)}$ $n(CH_3COCH_3) = \frac{1}{1} \times n(CH_3CH(OH)CH_3)$ $= 0.500$ mol
Use the formula $m = n \times M$ to determine the mass of the product if all of the reactant reacts. This is the theoretical yield of the product.	$m(CH_3COCH_3) = n \times M$ $= 0.500 \times 58.09$ $= 29.05$ g
Calculate the percentage yield for this reaction from the formula: percentage yield $= \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$	percentage yield $= \frac{20.00}{29.05} \times 100$ $= 68.85\%$

➤ Try yourself 12.7.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

80.0 g of propan-1-ol was oxidised to propanoic acid using an acidified solution of potassium dichromate ($K_2Cr_2O_7$). The propanoic acid obtained at the end of the reaction had a mass of 55.0 g. Calculate the percentage yield of this oxidation reaction.

Percentage yields in multistep synthesis

When a reaction proceeds by a number of steps, the overall percentage yield is reduced at each step. The yield for each step has an effect on the **overall yield**.

A low yield in one of the intermediate reactions can have a significant effect on the amount of final product obtained.

Comparison of the overall percentage yields for different pathways to the same product can be used to determine whether a particular synthetic pathway is the best way to produce an organic compound. Finding the most efficient pathway for the production of a desired chemical is critical to industry because wasting valuable reactants is not a good option, economically or environmentally.

Worked example 12.7.2

CALCULATING THE PERCENTAGE YIELD OF A MULTISTEP SYNTHESIS

Calculate the overall percentage yield for the preparation of C from A if it proceeds by a two-step synthesis:

$A \rightarrow B$ followed by $B \rightarrow C$

The yield of $A \rightarrow B$ is 80% and the yield of $B \rightarrow C$ is 70%.

Thinking	Working
Calculate the overall yield of C by multiplying the percentage yields together and expressing as a percentage.	The overall yield is: $\frac{80}{100} \times \frac{70}{100} \times \frac{100}{1}$ $= 56\%$

➤ Try yourself 12.7.2

CALCULATING THE PERCENTAGE YIELD OF A MULTISTEP SYNTHESIS

Calculate the overall percentage yield for the preparation of D from A if it proceeds by a three-step synthesis:

$A \rightarrow B$ followed by $B \rightarrow C$ followed by $C \rightarrow D$

The yield of $A \rightarrow B$ is 90%, the yield of $B \rightarrow C$ is 80% and the yield of $C \rightarrow D$ is 60%.

12.7 Review

SUMMARY

- The efficiency of a synthetic pathway is an important consideration for industrial chemists.
- Most chemical reactions are not 100% efficient.
- The theoretical yield is the maximum amount of the product that can be formed based on the stoichiometric mole ratios of the limiting reagent.
- The actual yield is less than the theoretical yield and is the amount of the product actually produced.
- The percentage yield can be calculated using:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

- The percentage yield in a multistep synthesis is the product of the percentage yield for each individual reaction. For example, for the multistep reaction $A \rightarrow B \rightarrow C \rightarrow D$ with the yields: 90%, 50% and 60%:

$$\text{overall yield} = \frac{90}{100} \times \frac{50}{100} \times \frac{60}{100}$$
$$= 27\%$$

KEY QUESTIONS

Retrieval

1 Define the percentage yield.

Comprehension

2 Explain the difference between theoretical and actual yield.

Analysis

3 Compound D can be synthesised by a reaction pathway that involves a number of intermediate steps. The yield for each step is shown:

$$A \xrightarrow{70\%} B \xrightarrow{50\%} C \xrightarrow{90\%} D$$

a Determine the overall yield for the preparation of compound D from compound A.

b Deduce how the overall yield would be affected if the yield for $B \rightarrow C$ was only 10%.

4 During a trial experiment for the industrial production of ethanol from ethene, 150 g of ethene was reacted with water to produce ethanol according to the equation:

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$

Calculate the theoretical yield, in grams, of ethanol for this reaction.

5 Calculate the percentage yield for the reaction in which 20.0 g of ethanol is oxidised to produce 21.5 g of ethanoic acid according to the equation:

$$C_2H_5OH \xrightarrow{K_2Cr_2O_7/H^+} CH_3COOH$$

12.8 Green chemistry



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- appreciate that green chemistry principles include the design of chemical synthesis processes that use renewable raw materials, limit the use of potentially harmful solvents and minimise the amount of unwanted products
- outline the principles of green chemistry and recognise that the higher the atom economy, the 'greener' the process
- calculate atom economy and evaluate the economic and environmental impact of chemical synthesis processes.

An important objective for an industrial chemist developing a synthetic pathway is to use a sequence of chemical reactions that minimises energy consumption, reduces waste and has a low impact on the environment.

In this way, 'green' chemistry aims to maximise the desired products and minimise by-products thereby improving the atom economy of a process. The design of new synthetic pathways is also important in developing sustainable chemical industries.

GREEN PRINCIPLES

There has been much research into the impact of humans on the sustainability of our environment, including the impact of anthropogenic processes on climate. All chemical processes, both natural and industrial, create waste that can pollute the environment. The following figures illustrate a variety of causes and effects that pollutants such as acid rain (Figure 12.8.1), acid mine drainage (Figure 12.8.2), pesticides (Figure 12.8.3) and oil spills (Figure 12.8.4) can have on the environment.

It is critical that scientists work to design and produce economically viable chemical products and devise processes that reduce pollution at its source. This is known as green chemistry.

Green chemistry provides principles that produce chemicals that are less hazardous to human health and the environment, reduce our dependency upon non-renewable resources and produce less waste material.

As a result, the **US EPA** has identified 12 green principles for chemical synthesis that demonstrate the concept of green chemistry:

1 Prevent waste. The chemical synthetic pathway should ideally prevent waste; however, if that is not possible the waste must be treated or cleaned up.

2 Maximise atom economy. Atom economy is important from an economic viewpoint but a higher atom economy also reduces the amount of raw materials required. Therefore, it is important that the final product contains the maximum proportion of the starting materials.

3 Design less hazardous chemical syntheses. Most chemical reactions will produce some unwanted by-products. It is better if these substances have little or no toxicity to either humans or the environment.

4 Design safer chemicals and products. As outlined in Modules 12.1 and 12.2, it is important to design pharmaceuticals that are completely effective, which may involve modifying their properties so that less product is required to have the same effect and with little or no toxicity.

5 Use safer solvents and reaction conditions. Where possible synthesis should avoid using solvents, separation agents or other auxiliary chemicals as these are often released into the environment.



FIGURE 12.8.1 Acid rain is formed downwind of industries that produce acidic gases such as sulfur dioxide. The acid rain leaches nutrients and toxic metals out of the soil, damaging vegetation. (a) This limestone statue has become pitted in recent years. Limestone (calcium carbonate) reacts more rapidly with the increased concentration of hydrogen ions in rainwater. (b) Aquatic plants and animals are killed when the pH falls too low. (c) The acid rain leaches nutrients and toxic metals out of the soil, damaging vegetation.



FIGURE 12.8.2 (a) The pool of red-coloured water at this mine site is typical of the effects of acid mine drainage; (b) Acid mine drainage from the disused Brukunga mine site in South Australia.

The causes and effects of pollutants on the environment



FIGURE 12.8.3 (a) A crop-dusting plane can quickly disperse different pesticides over crops. (b) Spraying an orchard to protect fruit from pests. Insects landing on the fruit are killed before they can lay eggs. (c) A village in Madagascar is sprayed with DDT to eradicate fleas. Fleas are linked to the transfer of a range of potentially fatal diseases, such as bubonic plague.



FIGURE 12.8.4 (a) An oil spill; (b) Effects of oil spills on wildlife and habitat; (c) After the explosion on the Deepwater Horizon oil rig in the Gulf of Mexico, oily sludge reached beaches around the Gulf of Mexico.

6 Increase energy efficiency. Operating at high temperatures and pressures often requires energy, so whenever possible chemical reactions should be performed at room temperature and pressure. To achieve an economically viable reaction rate this increases the need for catalysts.
7 Use renewable raw materials. Instead of using non-renewable resources, such as fossil fuels or mining ores, the use of renewable feedstocks, such as agricultural crops or wastes from other processes, is preferable.
8 Avoid chemical derivatives. The use of protecting groups on the chemical reduces the atom economy of the product as it requires additional reagents and creates waste.
9 Use catalysts, not stoichiometric reagents. Minimise waste by using catalysts. These are not used up in the reaction and are therefore only required in small quantities. In addition, they allow the reactions to operate at lower temperatures.
10 Design chemicals and products to degrade after use. Nowadays, more and more products are biodegradable, which means that after use they break down to simpler, harmless molecules and do not accumulate in the environment.
11 Analyse in real time to prevent pollution. Both the manufacturing process and treatment of any effluent should be monitored in real time so that it is possible to identify and control problems during the manufacturing process and minimise or eliminate by-products.
12 Minimise the potential for accidents. Design safer processes to minimise the potential for chemical accidents including explosions, fires and release to the environment.

ATOM ECONOMY

An important principle and consideration when planning reaction pathways is to maximise **atom economy**. The atom economy for a chemical reaction is a measure of how many of the atoms in the reactants end up in the desired product. As you can see in Figure 12.8.5, if the atom economy of a reaction is high, then there are few, if any, waste products. Any atom that does not go into the product must go into the waste product.

Calculating the atom economy of a reaction provides a method of accounting for the use of materials in a manufacturing process. It tracks all the atoms in a reaction and calculates the mass of the atoms of reactants actually used to form products as a percentage of the total mass of reactants. From this, the mass of reactant atoms that end up as waste can also be calculated.

Once the balanced equation for a reaction is known, the atom economy can be calculated using the formula:

$$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$

Since in a chemical reaction, the total mass of products is equal to the total mass of reactants, this alternative formula can also be used:

$$\text{atom economy} = \frac{\text{mass of desired product}}{\text{mass of all products}} \times 100$$

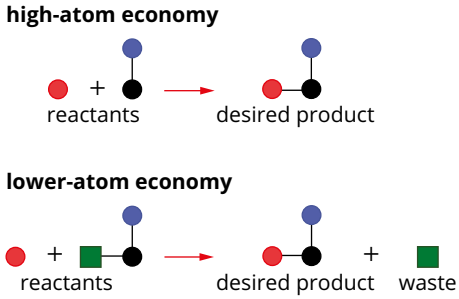


FIGURE 12.8.5 The different coloured symbols represent atoms or groups of atoms. In a high-atom economy reaction, all or most of the atoms in the reactant molecules end up in the desired product molecule. In a lower-atom economy reaction, not all of the reactant atoms end up in the desired product. The atoms that don't end up in the desired product are waste products of the reaction.

Worked example 12.8.1

CALCULATING ATOM ECONOMY

Calculate the atom economy in the production of ethanol from chloroethane. In this process, chloroethane is heated with a solution of sodium hydroxide.

The equation for the reaction is:

$$C_2H_5Cl(l) + NaOH(aq) \rightarrow C_2H_5OH(l) + NaCl(aq)$$

Thinking	Working
Calculate the total molar mass of the reactants.	$M(C_2H_5Cl) + M(NaOH)$ $= [(2 \times 12.01) + (5 \times 1.01) + (1 \times 35.45)] + [22.99 + 16.00 + 1.01]$ $= 104.52 \text{ g mol}^{-1}$
Calculate the molar mass of the required product.	$M(C_2H_5OH)$ $= [(2 \times 12.01) + (5 \times 1.01) + (1 \times 16.00) + (1 \times 1.01)]$ $= 46.08 \text{ g mol}^{-1}$
Calculate the atom economy for the reaction using the formula: $\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$	$\text{atom economy} = \frac{46.08}{104.52} \times 100$ $= 44.09\%$ So in this process, only 44.09% of the starting materials are converted to the desired product. The remainder of the chemicals used is waste.

➤ Try yourself 12.8.1

CALCULATING ATOM ECONOMY

Calculate the percentage atom economy in the formation of 1-iodopropane ($CH_3CH_2CH_2I$) from propan-1-ol. The equation for the reaction is:

$$CH_3CH_2CH_2OH(l) + NaI(aq) + H_2SO_4(aq) \rightarrow CH_3CH_2CH_2I(aq) + NaHSO_4(aq) + H_2O(l)$$

PA 4.2.1 WS 4.2.2

Green synthesis methods and atom economy

Prior to 1991, the efficiency of a chemical reaction was generally quantified in terms of the product yield, with a theoretical value of 100%. Nowadays, chemists view reactions in terms of how much of the reactants are converted into a desired product. This change came about following the development of a concept of atom economy by Barry M. Trost at Stanford University.

A good example of this concept is the production of ibuprofen. Ibuprofen is an over-the-counter NSAID (non-steroidal anti-inflammatory drug) painkiller sold at many supermarkets and pharmacies. Ibuprofen stops the body from producing large amounts of prostaglandins to help relieve pain and reduce inflammation when you have an illness or injury, such as headaches, toothaches, muscular aches or period pain. The structural formula of ibuprofen is shown in Figure 12.8.6

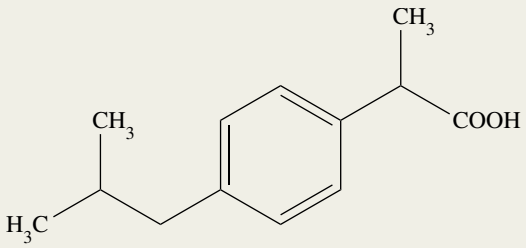


FIGURE 12.8.6 The IUPAC name for ibuprofen is 2-methylpropylphenylpropanoic acid.

An early synthetic pathway required six steps, beginning with the compound 2-methylpropylbenzene which is produced from compounds separated from crude oil. The remaining five steps are shown in Figure 12.8.7.

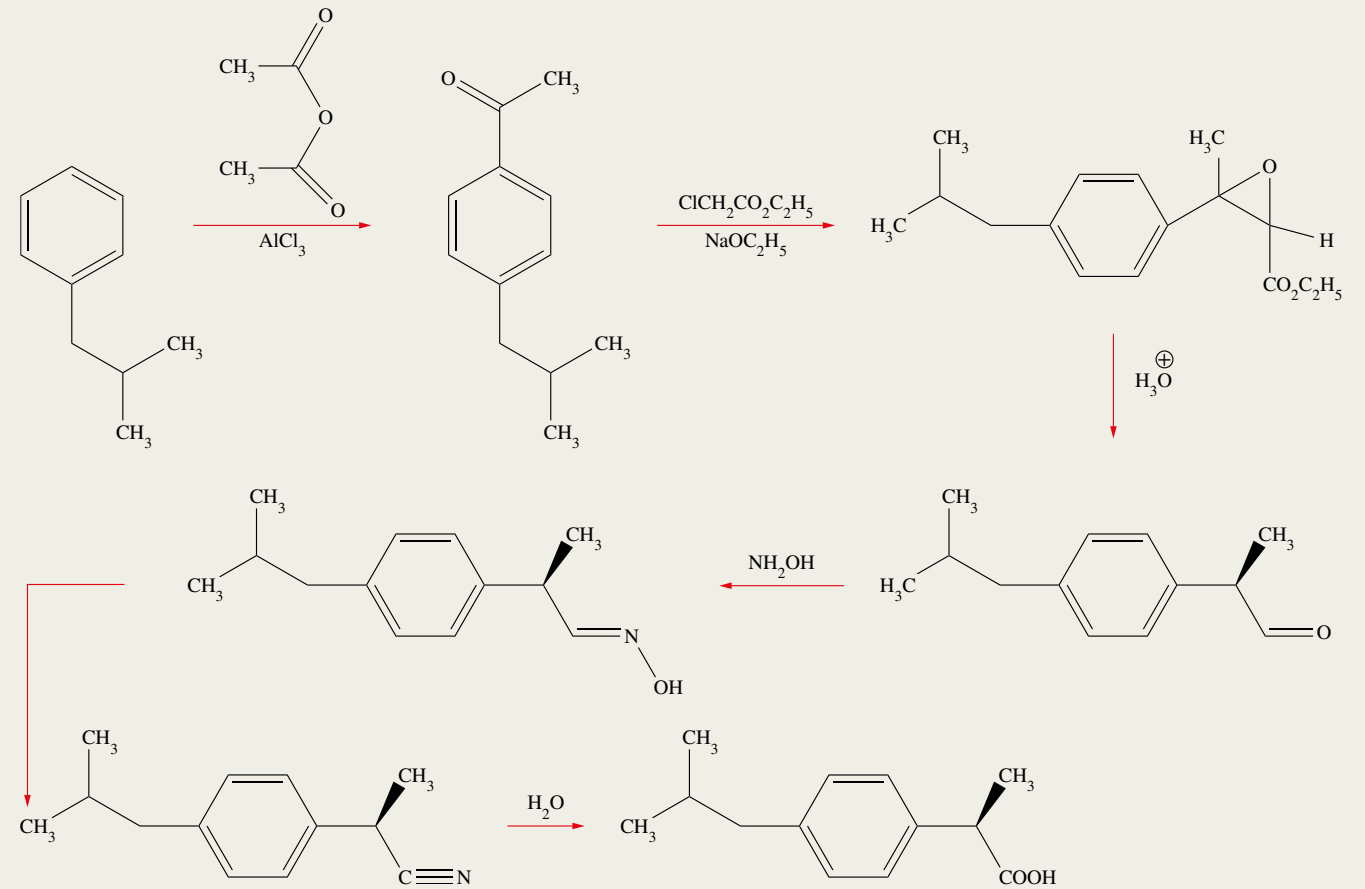


FIGURE 12.8.7 The Boots' synthetic pathway of ibuprofen

The efficiency of the pathway can be determined by calculating the atom economy. This involves looking at the mass of atoms from the starting material that end up in the final product. Table 12.8.1 shows the calculation of the atom economy of the overall reaction.

TABLE 12.8.1 Atom economy in the Boots' synthesis of ibuprofen

Reagent		**Used in ibuprofen**		**Unused in ibuprofen**	
Formula	**M_r**	**Formula**	**M_r**	**Formula**	**M_r**
$C_{10}H_{14}$	134.24	$C_{10}H_{13}$	133.23	H	1.01
$C_4H_6O_3$	102.10	C_2H_3	27.05	$C_2H_3O_3$	75.05
$C_4H_7ClO_2$	122.56	CH	13.02	$C_3H_6ClO_2$	109.54
C_2H_5ONa	68.06			C_2H_5ONa	68.06
H_3O	19.03			H_3O	19.03
NH_3O	33.04			NH_3O	33.04
H_4O_2	36.04	HO_2	33.01	H_3	3.03
Total		**Ibuprofen**		**Waste products**	
$C_{20}H_{42}NO_{10}ClNa$	514.98	$C_{13}H_{18}O_2$	206.31	$C_7H_{24}NO_8ClNa$	308.67

The atom economy for the reaction can be determined by:

$$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$

$$= \frac{206.31}{514.98} \times 100$$
$$= 40.06\%$$

The overall atom economy is 40%, which means that more than half of the chemicals used in the synthesis are wasted.

In 1990 a greener pathway was developed, which synthesised ibuprofen in three steps from the same starting material, 2-methylpropylbenzene acid. This is shown in Figure 12.8.8. Table 12.8.2 shows that the overall atom economy is 77%, which is almost double that of the previous synthetic method.

TABLE 12.8.2 Atom economy in the green synthesis of ibuprofen

Reagent		**Used in ibuprofen**		**Unused in ibuprofen**	
Formula	**M_r**	**Formula**	**M_r**	**Formula**	**M_r**
$C_{10}H_{14}$	134.24	$C_{10}H_{13}$	133.23	H	1.01
$C_4H_6O_3$	102.10	C_2H_3O	43.05	$C_2H_3O_2$	59.05
H_2	2.02	H_2	2.02		
CO	28.01	CO	28.01		
Total		**Ibuprofen**		**Waste products**	
$C_{15}H_{22}O_4$	266.37	$C_{13}H_{18}O_2$	206.31	$C_2H_4O_2$	60.06

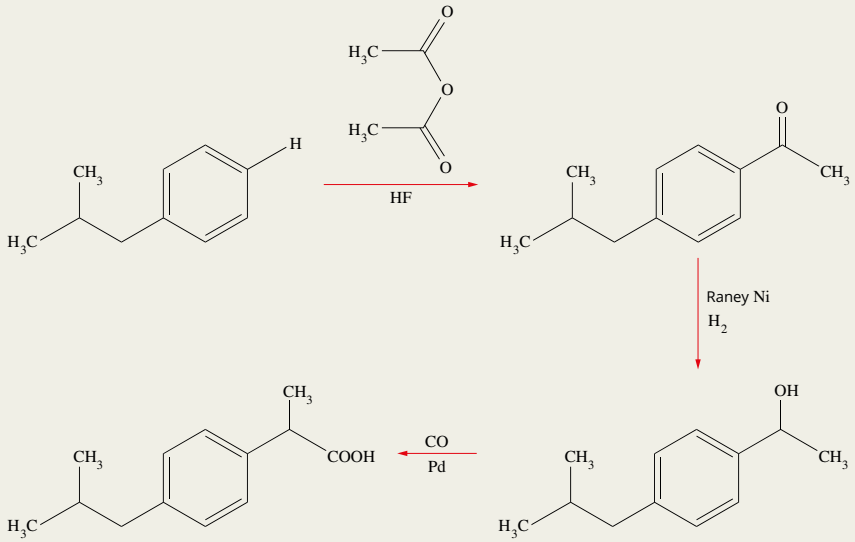


FIGURE 12.8.8 The 'greener' BHC synthetic pathway of ibuprofen

As before, the atom economy for the reaction can be determined by:

$$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$

$$= \frac{206.31}{266.37} \times 100$$

$$= 77.45\%$$

In addition to the fewer steps and greater atom economy, other advantages of the BHC pathway include the use of less hazardous material and use of catalysts. For instance, the hydrogen fluoride (HF) used in the first step is used in catalytic amounts and can be recovered and reused. These factors combine to provide significant economic and environmental benefits.

Review

1 **a** Explain the difference between atom economy and % yield. In your response consider the following reactions.

The oxidation of benzene has a 65% yield compared to the oxidation of but-1-ene, which only has a 55% yield.

b Calculate the atom economy for the two pathways and discuss your findings.

2 Calculate the atom economy for the first step in the Boots' pathway.

3 Calculate the atom economy of the second step in the BHC pathway.

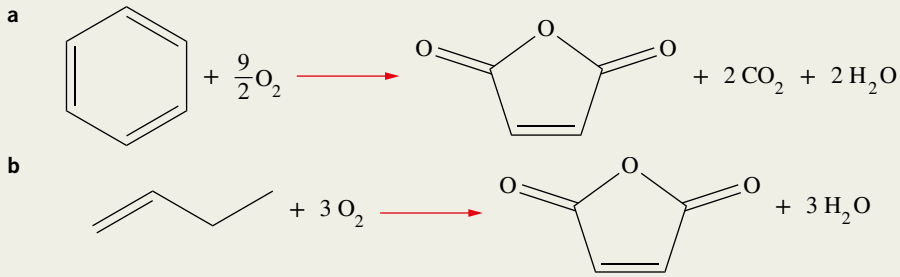


FIGURE 12.8.9 Formation of maleic anhydride by (a) oxidation of benzene, and (b) oxidation of but-1-ene.

12.8 Review

SUMMARY

- Green chemistry aims to maximise the desired products and minimise by-products thereby improving the atom economy of a process. In this way it is desirable to design and produce economically viable chemical products and devise processes that reduce pollution at its source.
- All chemical processes, both natural and industrial, create waste that can pollute the environment.
- The US EPA has identified 12 green principles for chemical synthesis:
  1. Prevent waste
  2. Maximise atom economy
  3. Design less hazardous chemical syntheses
  4. Design safer chemicals and products
  5. Use safer solvents and reaction conditions
  6. Increase energy efficiency
  7. Use renewable raw materials
  8. Avoid chemical derivatives
  9. Use catalysts, not stoichiometric reagents
  10. Design chemicals and products to degrade after use
  11. Analyse in real time to prevent pollution
  12. Minimise the potential for accidents
- The atom economy for a chemical reaction is a measure of how many of the atoms in the reactants end up in the desired product. Any atom that does not go into the product must go into the waste product. If the atom economy of a reaction is high there are few, if any, waste products.
- Atom economy can be calculated using the formula:

$$\text{atom economy} = \frac{\text{mass of desired product}}{\text{mass of all products}} \times 100$$

KEY QUESTIONS

Retrieval

1 Describe how the following green principles help to produce sustainable, economically viable products that reduce pollution.
- **a** using renewable raw materials
- **b** designing less hazardous chemical syntheses

2 Define the term 'atom economy'.

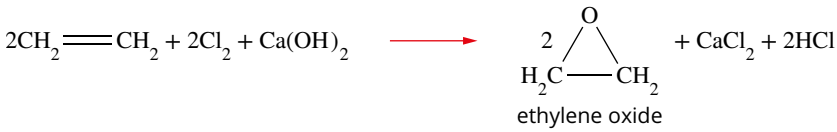
Comprehension

3 Explain the concept of green chemistry.

4 Explain how the use of catalysts can promote green chemistry.

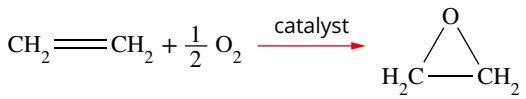
Analysis

5 Evaluate the 'greeness' of two pathways to ethylene oxide by calculating the atom economy of each pathway.
- **a** the chlorohydrin pathway



ethylene oxide

- **b** the catalytic pathway



6 When ethanamide is produced by the reaction of ethanoic acid and ammonia, the atom economy is 76.7%. Calculate the total mass of reactants, in kilograms, required to make 2.00 kg of ethanamide.

Chapter review

12

KEY TERMS

absorbed
actual yield
alkaline (solution)
atom economy
bioavailability
biocatalyst
biodegradable
biodegradation
biodiesel
by-products
cloud point
contact process
convergent synthesis
density
derivatives
distillation
emissions
energy content
energy density
enzyme
enzyme activity
fermentation
fuel cell
glycerol
green chemistry
Haber process
hygroscopic
intermolecular forces
materials-based storage
nitrogenase
non-renewable (fuel)
oleum
ores
overall yield
partially dissociate
percentage yield
petrodiesel
prodrug
promoters
regioselective
renewable (fuel)
retrosynthetic pathway
steam reforming
stoichiometric
synthetic pathway
TD_{50}
teratogenic
theoretical yield
thermostability
transesterification
US EPA
viscosity
yield
zymase

KEY QUESTIONS

Retrieval

1 Select the statement from the following options that best describes retrosynthesis.
- **A** The creation of a pathway that does not have an equilibrium.
- **B** The design of a scheme that uses older, traditional technology.
- **C** A synthetic strategy that works backwards from the product to simple starting compounds.
- **D** The reagents and conditions that convert a product back into the original starting compounds.

2 Select a definition of physical properties from the following options.
- **A** Physical properties can only be seen with our eyes.
- **B** Physical properties require special tools to observe them.
- **C** Physical properties can be observed without changing the identity of the substance.
- **D** Physical properties describe how a substance changes into a completely different substance.

3 While the carbon dioxide per gram emission from bioethanol combustion is less than that of octane (petrol), a car using bioethanol produces more carbon dioxide for the same journey as a car using octane. Select from the following options the statement that best explains this difference.
- **A** Bioethanol is more efficient than octane.
- **B** The energy content of bioethanol is less than that of octane.
- **C** The temperature of the engine favours the combustion of octane.
- **D** More energy transformations are required in the combustion of bioethanol.

4 Select which of the following options shows the half-equation for the reaction occurring at the cathode in a hydrogen–oxygen fuel cell with an alkaline electrolyte.
- **A** $H_2(g) \rightarrow H^+(aq) + 2e^-$
- **B** $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
- **C** $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$
- **D** $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

5 Ethanol is produced by fermentation of glucose, as shown in the following equation (M_r values for each molecule are provided).

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_6O(aq) + 2CO_2(g)$$

M_r	180	46	44

Determine which of the following expressions represents the atom economy for the reaction above.

A $\frac{46}{180} \times 100\%$

B $\frac{(46+44)}{180} \times 100\%$

C $\frac{(2\times46)}{180} \times 100\%$

D $\frac{(2\times46)+(2\times44)}{180} \times 100\%$

6 Select which of the following options is one of the 12 principles of green chemistry.

A reuse waste
B use only new solvents
C design commercially viable products
D use catalysts, not stoichiometric reagents

7 Define the term 'enantiomer'.

8 Identify the reagents and conditions that convert each starting material into the product.

	Reactant	Product
a	propan-2-ol	propanone
b	2-methyl-1-butene	2-chloro-2-methylbutane
c	$CH_3 - C \equiv N$	ethylamine
d	pentane	bromopentane

9 State whether the following are examples of a chemical or physical property.

a blue colour
b melting point
c density
d reacts with water
e flammability
f hardness
g solubility

10 State the name of the reaction in which a triglyceride is broken down to form biodiesel molecules.

11 List four advantages of using enzymes in industrial processes.

12 Define a biocatalyst.

13 Show the steps and conditions used in the industrial production of sulfuric acid.

14 Define percentage yield.

Comprehension

15 Determine whether the following are examples of a physical change or a chemical change.

a table salt (NaCl) dissolves in water
b milk sours
c silver (Ag) tarnishes
d sugar dissolves in water
e an apple is cut
f wood rots
g heat changes H_2O to steam

16 Explain the difference between a renewable and non-renewable fuel.

17 Describe the key difference between a fuel cell and a primary or secondary cell.

18 Describe two problems that make it necessary to research an alternative to fossil fuels for powering vehicles. For each explain how hydrogen would solve the problem.

19 Explain why fuel cells have a greater efficiency than thermal power stations.

20 Explain how soap removes oil.

21 Explain why biological washing powders are more effective than non-biological washing powders at low temperatures.

22 Compound D can be synthesised in the following pathway.

$$A \xrightarrow{50\%} B \xrightarrow{90\%} C \xrightarrow{65\%} D$$

Determine the overall yield for the preparation of compound D from compound A.

23 Explain the guiding principles of green chemistry.

24 Represent a retrosynthetic pathway for the formation of propanone from an alkene.

25 Represent a retrosynthetic pathway for the synthesis of ethyl propanoate.

Analysis

26 Determine the forward reactions used to produce n-butylpropanamide from propane. Use your knowledge of the retrosynthetic pathway and your knowledge of chemical reactions from Chapter 9.

27 Determine equations for the production of:

a chloroethane from ethane
b ethanol from ethene
c ethanol from chloroethane
d ethanoic acid from ethanol.

28 Classify each of the following as advantages or disadvantages of the use of bioethanol compared to petrol as an energy source.
- **a** It has a smaller carbon footprint.
- **b** It has lower energy density ($kJ\,g^{-1}$).
- **c** It can be produced from waste products.
- **d** It is a renewable resource.
- **e** A greater amount of CO_2 is emitted to travel a set distance.

29 Analyse why bioethanol is sometimes described as a 'carbon neutral' fuel. In your response support your answer with equations of photosynthesis, fermentation and combustion.

30 Trials are being conducted to source biodiesel from algae grown in the warm water of a power station cooling pond. The water is warm and carbon dioxide emitted from the power station can be trapped and bubbled through the water to enhance the growth of the algae. Classify the following as either an advantage or a disadvantage of large-scale production of biodiesel from algae.
- **a** fewer particulate emissions than petrodiesel
- **b** renewable
- **c** less reliance on fossil fuels
- **d** distribution outlets required
- **e** fewer net CO_2 emissions than petrodiesel
- **f** oil can be 'harvested' many times per year
- **g** reduction of CO_2 emissions from coal-fired power stations
- **h** more additives need to be added to the fuel in cold climates

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

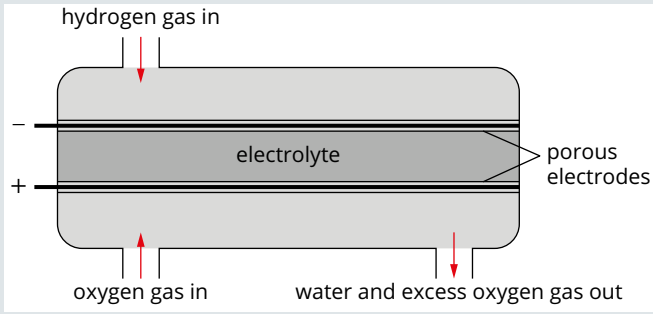
$$C_2H_4(g) + H_2O(g) \rightarrow CH_3CH_2OH(g)$$

- **a** Deduce whether ethanol produced by this method is a biochemical fuel.
- **b** Determine how ethanol, which is classified as a biochemical fuel, could be produced.

32 Compare the structures of petrodiesel and biodiesel to predict for which fuel incomplete combustion is more of a problem.

33 Predict if the following scenarios are more likely to refer to petrodiesel or biodiesel.
- **a** A sample of diesel has gone cloudy after being stored a long time.
- **b** The exhaust from this engine contains significant particulates.
- **c** The car will not start on a cold morning.
- **d** The water content of the fuel has reached a high level.

34 Explore why it is an advantage to use porous electrodes in hydrogen fuel cells, as shown in the diagram below.



35 Scientists have identified a number of other compounds, shown in the table below, that could be used in fuel cells.

Fuel and reactions occurring in the fuel cell.

Fuel		**Reaction occurring in the fuel cell**
ethane	C_2H_6	$C_2H_6 + 4H_2O \rightarrow 2CO_2 + 14H^+ + 14e^-$
methanol	CH_3OH	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$
ethanol	CH_3CH_2OH	$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$
ethane-1,2-diol	CH_2OHCH_2OH	$CH_2OHCH_2OH + 2H_2O \rightarrow 2CO_2 + 10H^+ + 10e^-$

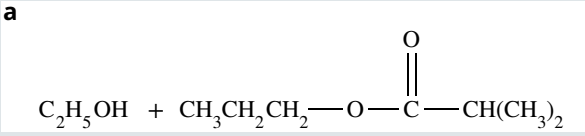
Evaluate which of these fuels is the most environmentally friendly based on the amount of CO_2 per coulomb of electrical charge generated. This is determined by dividing the number of moles of carbon dioxide by the number of electrons produced.

36 The equilibrium in which sulfur dioxide reacts with oxygen to form sulfur trioxide is one of the major reactions in the contact process (formation of sulfuric acid).
At one power plant, the concentration of sulfur dioxide before the reaction was $0.090\,mol\,L^{-1}$ and the concentration of oxygen was $0.040\,mol\,L^{-1}$. Once equilibrium was reached, the concentration of sulfur trioxide was $0.052\,mol\,L^{-1}$. Calculate the equilibrium constant, K, for the reaction.

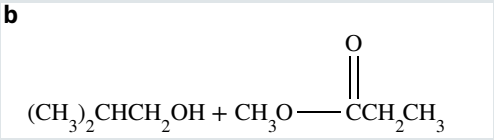
37 Assess the advantages and disadvantages of replacing petrol with renewable fuels such as ethanol.

38 Predict the structure of the ester produced through the following transesterification reactions.

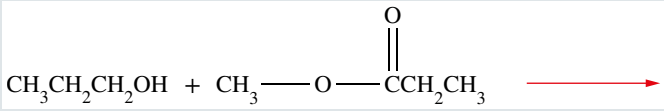
a



b



39 Determine the products for this transesterification reaction.



40 Identify why biological detergents are perceived to be better for the environment than non-biological detergents.

41 Identify factors that need to be considered when evaluating whether a chemical or biochemical catalyst is more suitable for a particular industrial application.

42 During a small-scale trial for the industrial production of ethanol from ethene, 200 g of ethene was reacted with excess water according to the following reaction.

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(l)$$

Calculate the theoretical yield of ethanol for this reaction.

43 Calculate the percentage yield for the following reaction in which 23.0 g is produced from 19.7 g of ethanol.

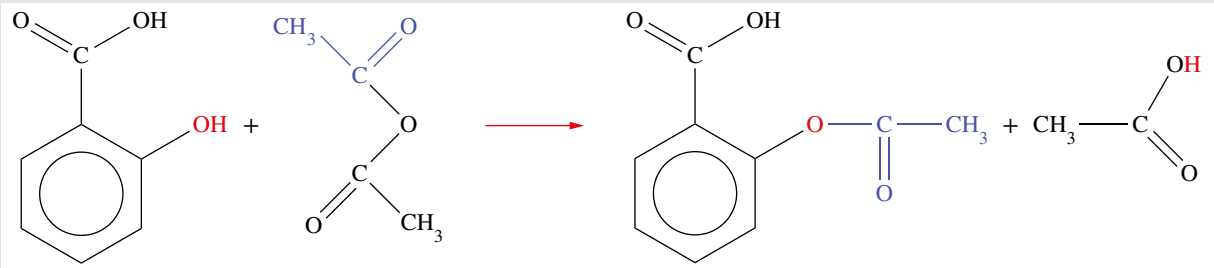
$$C_2H_5OH \rightarrow CH_3COOH$$

44 The reaction between ethane and chlorine in the presence of sunlight produces chloroethane (C_2H_5Cl), as shown in the following equation.

$$C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$$

Determine the atom economy for the production of chloroethane in this reaction.

45 Aspirin can be synthesised by an esterification reaction according to the pathway shown in the figure below.



A student reacted a 2.50 g sample of salicylic acid with an excess of ethanoic anhydride, using sulfuric acid as a catalyst. After purification a mass of 2.35 g of pure aspirin was obtained.

a Calculate the theoretical yield of aspirin for the reaction.

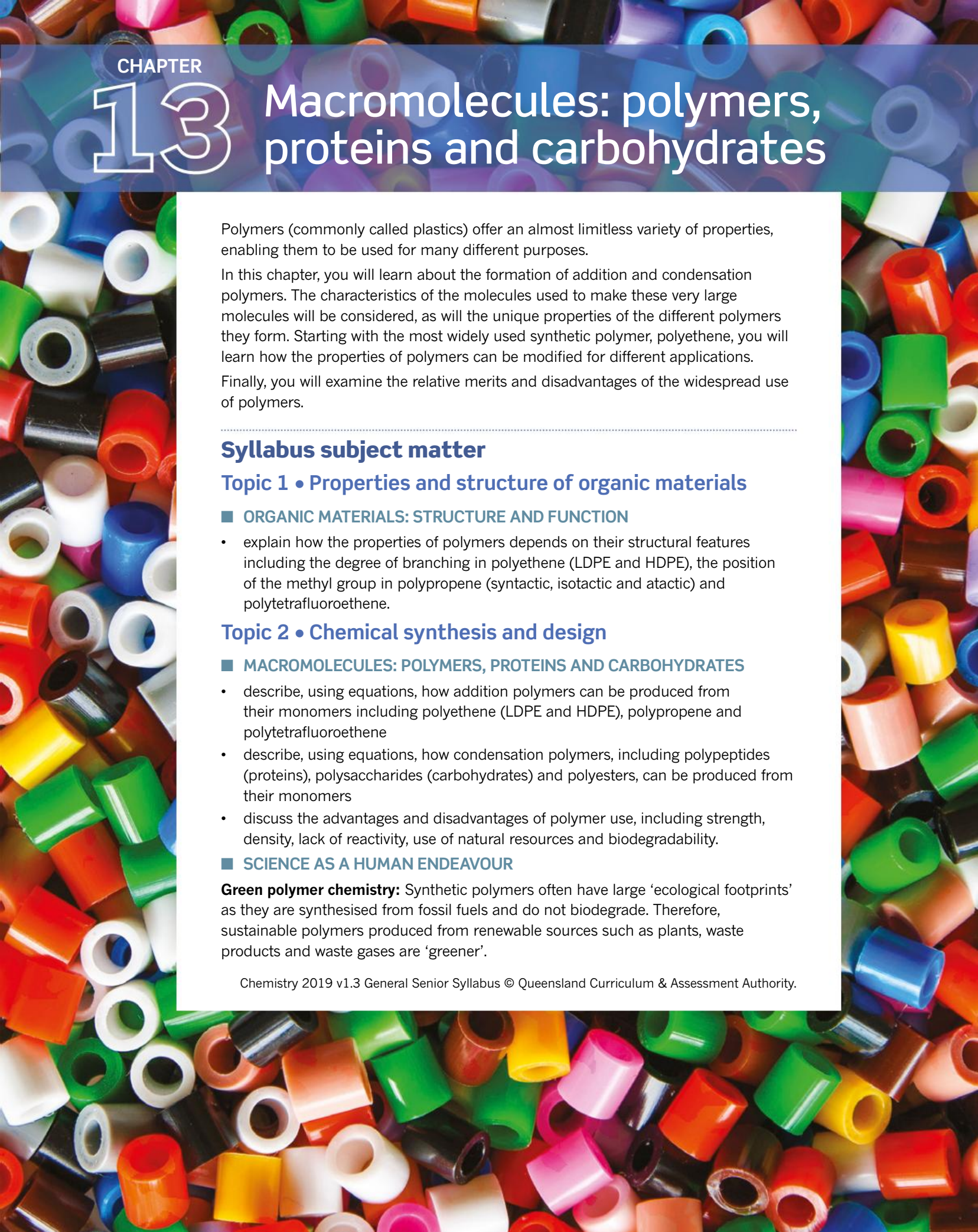
b Calculate the percentage yield of aspirin for the reaction.

46 While green chemistry has a large number of advantages over traditional synthetic approaches, identify some disadvantages of green chemistry.

Knowledge utilisation

47 Investigate the range of new technologies available to power vehicles and evaluate whether it would be possible for Australia to adopt hydrogen or electricity as the main vehicle fuel.





CHAPTER

13 Macromolecules: polymers, proteins and carbohydrates

Polymers (commonly called plastics) offer an almost limitless variety of properties, enabling them to be used for many different purposes.

In this chapter, you will learn about the formation of addition and condensation polymers. The characteristics of the molecules used to make these very large molecules will be considered, as will the unique properties of the different polymers they form. Starting with the most widely used synthetic polymer, polyethene, you will learn how the properties of polymers can be modified for different applications.

Finally, you will examine the relative merits and disadvantages of the widespread use of polymers.

Syllabus subject matter

Topic 1 • Properties and structure of organic materials

■ ORGANIC MATERIALS: STRUCTURE AND FUNCTION

- explain how the properties of polymers depends on their structural features including the degree of branching in polyethene (LDPE and HDPE), the position of the methyl group in polypropene (syntactic, isotactic and atactic) and polytetrafluoroethene.

Topic 2 • Chemical synthesis and design

■ MACROMOLECULES: POLYMERS, PROTEINS AND CARBOHYDRATES

- describe, using equations, how addition polymers can be produced from their monomers including polyethene (LDPE and HDPE), polypropene and polytetrafluoroethene
- describe, using equations, how condensation polymers, including polypeptides (proteins), polysaccharides (carbohydrates) and polyesters, can be produced from their monomers
- discuss the advantages and disadvantages of polymer use, including strength, density, lack of reactivity, use of natural resources and biodegradability.

■ SCIENCE AS A HUMAN ENDEAVOUR

Green polymer chemistry: 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’.

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13.1 Types of polymers



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- identify polymerisation reactions
- distinguish between addition and condensation monomers
- draw the chemical reaction that describes polymerisation
- determine the monomers required to form a polymer.

Polymers are often referred to by the general term **plastics**. You can probably identify many items that are made of polymers. Polymers are used in the construction of many different objects because they are cheap, versatile and easy to manufacture. Many products such as combs, pen casings and rulers do not require special properties. They do not have to withstand high temperatures or highly corrosive environments. These products can be made from cheap, lightweight polymer materials.

Figure 13.1.1 shows a range of familiar polymers. The polymers that make up these objects are selected for their strength, flexibility or other properties. In this chapter you will learn that scientists have developed very sophisticated polymers with high performance properties.







FIGURE 13.1.1 (a) The polymer used to make the toy soccer players in this game was selected for its strength and how easy it is to mould. (b) The polymer banknotes used in Australia are strong and flexible. (c) The polymers in the helmet, gloves and bottle are similar, but differences in processing have given them very different properties.

There are thousands of different polymers, many with specialised properties. However, in general polymers are:

- lightweight
- non-conductors of electricity
- durable
- versatile
- acid-resistant
- flammable.

The term 'plastic' is frequently used to describe many items, from cling wrap to detergent bottles. For chemists, the term 'plastic' describes the property of a material, not the material itself. A substance is described as being plastic if it can be moulded into different shapes readily. This is because the material from which it is made is a plastic material. Figure 13.1.2 shows two examples of objects made from polymers. The polymer used to make the basket has plastic properties because upon heating the polymer would melt, allowing it to be reshaped. However, the saucepan handle is hard and brittle and will not melt when heated.



FIGURE 13.1.2 A plastic basket has plastic properties, whereas a polymer frying pan handle does not.

POLYMER STRUCTURE

Polymers are covalent molecular substances composed of many small molecules all joined together. The word 'polymer' is made up of two parts, which come from Greek. *Poly* means 'many', and *mer* means 'part'. They are formed by joining together thousands of smaller molecules, called monomers (*mono* means 'one'), through a process called **polymerisation**, as shown in Figure 13.1.3.

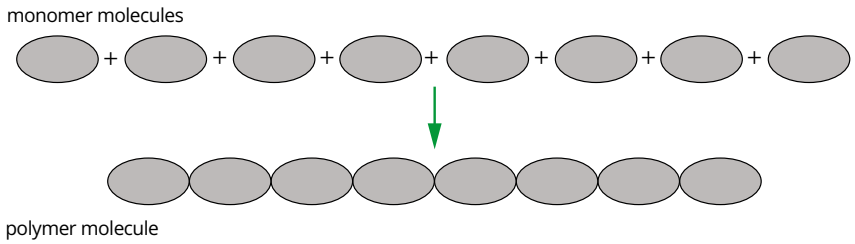


FIGURE 13.1.3 Monomers join to each other to form polymers.

Addition polymerisation

As you learnt in Chapter 9, addition reactions involve the reaction of an alkene with another molecule. All of the atoms of both molecules are present in the final molecule. Under some conditions alkenes can also undergo an addition reaction with themselves to produce long chains. The reaction of the monomer ethene with itself to form polyethene, shown in Figure 13.1.4, is an example of the addition polymerisation process. Several thousand ethene monomers usually react to make one molecule of polyethene.

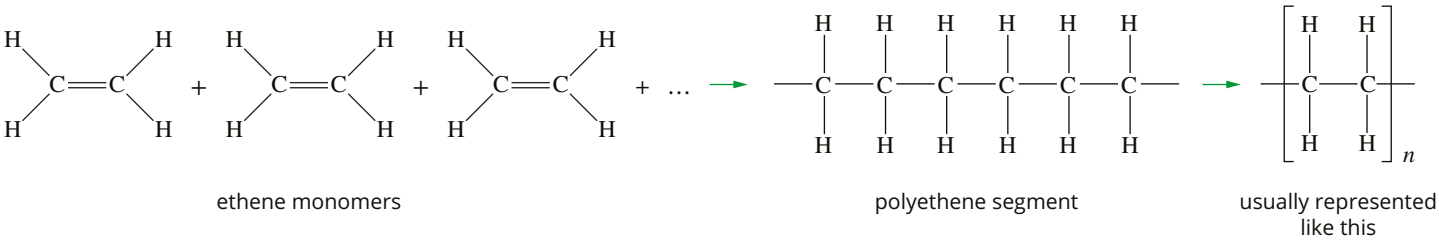


FIGURE 13.1.4 Thousands of ethene monomers join together to make one chain of polyethene. The standard notation shown simplifies the drawing of such a large chain.

Large square brackets and the subscript *n* are used to simplify the drawing of long polymer molecules. The value of *n* may vary within each polymer molecule, but the average molecular chain formed might contain as many as 20 000 carbon atoms. Polymers really are very large molecules!

Since all the atoms of the monomers are present in an **addition polymer**, the empirical formula of the monomer is the same as that of the polymer. Figure 13.1.5 provides an alternative representation of a polyethene chain segment, called a ball-and-stick model.

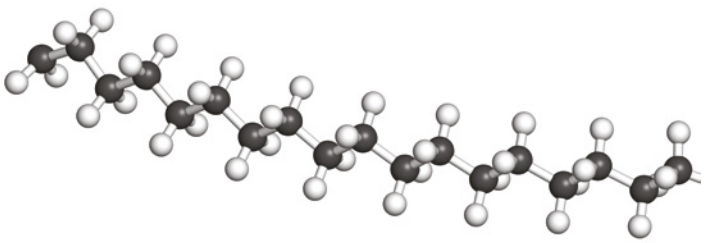


FIGURE 13.1.5 A ball-and-stick representation of a segment of polyethene

Ethene is an unsaturated molecule because it contains a carbon–carbon double bond. When ethene polymerises, the double bonds break and new covalent bonds are formed between carbon atoms on nearby monomers.

TABLE 13.1.1 Monomer and polymer names

Monomer	Polymer
ethene	polyethene
propene	polypropene
tetrafluoroethene	polytetrafluoroethene

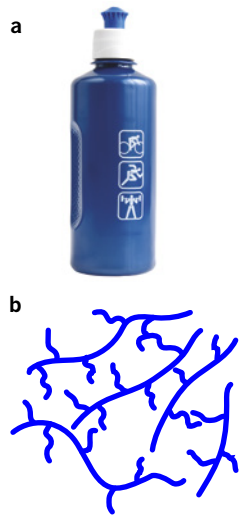


FIGURE 13.1.7 Low density polyethene (a) A drink bottle made from LDPE (b) LDPE branched structure

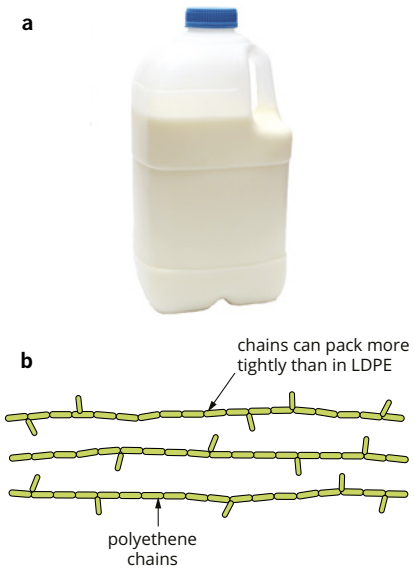


FIGURE 13.1.8 Properties and structure of HDPE (a) A bottle made from HDPE (b) HDPE structure

The polyethene formed does not contain any double bonds. The name of a polymer formed through addition polymerisation will often include the monomer that was used to make it. The names of three common addition polymers and their monomers are listed in Table 13.1.1.

LDPE

The earliest method of producing polyethene involved high temperatures (around 300°C) and extremely high pressures. Under these harsh conditions, the polymer is formed too rapidly for the molecules to be neat and symmetrical. Figure 13.1.6 shows that the product contains many small chains that divide off from the main polymer called branches.

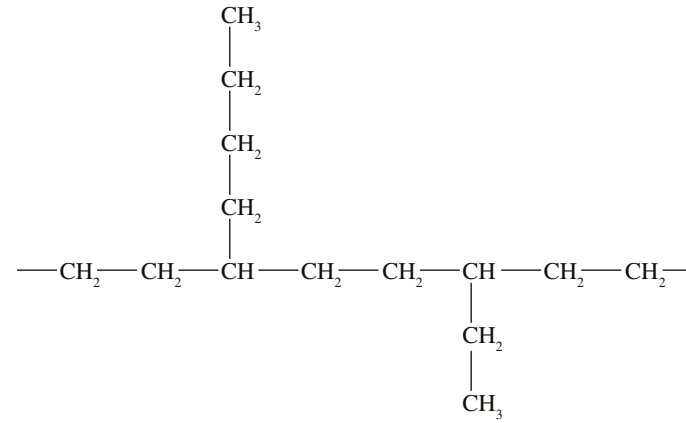


FIGURE 13.1.6 Polyethene made under high pressure and at high temperatures has short branches off the main chain.

The presence of these branches impacts upon the properties of the polymer as the molecules cannot pack closely together. The dispersion forces between molecules are weaker when the molecules are further apart. The arrangement of the polymer molecules can be described as disordered or non-crystalline. This form of polyethene is known as **low density polyethene** or LDPE. Its structure and an example of its use are shown in Figure 13.1.7. The properties of LDPE include that it:

- has low density
- is relatively soft
- has a low melting point
- is non-crystalline
- is opaque
- is a non-conductor of electricity.

HDPE

A low-pressure method of producing polyethene was developed by the Union Carbide company in the late 1960s. Highly specialised transition metal catalysts, known as **Ziegler–Natta catalysts**, are used to avoid the need for high pressures. The polymer molecules are produced under much milder conditions and there are very few branches.

The lack of branches allows the molecules to pack together tightly, increasing the density and the hardness of the polymer formed. The arrangement of the polymer molecules is more ordered, resulting in crystalline sections. This form of polyethene is known as **high density polyethene** or HDPE. Its structure and its uses are shown in Figure 13.1.8. The properties of HDPE include that it:

- has high density
- is hard
- has a relatively high melting point
- has crystalline sections.

Chain length

It is the length of polymer molecules that gives them many of their useful properties. Polyethene is essentially an extremely long alkane. In Module 8.6 you learnt that as the length of the carbon chain in organic molecules increases, the melting point of a substance increases. The weak dispersion forces (Figure 13.1.9) between the long polymer chains are sufficiently strong to cause polyethene to be a solid at room temperature.

Ultra-high molecular weight polyethene (UHMWPE) consists of extremely long polymer molecules. As a consequence, dispersion forces between chains are much stronger than in shorter chains of polyethene. Because of this, UHMWPE is such a tough polymer that it can be used to make artificial hip joints, safety helmets and even bulletproof vests.

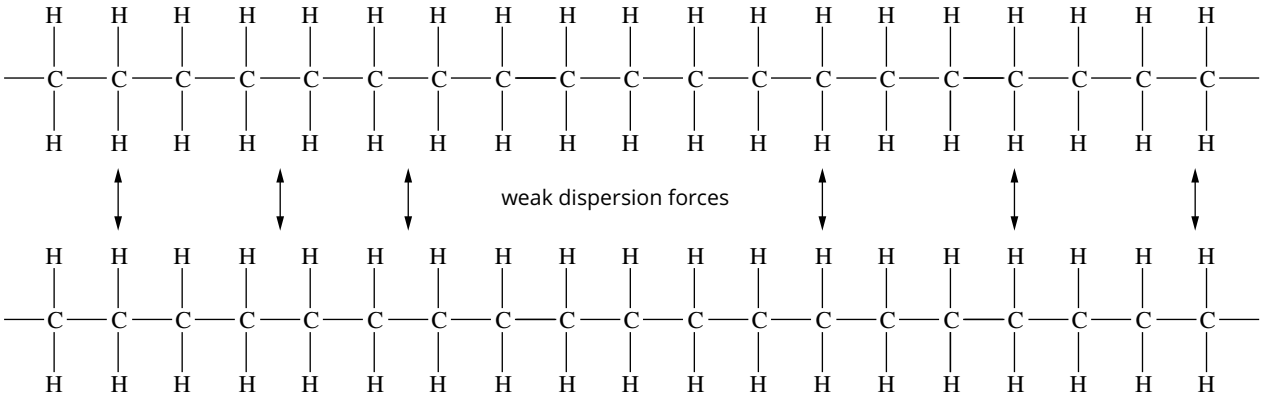


FIGURE 13.1.9 Dispersion forces between polyethene molecules are sufficiently strong to make it a solid at room temperature.

Extent of branching

The amount of branching in polyethene can be varied by changing the process used for its manufacture. When the monomers join in long chains with very few, short branches, the polymer molecules can pack together closely. This polymer material is called high density polyethene (HDPE) and can be seen in Figure 13.1.10. HDPE can have a percentage crystallinity as high as 95% and has excellent mechanical properties. HDPE is used to make pipes, buckets and food containers such as plastic milk bottles. Many car models have a fuel tank made from HDPE.

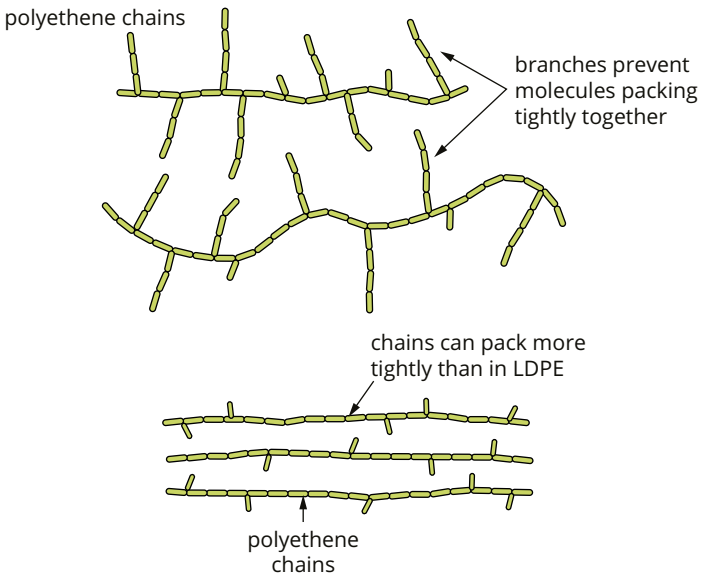


FIGURE 13.1.10 The arrangement of polymer molecules in low density polyethene (LDPE) and high density polyethene (HDPE)

Arrangement of side groups

Polypropene (PP) is an addition polymer made from the monomer propene (CH_2=$CHCH_3$), as shown in Figure 13.1.11.

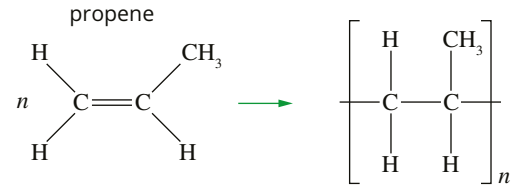


FIGURE 13.1.11 Propene undergoes addition polymerisation to form polypropene.

The way the methyl **side groups** ($-CH_3$) are arranged along the polymer chain has a significant effect on the properties and uses of this polymer. Figure 13.1.12 shows the three different structural forms of polypropene. You will learn more about the effect that the branching has on the properties in Module 13.2.

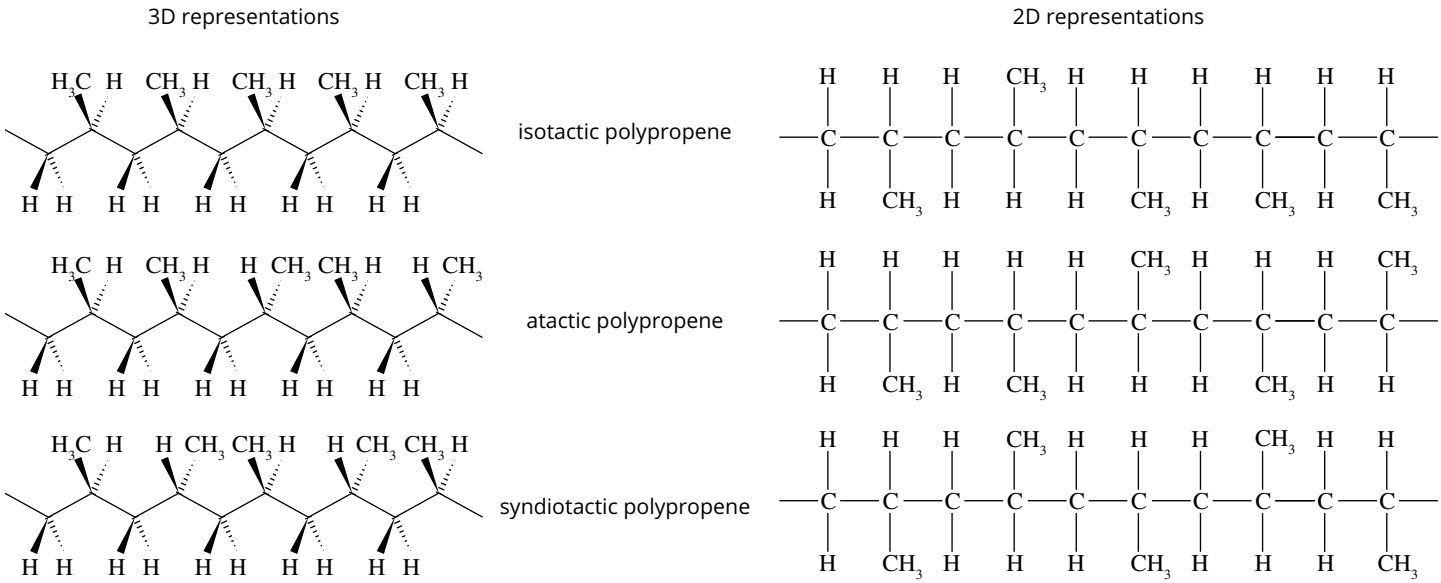


FIGURE 13.1.12 Sections of three different structural forms of polypropene

Isotactic polypropene has all the side groups on one side of the polymer chain. This allows crystalline regions to form, and significant attractive forces between the chains. This polymer material is used in many applications. For example, it is used to make babies' bottles that can be sterilised in boiling water without softening, Australian banknotes, very strong fibres and ropes, thermal underwear and polar fleece jackets.

Atactic polypropene has the side groups randomly distributed. This prevents the chains from stacking together well and forming crystalline regions. Atactic polypropene is very soft and has limited usefulness.

Syndiotactic polypropene has the side groups on regularly alternating sides of the polymer chain. This allows for good packing and the material is highly crystalline. It is a relatively new form of polypropylene and many new applications for it are currently being explored.

Other addition polymers

Many applications require polymers with more specialised properties than polyethene. For example, low flammability is essential for electrical wiring and a baby's bottle needs a polymer with a high melting point. As you will see in Module 13.2, one way to improve the properties of polyethene is to replace one or more of the hydrogen atoms on the monomer with more electronegative atoms or with a larger group of atoms.

As can be seen in Figure 13.1.13, when a chlorine atom replaces a hydrogen atom on ethene, the polymer polyvinyl chloride (PVC) is formed.



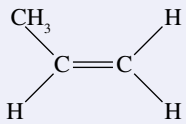
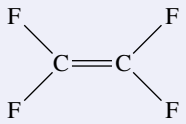
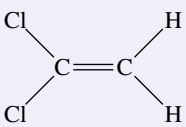
chloroethene (vinyl chloride) polyvinyl chloride (PVC)

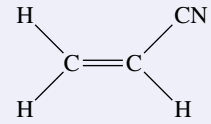
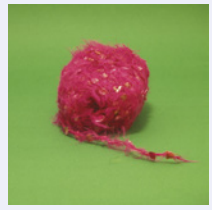
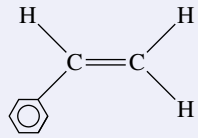
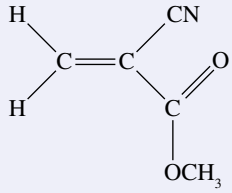
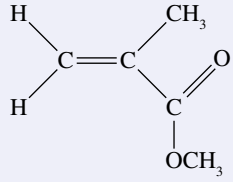
FIGURE 13.1.13 Polyvinyl chloride is made from the monomer chloroethene.

The chlorine atoms introduce dipoles into the long molecules. This increases the strength of the forces between polymer molecules, which leads to a higher melting point. PVC offers other advantages over polyethene: it has a low electrical conductivity and a low flammability. A PVC item burning in a flame will stop burning when it is removed from the flame. PVC is used in conveyor belts, cordial bottles, water pipes and the covering of electrical wiring.

There are thousands of commercial addition polymers. Table 13.1.2 shows a number of other polymers that may be familiar to you. Each of these polymers offers a unique property or properties that make them of commercial interest.

TABLE 13.1.2 Commercial addition polymers

Monomer	Polymer	Properties	Examples
propene	polypropene (polypropylene)	durable, cheap	artificial grass, dishwasher-safe plastic, ice-cream containers, rope
			
tetrafluoroethene	polytetrafluoroethene (PTFE, Teflon®)	non-stick, high melting point	frying pan and iron coatings, plumber's tape, Gore-Tex® fabric
			
dichloroethene	polyvinylidene chloride (PVDC)	sticks to self, transparent, stretchy	food wrap
			

Monomer	Polymer	Properties	Examples
propenenitrile	polypropenenitrile (acrylic)	strong, able to form fibres	acrylic fibres, fabrics
			
phenylethene (styrene)	polyphenylethene (polystyrene)	hard, brittle, low melting point	toys, packaging, expanded foams
			
methylcyanoacrylate	polymethylcyanoacrylate	polymerises on contact with water	superglue
			
methyl 2-methylpropenoate	polymethyl methacrylate	transparent, strong	Perspex® (a glass substitute)
			

Condensation polymerisation

Another method for producing polymers is to use monomers with functional groups on each end of the molecule. The monomers join when the functional groups react with each other. Polymers formed in this way are called **condensation polymers**. Nylon is a condensation polymer. The polymer is formed when two different monomers meet and join through a condensation reaction, as shown in Figure 13.1.14.

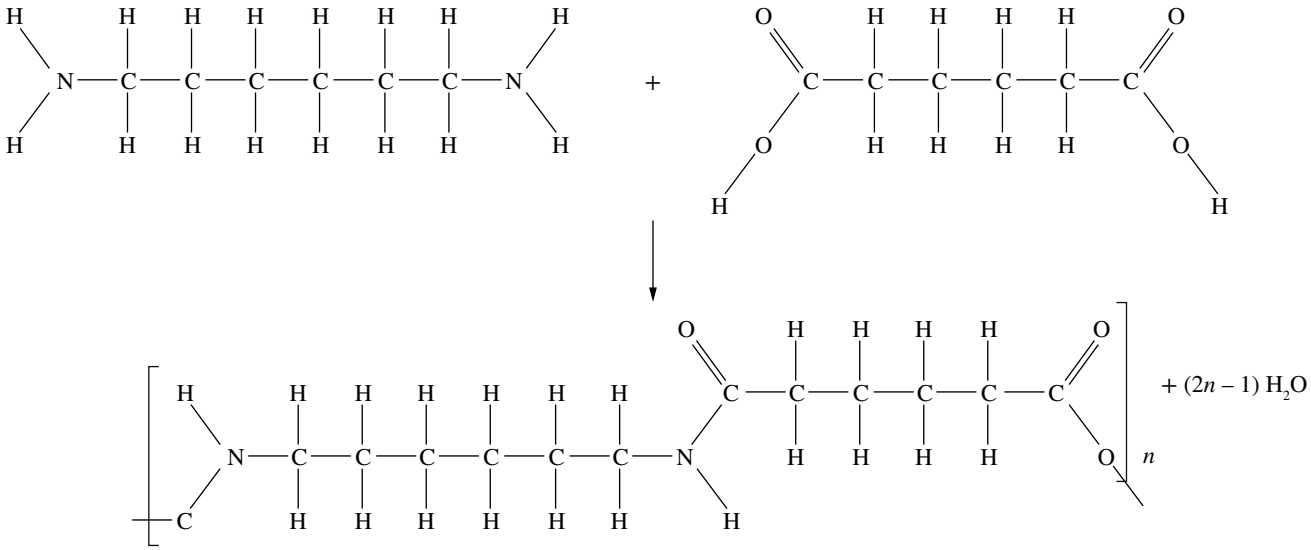


FIGURE 13.1.14 Production of nylon from the condensation reaction between two types of monomers

This form of nylon is described as a **copolymer** as it is formed from a reaction between two different monomers. A feature of condensation polymerisation is that small molecules, usually water, are also produced each time the monomer molecules join. Bakelite, polyester and Kevlar are other common condensation polymers.

In Module 9.3 you looked at condensation reactions between carboxylic acids and alcohols or amides. In a condensation reaction a small molecule, such as water, a hydrogen halide or ammonia, is eliminated.

To polymerise, condensation monomers must contain two functional groups. Alcohols contain an –OH group, which reacts with the –COOH group of carboxylic acids to form an ester linkage, –COO–, with the elimination of water. This is shown in Figure 13.1.15.

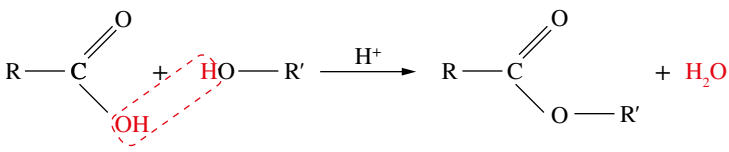


FIGURE 13.1.15 General condensation reaction between a carboxylic acid and alcohol to form an ester

A polyester, where each molecule is attached to the next by an ester group, is formed by the reaction between a diol (an alcohol with two OH groups) and a molecule that contains two carboxylic acids (dioic acids). An example is shown in Figure 13.1.16.

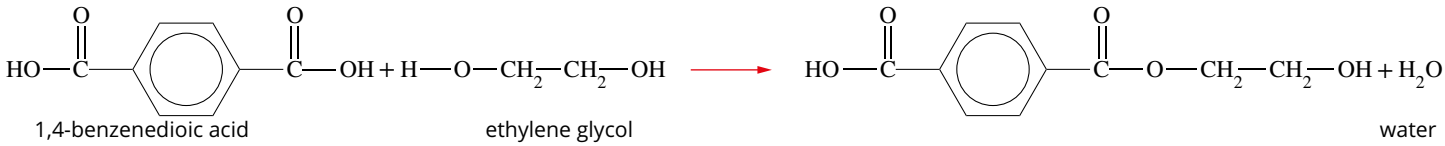


FIGURE 13.1.16 Formation of a polyester by the condensation reaction between 1,2-ethandiol and 1,4-benzenedioic acid

The formation of **starch** from α-glucose molecules forming glycosidic links between each glucose molecule (Figure 13.1.17) is a biologically important example of a condensation polymerisation reaction. Plants produce and polymerise α-glucose molecules to form starch and water as a by-product. Starch acts as an energy store that can be hydrolysed back into glucose to utilise the glucose as an energy source.

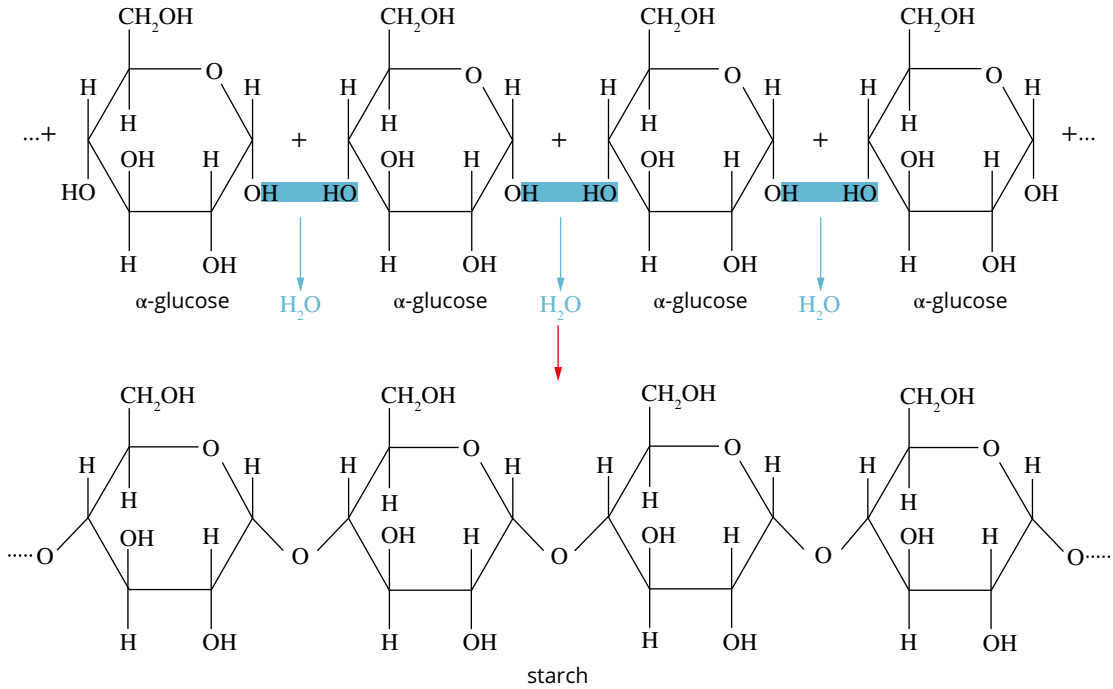


FIGURE 13.1.17 The condensation polymerisation of α-glucose to produce amylose, which is a form of starch.

The reaction between an amine and a carboxylic acid to form an amide is also a condensation reaction, as shown in Figure 13.1.18.

$$CH_3CH_2NH_2 + CH_3COOH \rightarrow CH_3C(O)NHCH_2CH_3 + H_2O$$

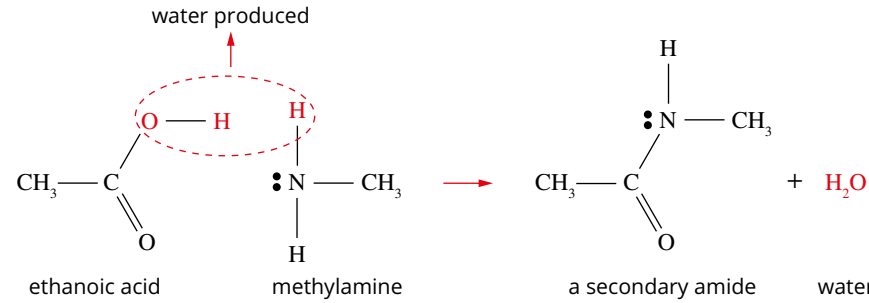


FIGURE 13.1.18 Condensation reaction between a carboxylic acid and amine to form an amide

This reaction is part of an important biological process. Proteins are formed by the polymerisation of amino acid monomers. Each amino acid is linked by an amide linkage, shown in Figure 13.1.19, similar to the reaction of amine groups and carboxylic acid.

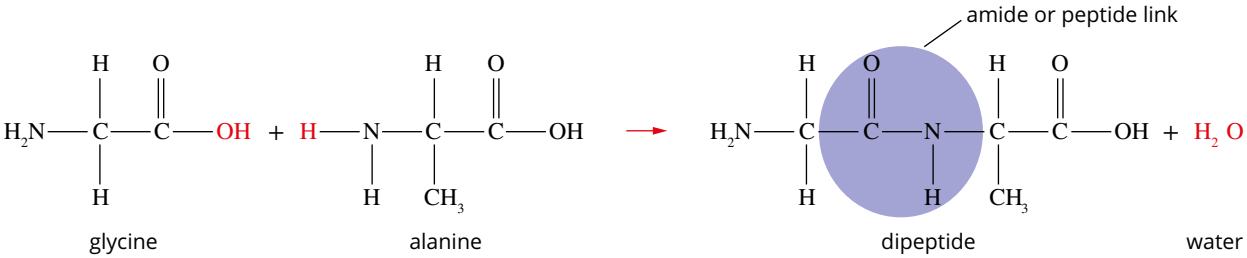


FIGURE 13.1.19 Polymerisation of amino acids

In a similar manner, several amino acids combine to produce a polypeptide. Proteins are large polypeptide chains containing approximately 50 or more amino acids. The polymerisation of amino acids is shown in Figure 13.1.20.

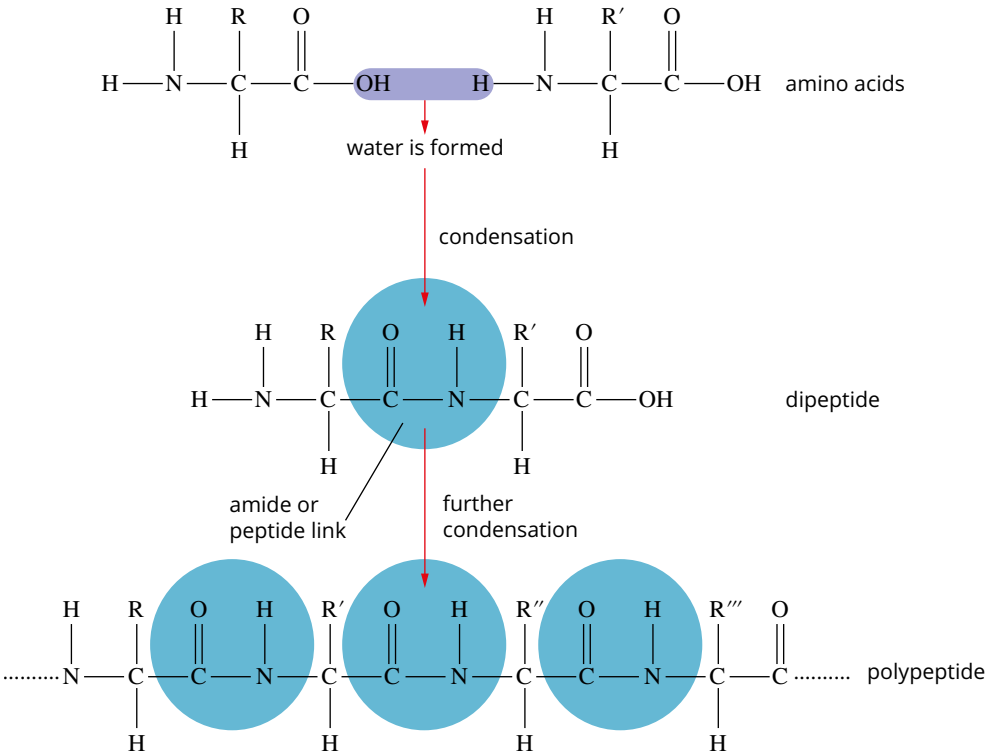


FIGURE 13.1.20 Condensation polymerisation of amino acids

In the same way that polyesters can be formed by the condensation of molecules with two identical functional groups, polyamides can be formed by the condensation of a molecule with two amine groups and a molecule with two carboxylic acid groups. An example is nylon, as shown in Figure 13.1.21.

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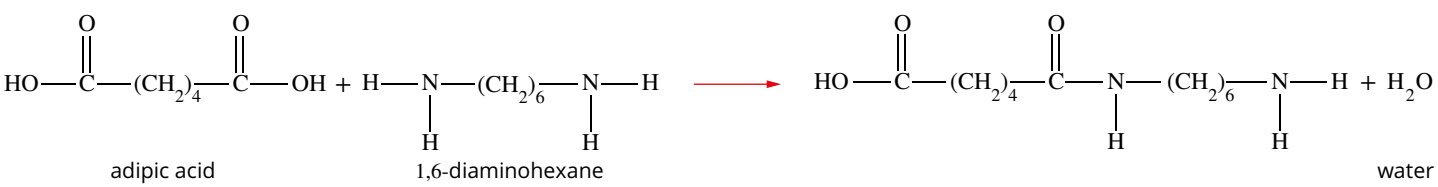


FIGURE 13.1.21 Formation of nylon by the condensation reaction between 1,6-hexanedioic acid and 1,6-diaminohexane

13.1 Review

SUMMARY

- A polymer is a covalent molecular substance composed of many small molecules joined together.
- A monomer is the smaller molecule that reacts with another monomer, of either the same compound or a different compound, to form the polymer.
- There are two main types of polymers—addition polymers and condensation polymers.
- To simplify the drawing of the polymer the repeating unit within the polymer is enclosed within large square brackets.
- Since polymerisation requires the formation of new bonds between the monomer units, addition monomers must be unsaturated compounds (i.e. fully saturated hydrocarbons cannot form addition polymers).
- Apart from the nature of the monomer linkage, the structure of the polymer is described in terms of the chain length, branching and the geometric arrangement of side groups (isotactic, atactic and syndiotactic).
- The properties of the polymer are related to the packing between the polymer chains and to the intermolecular forces between them.
- Condensation polymers, such as nylon, are formed when molecules with two functional groups meet and react together, eliminating a small molecule (often water).
- A copolymer is formed from a reaction between two different monomers.

KEY QUESTIONS

Retrieval

1 Define polymerisation.

2 Identify the structure of the repeating unit in the polyester formed from ethane-1,2-diol and benzene-1,4-dicarboxylic acid.

Comprehension

3 Draw the structure of a syndiotactic polypropene chain.

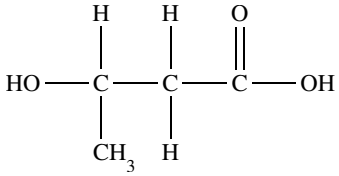
4 Describe the essential differences between the monomers that form addition polymers and the monomers that form condensation polymers.

5 Draw the reaction scheme and general structure of the polymer formed in the reaction between alcohols and carboxylic acids.

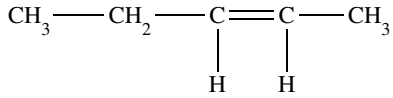
Analysis

6 For each of the following monomers, identify the polymer that is formed.

a



b



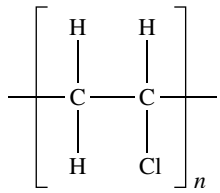
7 From the structures of the repeating units of the polymers below, identify the monomers from which they were produced.

a $-[CH_2-CH_2]-$

b $-[CO-CH(CH_3)NH]-$

c $-[NH(CH_2)_6NH-CO-(CH_2)_4CO]-$

8 The terms isotactic, atactic and syndiotactic are related to the relative geometric arrangement of the side groups. Deduce if polyvinyl chloride, shown below, should be classified using these terms.



13.2 Properties of polymers

BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- recognise the general characteristics of polymers
- differentiate polymers into two groups based on physical properties
- explain how changes to the monomer structure, the length of polymer chains, the amount of branching and the addition of other substances to the polymer can modify polymer properties
- describe and explain the factors that influence the physical properties of polymers
- differentiate between amorphous and crystalline arrangement of polymers and the effect on the physical properties
- describe the advantages and disadvantages of polymers.



POLYMER PROPERTIES

Characteristics of polymers

While each polymer may have distinct characteristics, most polymers share similar attributes.

- They have a high resistance to chemicals. A brief look at cleaning products around your house would highlight the corrosive nature of the chemicals used in cleaning products. This emphasises the need for the plastic packaging containers of these products to be inert to their chemical contents.
- They are thermal and electrical insulators. Consider all the appliances and electrical wiring around your house that are made of or covered by polymeric substances. Thermal resistance is evident in pot handles, the foam core of fridges and freezers as well as in polystyrene cups.
- They have a high strength to weight ratio. Generally, polymers are very light but incredibly strong. Polymers are used to make a diverse range of products, from toys to the frame structure of space stations and bulletproof vests. Compared to materials of similar strength, such as stone, concrete and steel, all plastics are very lightweight.
- They can be processed in many ways. Polymers are moulded or formed into a large variety of shapes. Extrusion produces thin fibres, films or food bottles. Injection moulding is used to produce very intricate parts or large panels for cars. Air can be blown into some polymers, such as polystyrene and polyurethane, to produce cushioning material. In addition, plastics can be mixed with solvents for use in paints and adhesives. Elastomers and some plastics are flexible and can stretch, whereas others hold their shape once they are formed.
- Additives can change the colour or characteristics of the polymer. While polymers have inherent properties, they can be changed by adding a range of additives to extend their uses and applications.
- Most polymers and plastics are derived from petroleum; however, in response to the recognition of the finite availability of oil, there is an increasing number of polymers made from renewable materials derived from agricultural products.
- They can be used to make unique items, particularly medical applications such as the use of PVC in medical tubing and blood bags, catheters as well as non-flammable flexible tubes used in oxygen masks.

Thermoplastic and thermosetting polymers

Polymers can be classified into two groups based on their behaviour when heated:

- thermoplastic polymers
- thermosetting (or thermoset) polymers.

Thermoplastic polymers soften when heated, which means they can be remoulded or recycled. Polymers are thermoplastic if the bonds between the long polymer chains are hydrogen bonds, dipole–dipole bonds or weak dispersion forces (Figure 13.2.1), which makes it ideal for flexible bottles and packaging material. When heated, the molecules in thermoplastic materials gain enough energy to overcome the intermolecular forces and become free to move and slip past one another. If the polymer can be remoulded, then it can probably be recycled easily, which is an important property in modern society.

Thermosetting polymers decompose or char when heated. They do not soften because the bonds between the chains are very strong (Figure 13.2.2). This means they are used to make a wide range of products. If the temperature becomes high enough to break the covalent bonds, the breaks may be at any point, causing the polymer to decompose. It is difficult to recycle thermosetting polymers as they cannot be remoulded into new shapes.

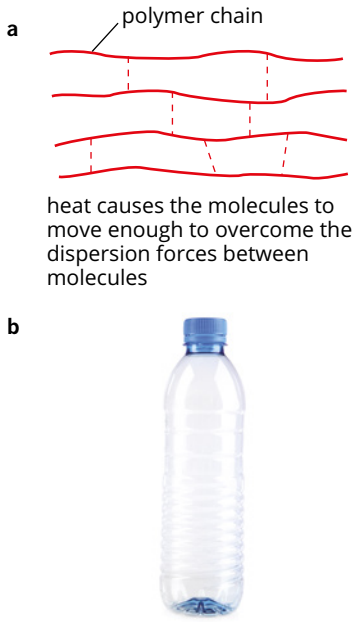


FIGURE 13.2.1 (a) A thermoplastic polymer has weak bonds between the chains. (b) Thermoplastic polymers are often used to make plastic bottles and food packaging.

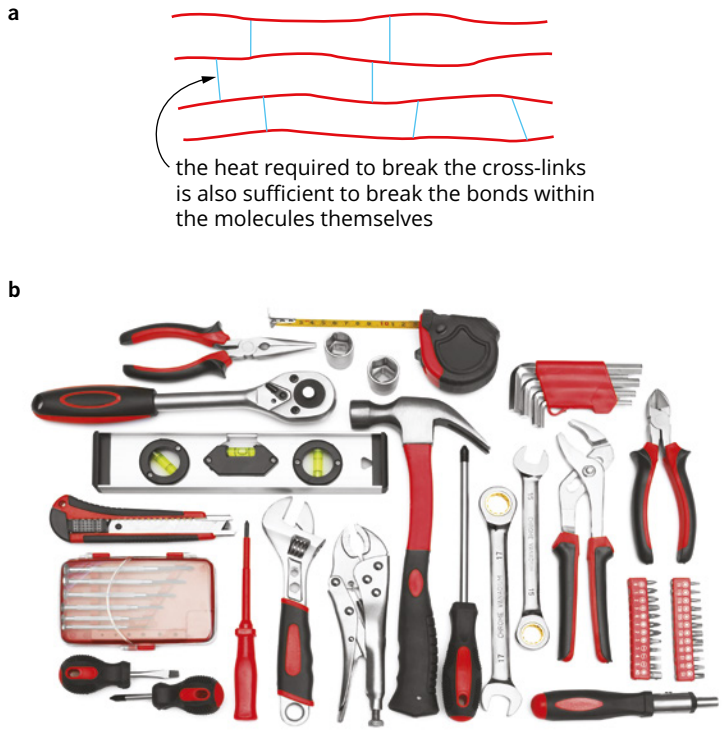


FIGURE 13.2.2 (a) A thermosetting polymer has strong covalent bonds between the chains. (b) A variety of products made from thermosetting polymers.

Covalent bonds between polymer molecules are called cross-links. Cross-links limit movement between the polymer molecules and make the polymer rigid, hard and heat resistant. Thermosetting polymers are used to make items such as saucepan handles, bowling balls and shatterproof crockery.

Elastomers are an interesting class of polymers that are formed when only occasional cross-links are present. The chains in these polymers can still move past each other when stretched but the cross-links return the chains to their original positions once the force causing the stretching is released. Elastic bands and other rubber items are made of elastomers. The cross-links stop elastomers from completely melting when heated and make recycling difficult. For example, the sulfur cross-links in the polymer in car tyres (Figure 13.2.3) make the tyres non-recyclable.

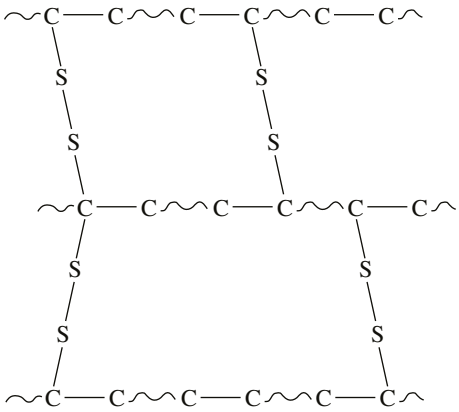


FIGURE 13.2.3 The elastomer chains in rubber car tyres are cross-linked by sulfur atoms.

DESIGNING POLYMERS FOR A PURPOSE

The development of new polymers has been motivated by the need to replace existing materials that are in short supply and to produce materials with improved physical and chemical properties. The widespread use of polymers brings many advantages, as well as challenges. A very important issue is the reduction of polymer waste, through either biodegradable polymers or recyclable polymers. Figure 13.2.4 shows apples packaged in biodegradable plastic and waste plastic waiting to be recycled.

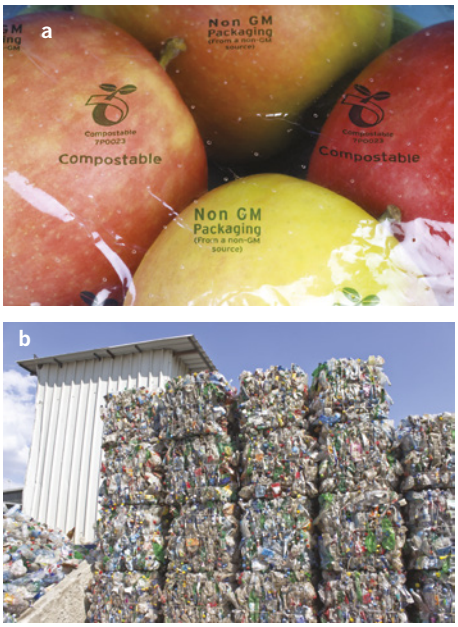


FIGURE 13.2.4 (a) Apples packaged in biodegradable plastic. (b) Waste plastic waiting to be recycled.

Selecting a monomer

The properties of a polymer depend largely on the monomer used to make them; therefore, it is important to consider the desired properties and which type of monomer is best suited to provide them.

Non-polar monomers

Polyethene is the most common polymer. It can be manufactured in two different ways to make two different products. Tetrafluoroethene (CF_2=CF_2), shown in Figure 13.2.5, is formed when all the hydrogen atoms in ethene are replaced by highly electronegative fluorine atoms.

Molecules of tetrafluoroethene react with themselves to form the polymer polytetrafluoroethene, known as Teflon®. Teflon has quite exceptional properties that are very different from those of polyethene. Teflon can be used to make non-stick frying pans, medical implants and gears. The electronegative fluorine atoms reduce the strength of intermolecular bonds with other substances.

Another innovative application of Teflon is in Gore-Tex® (Figure 13.2.6). Gore-Tex is a fabric that 'breathes'. Rain cannot penetrate a Gore-Tex raincoat, but water vapour from sweat can escape through it. High-quality camping clothing is often made from Gore-Tex.

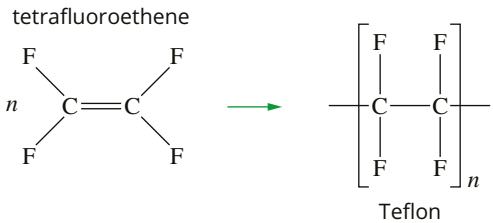


FIGURE 13.2.5 Addition polymerisation of tetrafluoroethene makes the polymer Teflon.

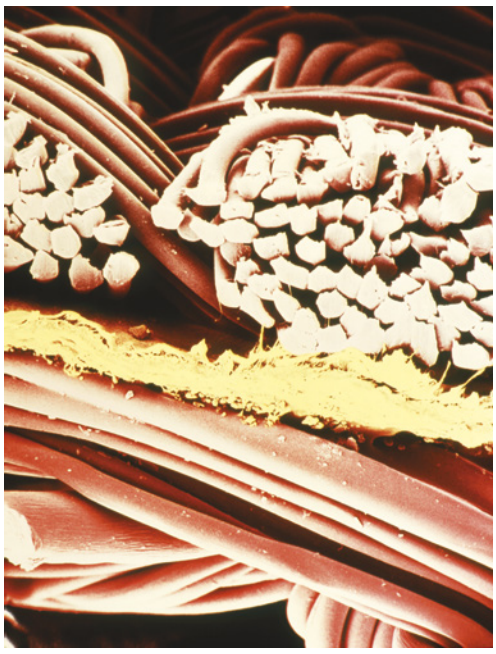


FIGURE 13.2.6 Scanning electron micrograph of Gore-Tex fabric. The small yellow and white particles are Teflon. The small holes between these particles allow vapour to pass through the fabric but not liquid.

The properties of Teflon are summarised in Table 13.2.1.

TABLE 13.2.1 A summary of the properties of Teflon

Property	Description
non-stick	Teflon repels all other substances, both hydrophobic (oil, fat) and hydrophilic (water).
heat resistant	The melting point of Teflon is 335°C and the upper operating temperature for this polymer is 260°C.
chemical resistant	Teflon is extremely resistant to all known chemicals. It is not attacked by strong acids and bases and is inert towards all organic solvents.
good mechanical properties	Teflon is strong and durable, but not as hard as PVC.
low friction coefficient	Teflon is slippery to the touch. The friction coefficient between two pieces of Teflon is very low.
flame resistant	Teflon is non-flammable.

Polar monomers

Ethene and tetrafluoroethene molecules are non-polar, meaning that the intermolecular forces present between polyethene and Teflon molecules are weak dispersion forces. When a polymer is made from polar monomers, the chains will be held together by stronger polar attractions, such as dipole–dipole interactions or hydrogen bonds. Polyvinyl chloride (PVC) is made from the polymerisation of chloroethene ($CHCl{=}CH_2$), as shown in Figure 13.2.7.

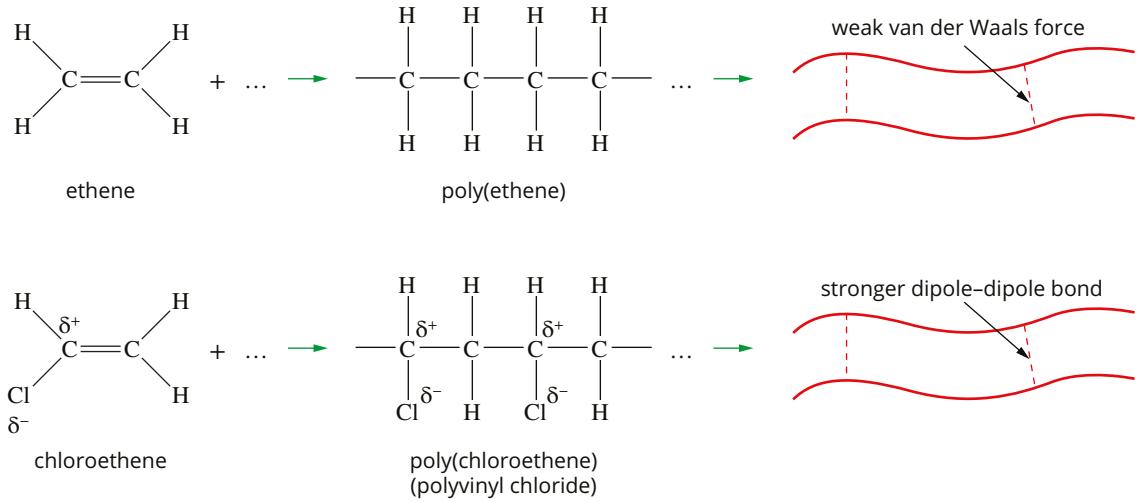


FIGURE 13.2.7 Polyvinyl chloride (PVC) is formed from polymerisation of polar chloroethene monomers, and has dipole–dipole attractions between chains.

The carbon–chlorine bonds in a PVC molecule are polar and allow dipole–dipole attractions to occur between polymer chains. Because of this, PVC is harder and more rigid than polyethene and Teflon. One of the main applications of PVC is in drain pipes. Incorporating additives, which is discussed later in this module, allows even more widespread use of PVC.

Copolymers

In recent years, a new generation of versatile materials has been developed by combining two or more monomers together into one polymer. A copolymer is a polymer made from at least two different monomers. The Water Cube Stadium built in Beijing for the 2008 Olympic Games (Figure 13.2.8) was made with a copolymer of ethene ($CH_2{=}CH_2$) and tetrafluoroethene ($CF_2{=}CF_2$) monomers. The copolymer

is known as ethene tetrafluoroethene (ETFE). The stadium has over 100 000 m^2 of very thin ETFE 'bubble walls'. The walls allow more light and heat to penetrate than traditional glass does, lowering energy costs. ETFE weighs only 1% of the weight of glass and is a better thermal insulator. It was designed by a consortium including two Australian companies, PTW Architects and Arup engineers.



FIGURE 13.2.8 The outer shell of the Water Cube Stadium in Beijing, China, is made of ETFE, a new copolymer building material.

Another copolymer called styrene-butadiene rubber (SBR) (Figure 13.2.9) is formed from styrene (CH_2=CH(C_6H_5)) and butadiene (CH_2=CHCH=CH_2). Pure polybutadiene is an elastomer used in the production of synthetic rubbers for applications such as tyres and golf balls.

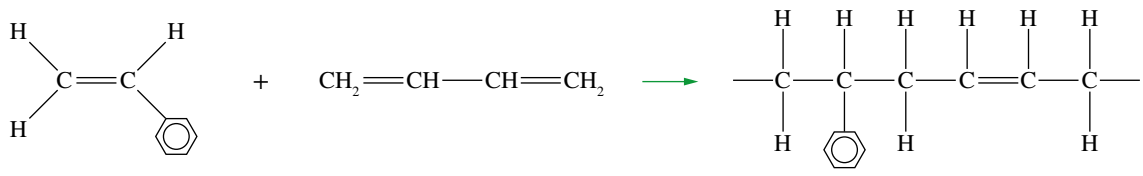


FIGURE 13.2.9 Formation of the SBR copolymer chain from two monomers, styrene and butadiene.

A variety of polymers with different properties can be produced simply by altering the ratio of the monomers. For example, an elastomer similar to natural rubber is produced when two monomers are present in close to equal amounts. The styrene monomers increase the abrasion resistance of the polymer and make it suited for use in car tyres, its main application.

The addition of a third monomer, acrylonitrile (CH_2=CHC≡N), produces the polymer acrylonitrile-butadiene-styrene (ABS), which is used to make LEGO® blocks. This polymer is rigid and strong but can be melted easily. These properties have made this thermoplastic polymer very popular for use in 3D printing. In Figure 13.2.10, a 3D printer melts a thin cord of ABS called a filament. The molten ABS is built up in layers, where it sets to make the object solid.

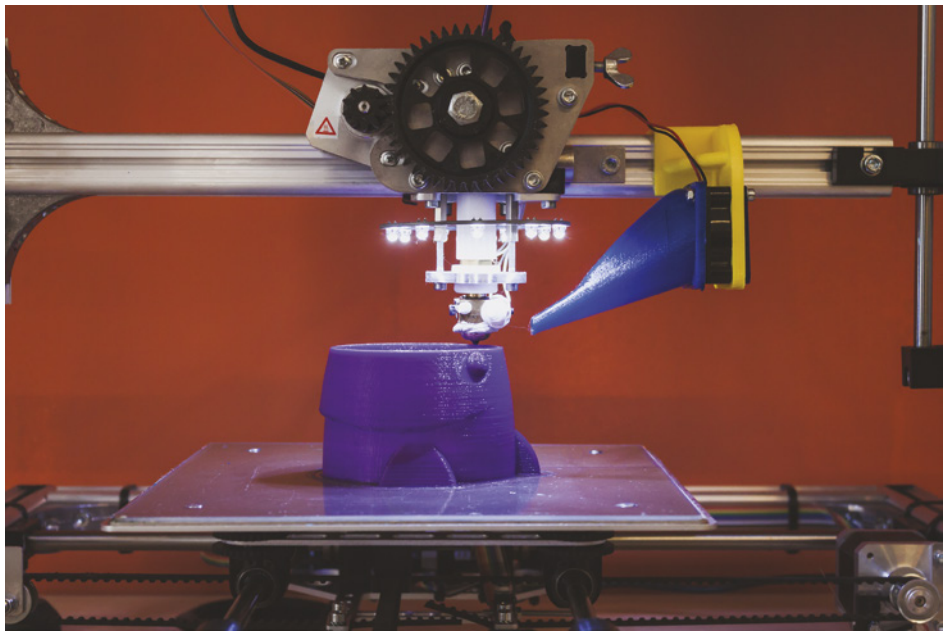


FIGURE 13.2.10 3D printer using an ABS copolymer filament to make an object

Conductive polymers

Polymers are usually known for their insulating properties. In 2000, the Nobel Prize in Chemistry was awarded to Alan MacDiarmid (born in New Zealand), Hideki Shirakawa (Japan) and Alan Heeger (USA) for their discovery of electrically conducting polymers. These ground-breaking **conductive polymers** have opened the way to lighter, polymer-based circuits that are now being used in biosensors.

When ethyne (CH≡CH) polymerises, one of the carbon–carbon bonds is rearranged to bond to neighbouring monomers. As you can see in Figure 13.2.11, each repeating monomer unit in polyethyne has alternating double and single carbon–carbon bonds.

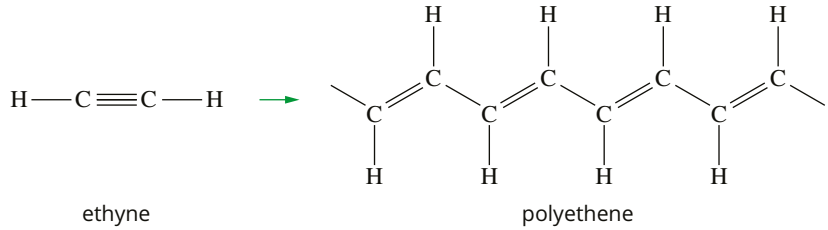


FIGURE 13.2.11 Addition polymerisation of ethyne produces polyethyne with alternating double and single carbon–carbon bonds, a polymer that becomes conductive in some conditions.

Photoconductive polymers

The process of making a photocopy relies on polymers that are **photoconductive**. The electrical conductivity of these polymers increases when they are exposed to light. Figure 13.2.12 shows how they are used to make a photocopy.

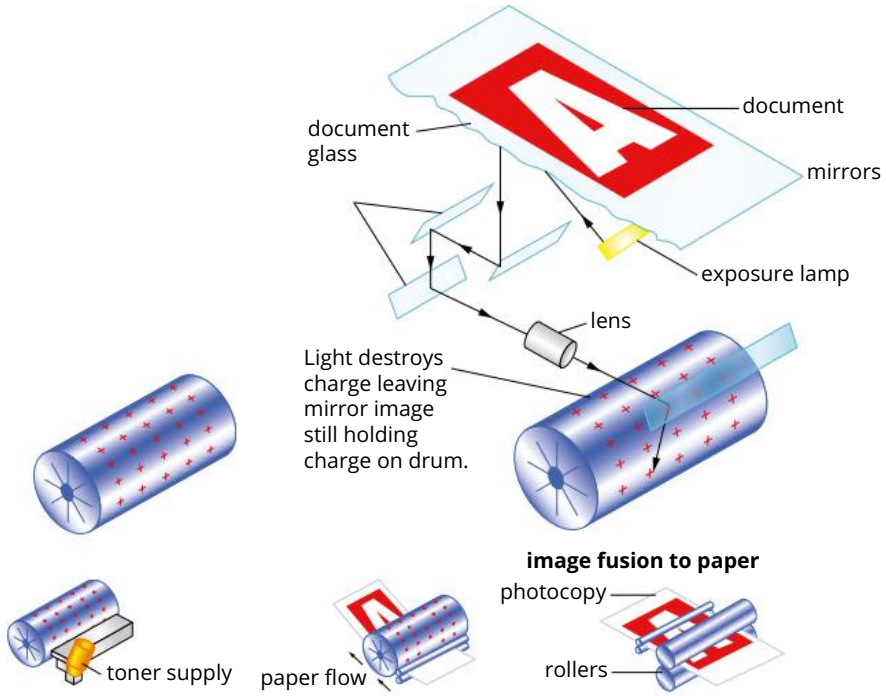


FIGURE 13.2.12 The process of producing a photocopy

Crystallinity

By manipulating the molecular structure of the polymer and introducing additives and fillers scientists can change the properties of the polymer produced.

Figure 13.2.13 shows spaghetti on a plate. Linear polymer strands also display this type of irregular arrangement. The amorphous arrangement of the molecules has no specific form and is the result of the rapid quenching of the molten polymers. As a result, linear polymers are generally transparent, which makes them suitable for use as food wrap, plastic windows and contact lenses.

However, polymer chains can be ordered into a crystalline arrangement where the polymer molecules are arranged in distinct patterns. This results in polymers that are not transparent. The degree of crystallinity can be controlled in some polymers. Generally, the higher the degree of crystallinity the less light can pass through the polymer meaning that crystalline polymers are typically opaque. In addition, crystallinity affects the strength, stiffness, stability and chemical resistance of the polymer.

Materials made from polymers consist of many long chains that twist around each other, with intermolecular forces between one chain and another. Many polymeric materials contain both **crystalline regions** and **amorphous regions**.

Where the chains are lined up in a regular arrangement, they create crystalline regions, as shown in the ordered section of the polymer in Figure 13.2.14. Being regularly arranged brings the polymer chains closer together. The intermolecular forces between the closely packed chains are stronger and the presence of crystalline regions strengthens the material overall. Crystalline regions in a polymer prevent the transmission of light through the material, making it appear opaque (cloudy), so that light does not pass directly through it.

An amorphous region is an arrangement where the polymer chains are randomly tangled and unable to pack very closely. The polymer chains shown in Figure 13.2.15 are amorphous because they have no orderly arrangement.

In some polymer materials, the entire solid is amorphous. Amorphous polymers are usually less rigid, weaker and often transparent (see-through). The percentage of the polymer that is crystalline, rather than being amorphous, influences the properties of the polymer. Increasing the percentage crystallinity of a material makes it stronger and less flexible. This also makes the material less transparent as the crystalline regions scatter light.

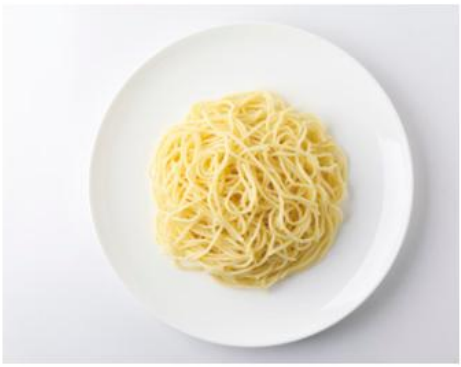


FIGURE 13.2.13 Spaghetti on a plate resembles the unorganised nature of amorphous polymer chains.

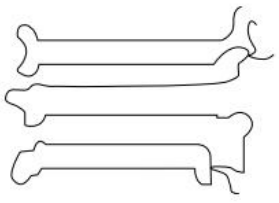


FIGURE 13.2.14 A crystalline region of a polymer material forms where the polymer chains are arranged in an ordered fashion.

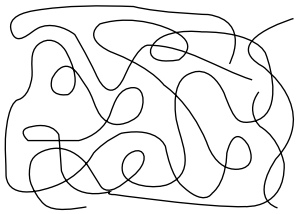
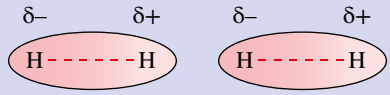
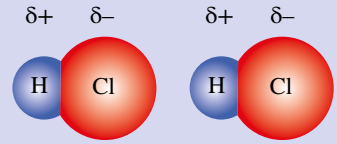
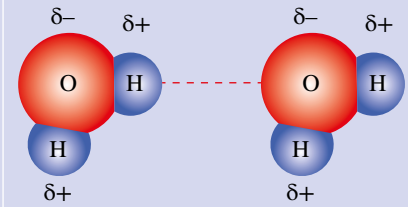


FIGURE 13.2.15 An amorphous region forms when polymer chains are disordered.

As outlined in Module 13.1, the properties of polymers are related to a number of different factors such as chain length and the nature and arrangement of the side groups. The property of the polymer is closely related to the strength of the intermolecular forces between the polymer chains. As you learnt in Unit 2, there are three types of intramolecular forces. Table 13.2.2 shows these forces, which vary in strength from the weakest van der Waals forces (also known as London forces), to dipole–dipole forces, to the strongest hydrogen bonding between molecules containing nitrogen, oxygen and fluorine atoms.

TABLE 13.2.2 Summary of the three types of intermolecular forces

	van der Waals dispersion forces	Dipole–dipole forces	Hydrogen bonding
definition	• attraction between two instantaneous dipoles • asymmetrical electron distribution • all atoms and molecules	• attraction between two permanent dipoles • polar molecules	• attraction between molecules with N–H, O–H and F–H bonds • extremely polar bonds—very strong dipole–dipole force
diagram			
relative strength	• weakest	• medium strength	• strongest
other information	• increase in strength as molar mass increases (more electrons)	• stronger when molecules are closer together	• not chemical bonding

Chain length

Polymers are made of strands of individual polymer chains that interact and pass over each other. Thus, the physical properties of polymers are strongly dependent on the length of the polymer chain. Not only are longer chains more likely to get tangled in each other than short chains but the number of intramolecular forces also increases with the number of atoms. This means that long-chained polymers tend to have higher melting points and lower mobility than the short-chained polymers.

The shorter-chained polymers can pass over each other more easily and so tend to be softer, whereas the reduced mobility of the longer chains increases strength, toughness and glass transition temperatures. As a rule, mechanical properties such as ductility, tensile strength and hardness rise and eventually level off with increasing chain length.

In Module 13.1 you learnt that low density polyethylene (LDPE) is composed of shorter polymer chains than high density polyethylene (HDPE). LDPE is therefore softer, weaker, less dense and more easily deformed than HDPE.

Side groups

The length of the polymer chains means that the attractive intermolecular forces between molecules are amplified compared to simple molecules like water and methane. However, just like the nature of the atoms increases the intermolecular bonding and changes the boiling point (e.g. water 100°C versus methane –161.5°C), the attractive forces between polymer chains play a large part in determining a polymer's properties.

As in simple organic molecules, polar side groups increase the attraction between neighbouring polymer chains. The stronger intermolecular forces between polymer chains containing polar side groups (especially those capable of hydrogen bonding) typically result in polymers with higher tensile strength and higher crystalline melting points.

This can be seen when comparing polyethylene (PE) with polyvinyl chloride (PVC). The electronegativity difference between the carbon atom and the chlorine atom (0.9) in PVC creates dipole–dipole interactions between the polymer chains in PVC. As a result, the glass transition temperature (T_g) for PVC is 81°C compared to a T_g of −125°C for PE, which only has van der Waals forces between the polymer chains.

Hydrogen bonds are the strongest non-covalent forces and, as you learnt in Unit 2, these require a hydrogen atom on one polymer, molecule or chain, interacting with a highly electronegative atom, nitrogen, oxygen or fluorine on another polymer, molecule or chain. For instance, in nylon there are NH groups that can form hydrogen bonds with the C=O groups of another chain. The large number of interchain hydrogen bonds make the nylon polymer rather stiff.

As seen in Chapter 10, hydrogen bonds are present in proteins and are responsible for holding the DNA double helix together, as shown in Figure 13.2.16. Additionally, they are responsible for the association between complementary nucleotides, so that DNA chains can replicate.

Earlier in this module you learnt that polymers with cross-linking between the polymer chains (thermoplastic polymers) are very strong polymers; for instance the sulfur in natural rubber. With light cross-linking, the polymer is rubbery and flexible, but with heavy cross-linking it is stiff, like an epoxy resin or cured silicone.

However, if you compared polymers with the same type of polymer skeleton (i.e. polyalkanes), the amount of branching in the polymer will affect the polymer's properties. Polymers that do not have side chains on their molecules have a higher density because more polymer chains can pack into the same amount of space. The chains can slide over each other more easily if there is nothing in the way to stop them, compared to when there are side chains or branches in the way.

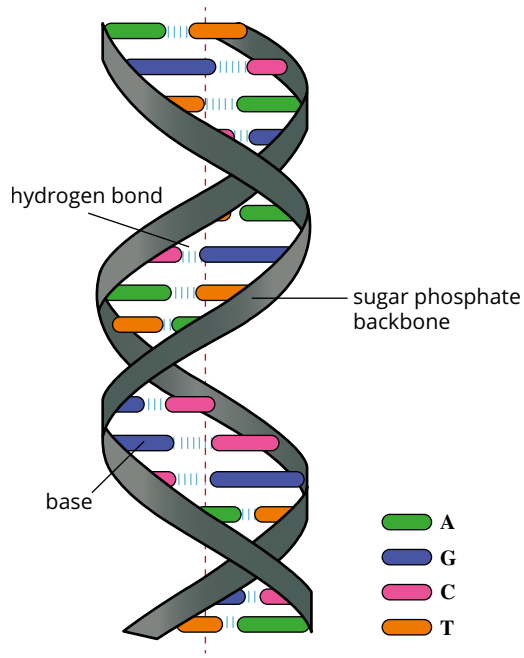


FIGURE 13.2.16 A section of DNA showing the hydrogen bonds holding the double helix together

Arrangement of side groups

Polymers are usually made by heating the monomer and passing it over a catalyst. The sort of catalyst used can affect how much the polymer chain branches. Polymer branches are like the branches of a tree—they are made of the same material as the main chain but go off in a different direction. If the polymer chains have no branches, they pack in close to each other and the material has a high density. The chains can pass over each other easily so the material is very stretchy. If the polymer chains have a lot of branches, then the chains cannot pack together as closely and the material has a lower density. The branches catch on each other, preventing the chains from sliding easily past one another. This makes the plastic less stretchy.

Polymer chains branching affects their ability to slide past one another and in turn alter bulk physical polymer properties. While long chain branches can increase the number of entanglements per chain and thereby increase polymer strength, toughness and the glass transition temperature, short chain branches can reduce polymer strength due to disruption of organisation and may decrease the degree of the crystallinity of the polymer.

Size of side group on monomer

Bulky side groups in polymer chains make it difficult for the chains to slide over one another or stack closely together. This prevents the formation of crystalline regions that refract light. As a result, an amorphous material is produced that is often transparent, making it a useful substitute for applications where glass has traditionally been used.

Polystyrene

The side group in styrene is a flat ring of six carbon atoms, often called a benzene ring, as shown in Figure 13.2.17.

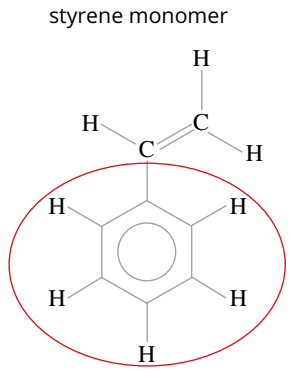


FIGURE 13.2.17 The chemical structure of the styrene monomer showing the bulky side group circled in red

Styrene polymerises as shown in Figure 13.2.18, where benzene rings are covalently bonded to every second carbon atom in the polymer chain. This causes polystyrene to be a hard but quite brittle plastic with a low density. It is used to make food containers, picnic and refrigerator parts.

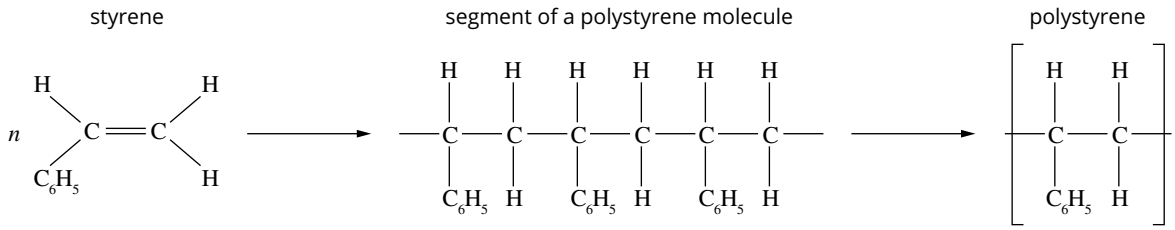


FIGURE 13.2.18 The polymerisation of styrene to form polystyrene

Polymethyl methacrylate

Polymethyl methacrylate (PMMA) also has large side groups, as you can see in the structure of its monomer in Figure 13.2.19. Due to the absence of crystalline regions that refract light, PMMA is transparent like polystyrene.

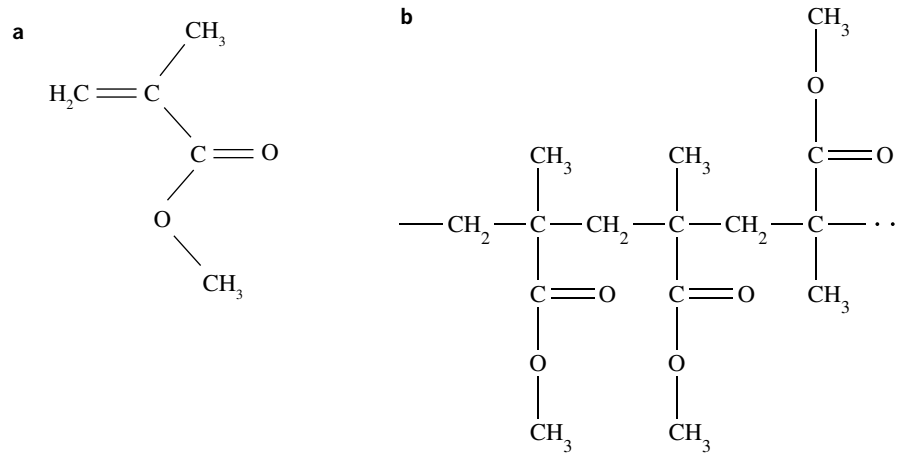


FIGURE 13.2.19 (a) Methyl methacrylate; (b) polymethyl methacrylate in which the bulky methyl and ester side groups of methyl methacrylate prevent the polymer chains from forming compact crystalline structures

Polymethyl methacrylate is much lighter than glass, more malleable and less prone to shattering. It is the ideal polymer for car headlamps, safety glasses and safety shields used by riot police (Figure 13.2.20).



FIGURE 13.2.20 Polymethyl methacrylate is an amorphous material that is used in safety glasses and the shields used by riot police.

Additives

Very few polymers are used in their pure form. Most include additives that improve or extend the properties of the polymer. They include pigments (to add colour), UV stabilisers (to prevent deterioration in sunlight), flame retardants and plasticisers.

Plasticisers

Plasticisers are small molecules that can be added to polymers during their manufacture. The polymer molecules are forced slightly further apart, weakening the forces between the chains and making the material softer and more flexible.

Because of the polar carbon–chlorine bond in polyvinyl chloride (PVC), the polymer chains are held together strongly by dipole–dipole attractions. Pure PVC is quite rigid at room temperature.

When a plasticiser is introduced between the chains, the chains can slide past each other, making the polymer softer and more flexible. By varying the amount of plasticiser used, PVC can be produced with a wide range of flexibilities. You can see the difference between the packing of PVC with and without plasticiser in Figure 13.2.21. Diisononyl phthalate is a plasticiser that is used to make PVC into vinyl floor coverings.

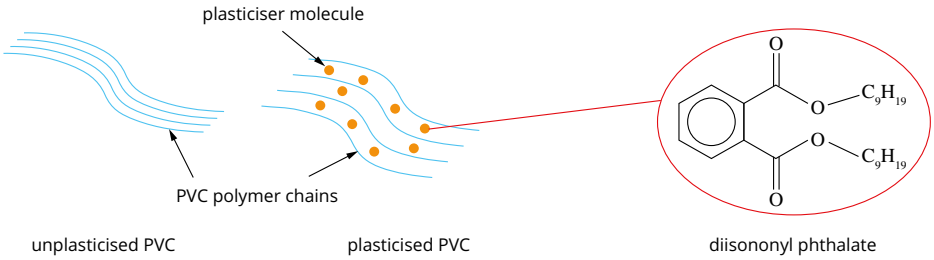


FIGURE 13.2.21 The presence of a plasticiser between the polymer chains weakens the attractive forces.

Foamed polymers

Foamed polymers are formed by blowing a gas through melted polymer materials. Foaming can drastically change the physical properties of a polymer material, as shown by the two examples of polystyrene in Figure 13.2.22. Polystyrene foam is produced by introducing pentane into melted polystyrene beads. The beads swell up to produce the lightweight, insulating, shock-absorbing foam that is commonly used for takeaway hot drink containers, bean bag beans and packaging materials.



FIGURE 13.2.22 A model plane made of rigid polystyrene sitting on a block of foamed polystyrene

ADVANTAGES AND DISADVANTAGES OF POLYMERS

Polymers have become the dominant material used in our society. There are many reasons why this has occurred and it is wise to be aware of potential drawbacks that arise from their use. Some of these advantages and disadvantages are shown in Table 13.2.3.

TABLE 13.2.3 Some advantages and disadvantages of using polymers

Advantages	Disadvantages
They are available in an enormous variety of forms, each with distinctive properties.	Many are derived from petroleum, a non-renewable resource.
They are generally biologically inert, chemical and corrosion resistant.	Microorganisms cannot break down most synthetic polymers (they are not biodegradable).
They are easy to process by moulding.	Thermoplastic polymers have a limited thermal stability.
They have low density.	Some plastic products crack, scratch or break easily.
They display good mechanical strength.	Many plastics produce toxic gases, such as hydrogen chloride, hydrogen cyanide and dioxins, when burnt.
Their properties can be modified (by foaming or adding plasticisers).	Some plasticisers can leach out of containers or wraps and pose a health risk.
Many can be recycled.	Thermosetting polymers are currently difficult to recycle.

Plastic waste



FIGURE 13.2.23 Plastic persists for a very long time in the environment.

Australians consume more than 1.5 million tonnes (1.5 billion kilograms) of polymer materials every year, which includes many different plastics. The disposal of waste polymer material is a serious issue in our society.

Plastics are durable, chemically resistant and lightweight. These properties make plastics very useful, but they also have a serious environmental impact. The biodegradation of plastics is very slow. Once discarded, plastics persist for a very long time, possibly hundreds of years. Because synthetic polymers have low density, waste plastic takes up more volume than other kinds of waste. They occupy the limited space available in landfills and litter the environment (Figure 13.2.23). Burning plastics raises concerns about pollution from harmful combustion by-products. One of these is hydrogen chloride, which is formed by the combustion of waste containing PVC.

Biodegradable plastics

Biodegradable materials break down naturally by the action of microorganisms. New types of biodegradable plastics are being developed but these are still a very small proportion of the plastics in everyday use. Most biodegradable plastics are condensation polymers that are made from renewable plant materials such as corn and starch. Other biodegradable plastics involve including additives in their manufacturing process, such as transition metals, in the polymers used to make food wrappings and shopping bags. These additives promote degradation of polymer chains to smaller, biodegradable compounds over time.

One example of a biodegradable addition polymer is polyvinyl alcohol. It is made by replacing side groups in polyvinyl ethanoate with hydroxyl groups as shown in Figure 13.2.24. The hydroxyl side groups form hydrogen bonds with water molecules, making the polymer soluble in water. It can be used to make water-soluble hospital laundry bags, sealed sachets containing laundry detergent or pesticides, and bags for waste disposal.

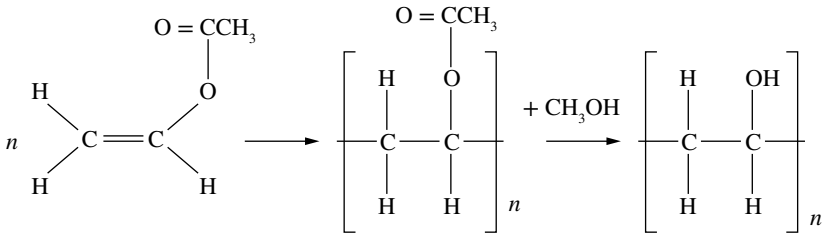


FIGURE 13.2.24 Polymerisation of vinyl ethanoate produces polyvinyl ethanoate, which is then reacted with an alcohol to produce polyvinyl alcohol.

Recycling plastics

There are two ways of recycling plastics. Reprocessing involves shredding, melting and reshaping used plastic into new, clean products as shown in Figure 13.2.25. This method can be used only with thermoplastic polymers. For example, reprocessed polyethene can be used for manufacturing plastic bags, rubbish bins and bottle crates.

The other method of plastic recycling involves depolymerisation, in which polymers are broken down into monomers. These monomers are then used in the production of new polymers. Figure 13.2.26 shows the depolymerisation of polystyrene back into individual styrene monomers. Depolymerisation requires a large amount of energy and the yield is usually low, making this recycling method less economically viable than reprocessing.

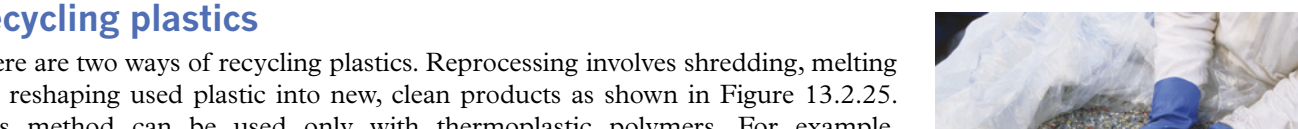


FIGURE 13.2.25 Reprocessing plastic by shredding and blow moulding new products

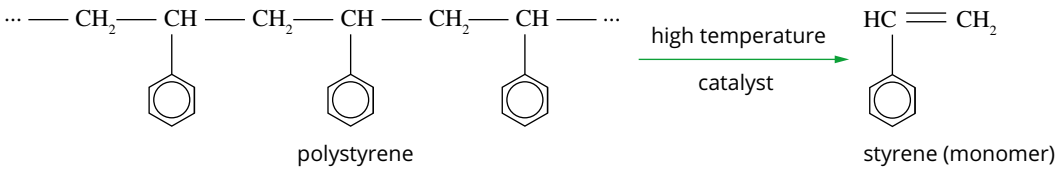


FIGURE 13.2.26 Depolymerisation of polystyrene at high temperature with a catalyst re-forms styrene monomers.

A numbering scale is used to identify plastics for recycling, as shown in Figure 13.2.27.



Polyethene terephthalate	High density polyethene	Polyvinyl chloride	Low density polyethene	Polypropene	Polystyrene	Includes polycarbonates, ABS, Teflon, various copolymers, nylon and other condensation polymers
bottles for soft drinks, water, shampoo, takeaway food containers	garbage bins, fuel tanks, hard hats, banners, water pipes, food storage containers	plastic wrap, cordial bottles, electrical wire covers, water pipes, floor tiles	plastic wrap, squeeze bottles, plastic tubing, shopping bags	rope, clothing, ice-cream containers, flip-top bottle lids	yoghurt containers, fridge shelves, drink cups, insulating beads, packaging	

FIGURE 13.2.27 International number code used to identify recyclable plastics

PA 4.2.4

Green polymer chemistry

Green polymer chemistry is a very popular field with research focused on eight main areas, as shown in Table 13.2.4. This field of chemistry is becoming increasingly popular for many reasons including:

- the need for decreased dependence on crude oil
- less fluctuation in the price of agricultural-based products compared to petrochecmical-based polymers
- the need for improved biodegradability
- support for farmers and rural communities.

Advances have been made in many areas, including new uses of bio-based feedstock, green reactions, green processing methodologies and green products.

TABLE 13.2.4 The eight major focus areas for green polymer chemistry

Major pathways	Examples
green catalysts	biocatalysts, including enzymes and whole cells
diverse feedstock base	bio-based building blocks and agricultural feedstocks, including sugars, peptides and triglycerides
degradable polymers and waste minimisation	agri-based renewable materials, including some polyesters and polyamides
recycling of polymer products and catalysts	many degradable polymers may be able to be recycled including the reuse of immobilised enzymes
optimising of molecular design and activity	polymers with designed structures or functions; improved biocatalysts; protein synthesis; genetic/metabolic engineering
non-hazardous solvents	water, ionic liquids or reactions occurring without solvents
energy generation or minimising energy use	biofuels; energy-saving processes, such as microwave and jet cooking
improved synthetic processes	atom economy, reaction efficiency, decreased by-products, toxicity reduction

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'.

Biocatalysis

Biocatalysis usually involves the use of enzymes, micro-organisms and even higher organisms to speed up or favour various reaction pathways. Since most biocatalytic reactions take place in water or without solvents, at lower temperatures (below 60°C) and produce fewer by-products, they represent excellent green methods to carry out polymerisation and polymer reactions.

Green processing

The increasing cost of energy and greater scrutiny on environmental considerations have resulted in industry adopting processes that increase yield and decrease energy usage and chemical waste. Improved reaction planning and process design can facilitate greener processing and reduce logistical problems. This can include the use of agriculturally based starting materials such as carbohydrates, triglycerides and other natural compounds. This has the advantage of reducing toxicity and results in safer handling of reactants and products.

Green products

In general, the polymers derived from natural agriculturally based sources are more likely to be degradable and possibly recyclable. For example, polylactic acid (PLA), shown in figure 13.2.28, is a biodegradable and bioactive thermoplastic polymer derived from renewable materials, such as corn starch and sugar cane. PLA is transparent and has similar properties to polyethylene and polypropylene. In 2010 PLA was the second most consumed biopolymer. Global demand for biopolymers is forecast to rise to about six million tonnes by 2021, growing at an annual rate of around 19%.

For five decades PLA has been used in biomedical applications; however, recent developments have led to its use as a feedstock material and decomposable packaging material (Figure 13.2.29). PLA can be recycled by thermal depolymerisation or hydrolysis back to the monomer.

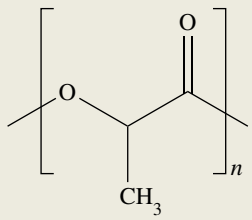


FIGURE 13.2.28 Chemical structure of polylactic acid (PLA)



FIGURE 13.2.29 Corn-made plastic cup produced from polylactic acid

PLA production emits less CO_2 per kilogram and uses less energy than most other polymers. Recent estimates predict that if the United States replaced production of high density polyethylene it would result in a reduction of almost six million tonnes of carbon emissions annually.

Other green products include the use of enzymes and enzyme-based conjugates for the treatment of waste water and enhanced oil recovery, encapsulation and production of biocompatible films and fibres.

Review

1. Discuss how green chemistry is beneficial to human health.
2. Identify any disadvantages of green chemistry.
3. Investigate some of the following applications of green chemistry.
   - polysaccharide polymers
   - formation of commodity chemicals from glucose
   - synthesis of aromatic amines without using halogenated compounds
   - green solvents, such as CO_2 or immobilised solvents

13.2 Review

SUMMARY

- A polymer is thermoplastic if it will soften when heated, allowing it to be reshaped. A thermoplastic polymer can be recycled by moulding it into a new shape. Thermoplastic materials have no strong bonds between polymer chains.
- Some polymers have covalent bonds, or cross-links, between polymer chains. Such thermosetting materials do not melt and they cannot be reshaped. If they cannot be reshaped, recycling is limited.
- Elastomers are polymers with special cross-links that allow them to stretch.
- Materials composed of polymers offer an almost limitless variety of properties, enabling them to be used for many different purposes.
- The percentage crystallinity of a polymer is a measure of the relative amounts of crystalline (ordered) regions and amorphous (disordered) regions in the material.
- No polymer is entirely crystalline. Some are entirely amorphous; most consist of both structures.
- Polymers can be designed for a particular purpose by selecting suitable monomers, reaction conditions or additives.
- Factors that affect the physical properties of polymers include the:
  - polarity of side groups in the polymer
  - use of more than one monomer (copolymers)
  - polymer chain length
  - extent of branching of polymer chains, e.g. LDPE and HDPE
  - arrangement of side groups in the polymer chain
  - inclusion of additives such as plasticisers with the polymer.
- A copolymer is a polymer that is made from more than one monomer.
- Plasticisers are organic molecules that soften a plastic because they weaken intermolecular attractions between polymer chains.
- As most polymers are made from non-renewable resources and are not biodegradable they pose an environmental risk.

KEY QUESTIONS

Retrieval

1 Describe what elastomers are.

2 Recall what a copolymer is.

Comprehension

3 The polymer chains of a certain material can be cross-linked to varying extents.

a Draw the polymer chains when there is:

i no cross-linking

ii a little cross-linking

iii a large degree of cross-linking.

b Use diagrams to show the effect of stretching each of these materials.

4 Explain how the structure of PVC chains gives rise to its suitability for use as a cover on electrical cables.

Analysis

5 Distinguish between a thermoplastic and a thermosetting polymer.

6 Elastic bands, golf balls and saucepan handles are made from polymers with some cross-linking.

a Identify which of these materials has the greatest degree of cross-linking.

b Describe the properties of the material you chose in part **a** to support your answer.

7 A polymer chemist is investigating the properties of polymers by increasing the length of chains in a controlled way. The chemist identified the effect on the relative molecular mass, melting point, strength of interchain forces and electrical conductivity. Predict the results for each property test.

Chapter review

WS 4.1.11 WS 4.1.12

13

KEY TERMS

addition polymer
amorphous region
atactic
biodegradable
condensation polymers
conductive polymer
copolymer
crystalline region
high density polyethene (HDPE)
isotactic
low density polyethene (LDPE)
photoconductive
plastic
polymerisation
side group
syndiotactic
unsaturated
Ziegler–Natta catalyst

KEY QUESTIONS

Retrieval

1 Identify the description that best defines a polymer.
- **A** a very long covalent molecule constructed from a repeating unit
- **B** a very long molecule with no pattern to its structure
- **C** a giant lattice of atoms in a repeating pattern
- **D** a very long molecule

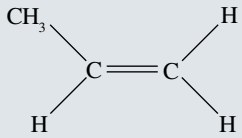
2 Identify the statement that best describes HPDE as compared to LDPE.
- **A** cross-links that leads to a lower melting point
- **B** much longer molecules with stronger covalent bonds
- **C** more polar molecules resulting in a higher boiling point
- **D** fewer branches in the chains resulting in a higher melting point

3 Define the term 'syndiotactic'.

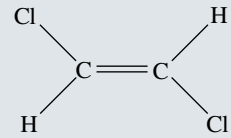
Comprehension

4 Draw the polymers formed from each of the following monomers.

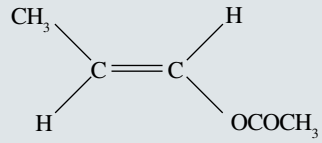
a



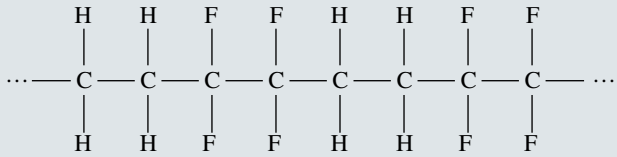
b



c



5 Determine how many monomer units the following polymer contains.



6 Explain the following terms using polyethene as an example.
- **a** addition polymerisation
- **b** unsaturated and saturated
- **c** empirical formula

7 **a** In terms of their structures, explain the difference in properties between HDPE and LDPE.
- **b** Determine whether HDPE or LDPE would be a suitable material for a:
  - **i** soft, flexible plastic wrap
  - **ii** two-litre drink container
  - **iii** wrapping material for frozen food.

8 Explain how the strength of the interchain bonding differs between thermosetting and thermoplastic polymers.

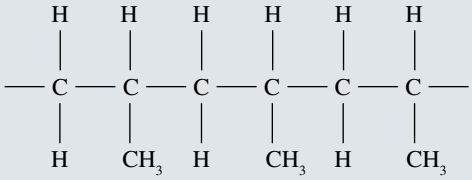
9 Explain why thermosetting polymers decompose rather than melt when heated.

Analysis

10 Identify the strongest type of intermolecular force present between polymer molecules produced from the following monomers.

- **a** ethene ($CH_2=CH_2$)
- **b** vinyl chloride ($CH_2=CHCl$)
- **c** styrene ($CH_2=CHC_6H_5$)
- **d** propene ($CH_2=CHCH_3$)
- **e** acrylonitrile ($CH_2=CHCN$)

11 A typical section of a polymer is shown below.



- **a** Name the term used to describe the arrangement of the side groups in the polymer.
- **b** Draw the monomer from which this polymer is produced.
- **c** Identify the number of repeating monomer units shown.
- **d** Determine whether this polymer would be part of a crystalline or amorphous region of the polymer.

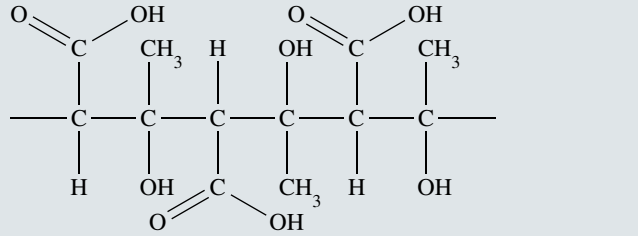
12 Determine whether the following features of a polymer chain will increase or decrease the crystallinity of the polymer material.

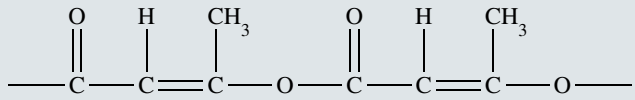
- **a** isotactic alignment of side groups
- **b** less branching
- **c** larger side groups

13 Conclude whether a recycled plastic is more likely to be thermoplastic or thermosetting.

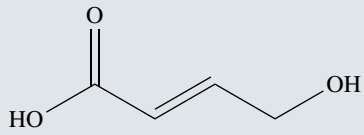
Knowledge utilisation

14 a Determine which of the following monomers, labelled A–C, could be used to produce both of the polymer chains shown below.

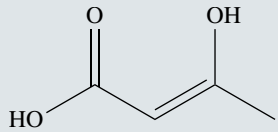




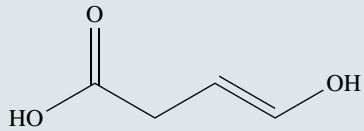
A



B



C



- **b** Justify why the remaining monomers would not be applicable.

CHAPTER

14 Molecular manufacturing



Molecular manufacturing is the design and production of molecules that have a particular composition, shape and function. It relies on an in-depth understanding of how the positioning of atoms and functional groups will result in the substance forming a particular shape and proceeding to interact with its environment. Once the structure has developed its unique three-dimensional shape, the molecule has effectively organised itself. It is now ready to act as an extremely small machine or device in the human body or in the environment.

Syllabus subject matter

Topic 2 • Chemical synthesis and design

MOLECULAR MANUFACTURING

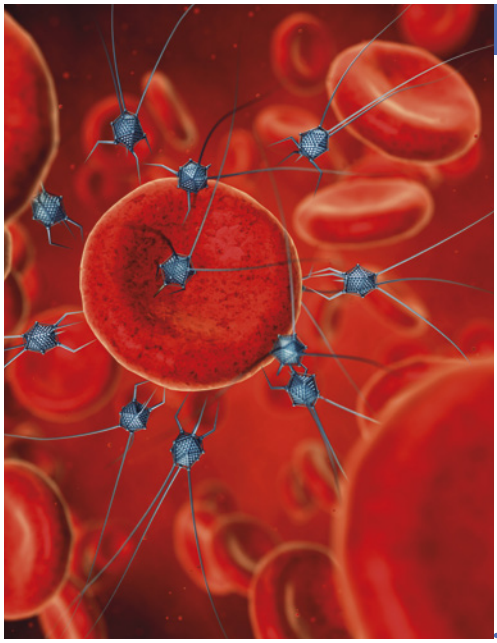
- appreciate that molecular manufacturing processes involve the positioning of molecules to facilitate a specific chemical reaction; such methods have the potential to synthesise specialised products, including proteins, carbon nanotubes, nanorobots and chemical sensors used in medicine.

SCIENCE AS A HUMAN ENDEAVOUR

- **Development of molecular manufacturing processes:** Molecular manufacturing (or molecular assembly) involves building objects to atomic precision using robotic mechanisms to position and react molecules. Molecular manufacturing arguably has the potential to quickly develop products (such as stronger materials, and smaller, faster and more energy-efficient computers) and address a range of global issues through provision of vital materials and products at a greatly reduced cost and environmental impact.

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14.1 Designer chemicals



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- understand that scientists can produce nanoparticles from smaller particles or even individual atoms
- understand that scientists can control molecular interactions by managing the shape of molecules and their binding sites
- understand that hydrogen bonding between molecules and within molecules can create structures with a particular shape
- understand that a specific reaction can be promoted using the orientation effect where two species will interact because of physical proximity
- recognise that unwanted 'side-reactions' can be prevented by temporarily attaching a protecting group
- recognise that a specific DNA sequence allows the creation of structures of known shape due to nucleotide base pairing
- understand that molecular machines, such as nanotubes, nanorobots and chemical sensors, can interact with, and sometimes change, their environment.

In the macroworld we use many machines that require energy in the form of fuel or electricity to complete their tasks. In the nanoworld, at the level of tens or hundreds of atoms, little or no energy is required to undertake tasks because the chemical change is initiated by the interaction of part of their structure with a molecule it 'meets'. Molecules manufactured in this way are able to traverse their environment as free entities, ready to respond when presented with the correct substrate. These structures are sometimes referred to as **nanorobots**.

Researchers in molecular manufacturing recognise that developing precise molecular structures, so-called 'designer chemicals', is key, and many see far-reaching consequences for even small gains in this field. These revolutionary molecules could provide smarter pharmaceuticals, faster drug delivery and more sensitive diagnostic tests.

MANIPULATING MOLECULAR ASSEMBLY—POSITIONING OF MOLECULES

Researchers have used two methods to custom build very small particles, between 1 and 100 nm, known as **nanoparticles**. The first method involves processing a larger mass of bulk substance (the **top-down approach**). Since physical or chemical means are used to break the material down to nanoscale particles, this often wastes a lot of the starting substance.

The other method builds the molecule by combining smaller structures, sometimes atom-by-atom (the **bottom-up approach**). The practicalities of this procedure mean that the molecule must essentially assemble itself using intrinsic forces—it is too small for human manipulation. These intrinsic forces are a result of the chemical and physical properties of the atoms involved. Covalent bonding and intermolecular forces based on electrostatic attraction (discussed in Units 1 and 2) are examples of these forces.

In nature, most materials are produced bottom-up. An important example is carbohydrate synthesis by chlorophyll in plants (**photosynthesis**) that produces simple and complex sugars followed by other reactions that produce larger molecules, such as cellulose. The strong and durable threads that spiders and silkworms produce from chemicals within their bodies are another example of materials produced bottom-up.

The process of deliberate and purposeful synthesis of molecular structures relies on understanding fundamental molecular and atomic interactions, such as stereospecificity, the orientation effect and hydrogen bonding.

Stereospecificity and the orientation effect

In Unit 2 you learnt about macromolecules, such as enzymes, containing **binding sites** specific to a **substrate molecule**. The substrate molecule fits the binding site in a way similar to a key fitting a lock—the shape is vital. In molecular manufacturing, scientists can use their understanding of stereochemistry (the three-dimensional arrangement of atoms) to make structures with binding sites specific to a molecule or atom of interest. This specificity based on shape is called **stereospecificity**.

Complexes containing a substrate molecule or particle specifically bound to a site on a larger molecule are often called **host–guest systems**. They can be used to bind to and remove hazardous substances from the environment. An example of this is the BOBCalix6 molecule shown in Figure 14.1.1. It is part of a group of substances known as calixarenes. The cavity in its structure has the correct size and shape to accommodate and bind a caesium ion. In addition, dipoles formed at the six oxygen atoms lining the binding site provide electrostatic forces holding the caesium cation in place. BOBCalix6 will potentially be able to remove radioactive caesium-137 contamination from large volumes of liquid nuclear waste. Scientists are working to develop an improved structure with a shape that will hold two caesium ions rather than just one.

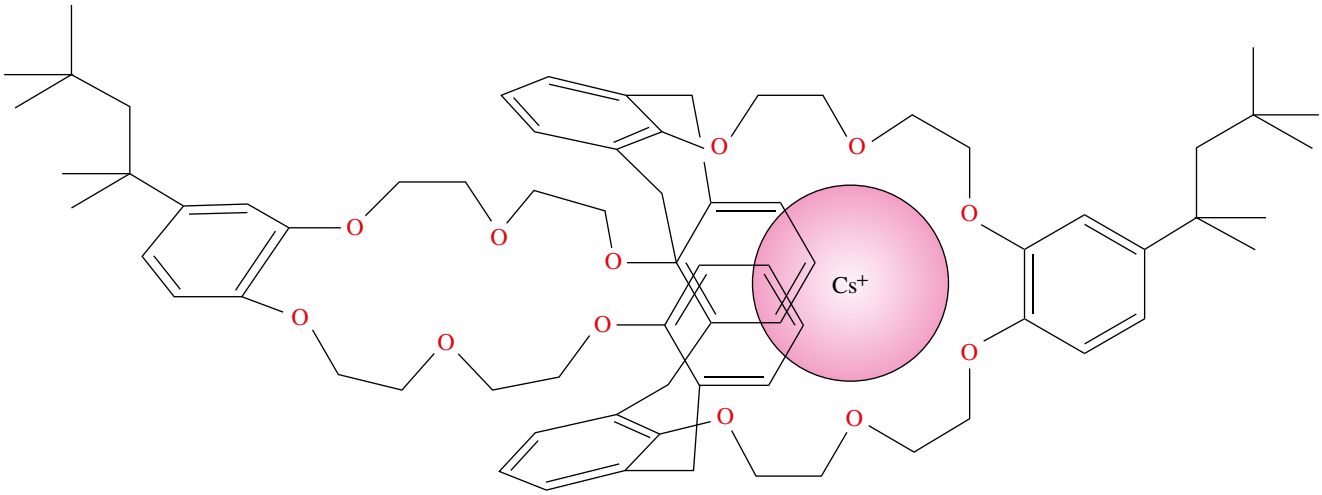


FIGURE 14.1.1 Host molecule (BOBCalix6) shown with a positively charged caesium ion held in one of its cavities

The effectiveness of structures containing a stereospecific binding site is due to the **orientation effect**. This means that molecules, or sections of molecules, are aligned so that a particular association and/or chemical reaction is promoted. The proximity or 'forced association' of the functional groups of two molecules allows collisions of sufficient energy and orientation for a reaction to occur.

Ribosomes are an example of naturally occurring biomolecular machinery that uses the orientation effect to align reactants and promote protein synthesis. In ribosomes, amino acid monomers are aligned in the correct orientation to allow them to bond and create a protein polymer. The ribosomal machinery also uses tRNA structures to create the correct sequence relative to the RNA strand attached to the ribosome. Figure 14.1.2 shows a molecular machine (ribosome) producing a protein polymer using amino acids (coloured circles). The correct amino acids are orientated close to each other using tRNA molecules (green) leading to the formation of a peptide bond.

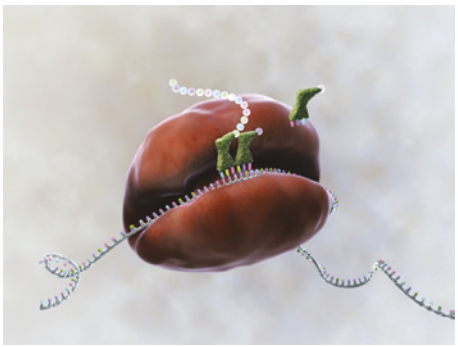


FIGURE 14.1.2 A ribosome is an example of a biomolecular machine.

When scientists aim to synthesise a molecular machine that facilitates a particular reaction, they need to devise ways that ensure the reacting species will associate with the molecule in the correct orientation. This involves positioning individual molecules close together so stronger chemical attractions can overcome weaker ones in a controlled way, depositing or removing atoms as desired.

Scientists have been able to mimic at least some of the impressive abilities of the ribosome using a **rotaxane**. A rotaxane is a molecule that has a circular structure (called a macrocycle) associated with a linear dumbbell-shaped molecule (molecular axle). The two molecules are interlocked but not bonded, allowing movement. This is represented in Figure 14.1.3.

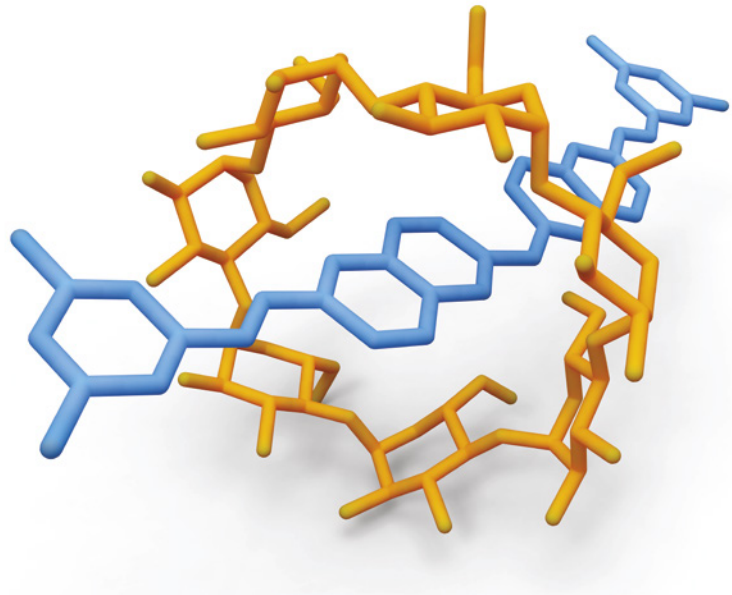


FIGURE 14.1.3 A rotaxane is an example of a molecular machine.

Researchers at the University of Manchester have produced a rotaxane-based small molecule machine that produces a peptide in a process known as non-ribosomal protein synthesis. The polymer is built as the macrocycle travels along the central molecule 'picking up' amino acids and synthesising a peptide. Natural chemical attachment of the amino acids is promoted by the way the macrocycle of the rotaxane is linked with and moves along the molecular axle (Figure 14.1.4).

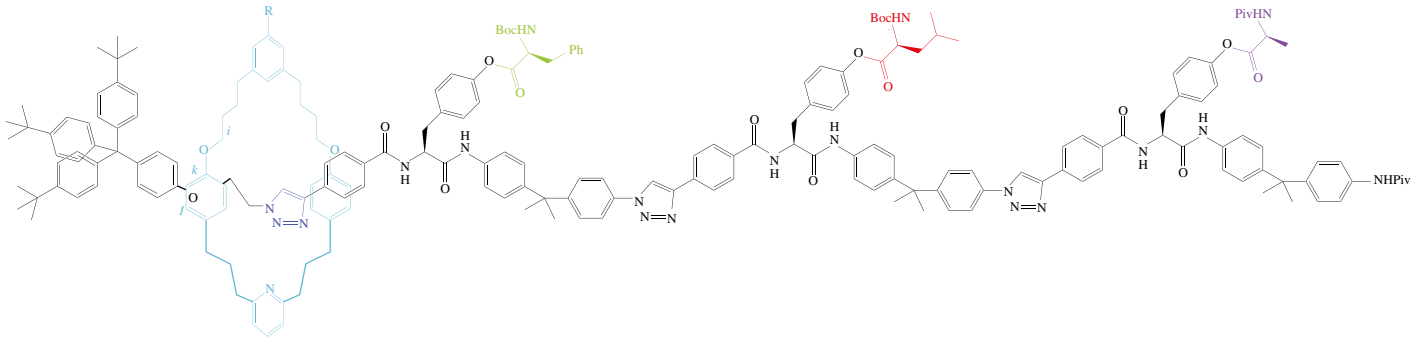


FIGURE 14.1.4 A peptide-synthesising rotaxane showing the macrocycle (blue) encircling the molecular axle (black), which contains three amino acids (green, red, purple)

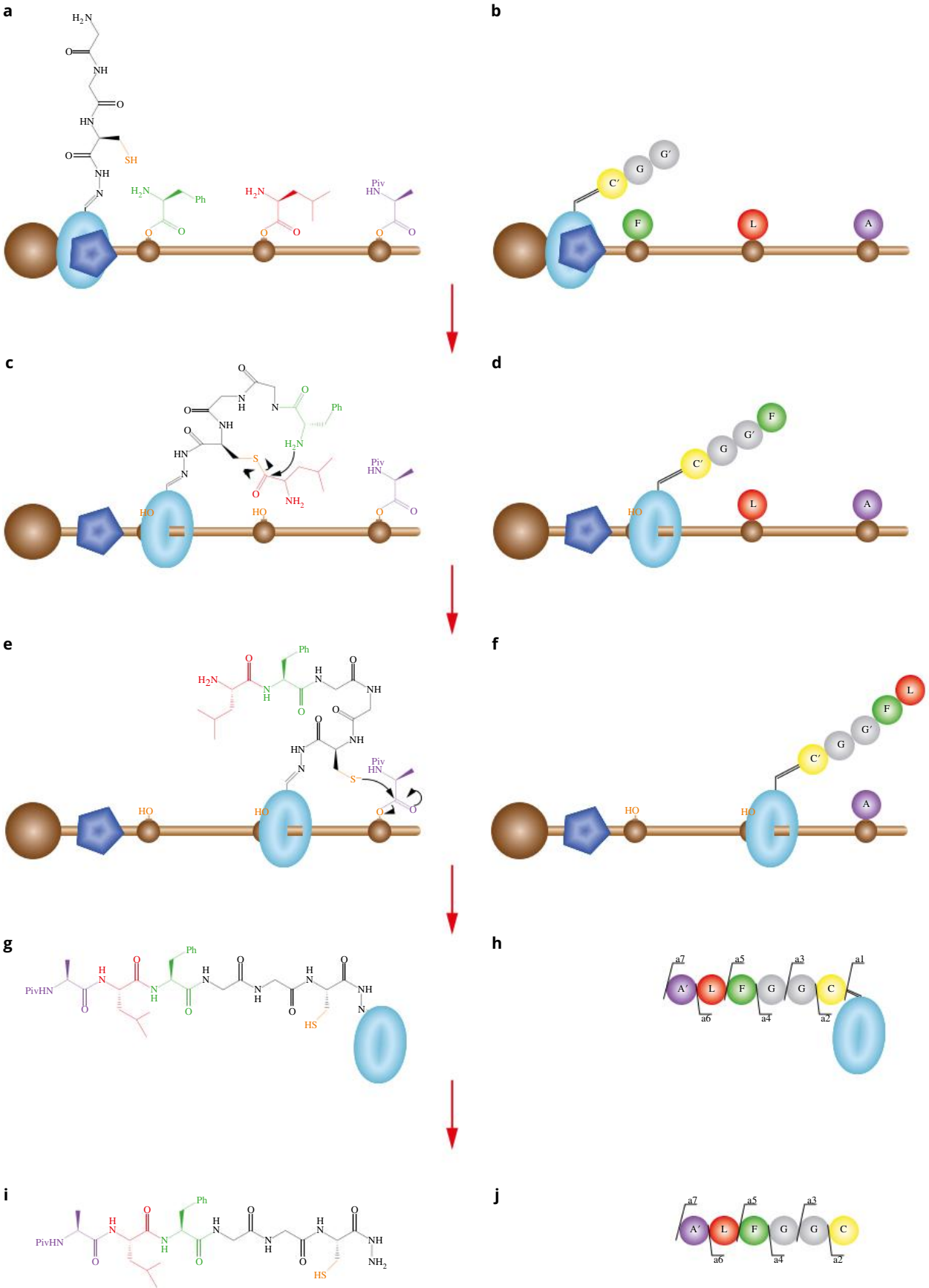


FIGURE 14.1.5 Non-ribosomal peptide synthesis by a rotaxane. (a) and (b) show the structure of the rotaxane with macrocycle, starter peptide and molecular axle containing three amino acids; (c) (d) (e) and (f) show the macrocycle moving to the left allowing close association of the growing peptide chain with each consecutive amino acid on the molecular axle; (g) and (h) show the completed peptide still attached to the macrocycle; (i) and (j) show the peptide chain after removal from the macrocycle.

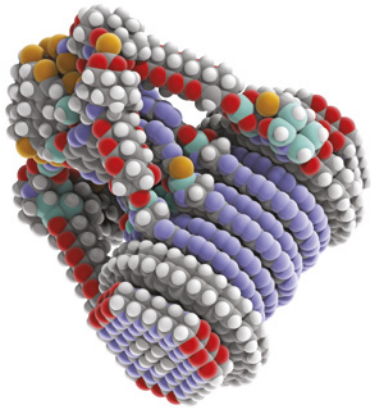


FIGURE 14.1.6 Representation of the atomic structure of a hypothetical molecular machine

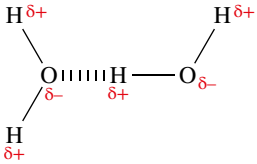


FIGURE 14.1.7 Hydrogen bonds in water, shown by dashed lines, are an electrostatic attraction between two polar regions. A slightly positive hydrogen atom on one molecule is attracted to a slightly negative fluorine, oxygen or nitrogen atom on another molecule.

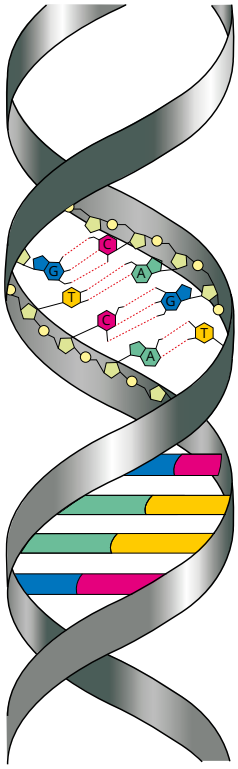


FIGURE 14.1.8 Illustration of the structure of a DNA molecule

This recent success in partially mimicking a biochemical process as important as peptide synthesis will potentially lead to molecular machines that can perform other important functions. Raw materials can be used to produce useful structures, or modify existing ones, at the nanoscale. Figure 14.1.6 shows an artist's representation of a hypothetical nanomachine.

Hydrogen bonding and sequence defined polymers

Forces such as covalent bonding and intermolecular forces, while complex, are bonding theory that is well understood. The strongest of the intermolecular forces (forces between molecules) is hydrogen bonding, which occurs when fluorine, oxygen or nitrogen interact with a hydrogen atom on a neighbouring molecule (Figure 14.1.7). Hydrogen bonding is an electrostatic charge attraction. The force of attraction can often be overcome when molecule(s) have greater kinetic energy after heat is applied.

One of the most important examples of electrostatic forces in the form of hydrogen bonding is the interaction between nucleotide bases in DNA (**deoxyribonucleic acid**, Figure 14.1.8). DNA is composed of chains of **nucleotides** (thymine, adenine, guanine and cytosine) formed into a double-stranded structure, as shown in Figure 14.1.9. A unique DNA sequence codes for a gene.

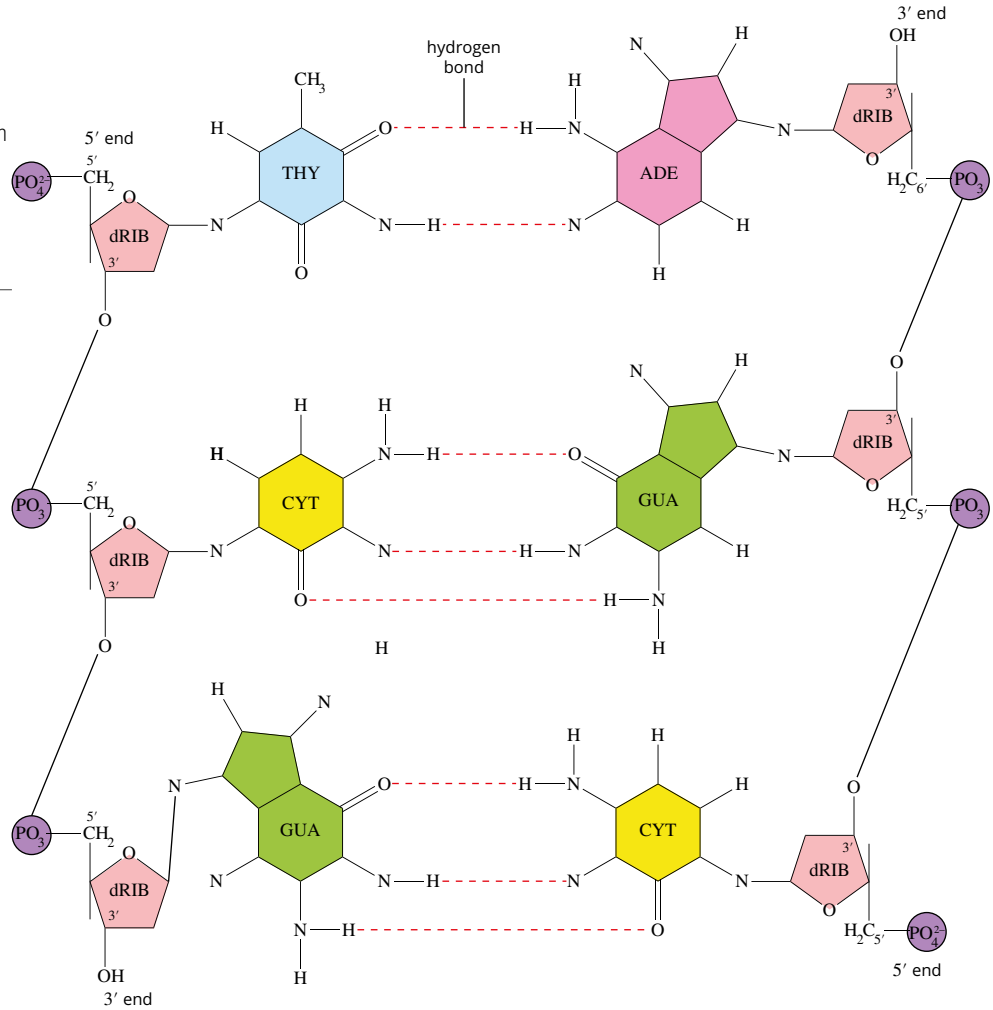


FIGURE 14.1.9 Two DNA strands showing nucleotide base pairing and hydrogen bonding

DNA has become a useful tool in synthesising molecular machines because a predetermined sequence can be constructed, and it will fold to a particular shape when complementary sequences align and form hydrogen bonds. These sequence-specific polymers have become known as '**DNA origami**'. First used by Nobel Prize winner Paul W. K. Rothemund in 2006, tent-shapes, barrels, baskets and

hinged structures like tweezers have been built. Longer pieces can be folded and 'stapled' with custom-built shorter pieces (Figure 14.1.10). These staples use the familiar base pairing and hydrogen bonding found in the DNA of every living cell.

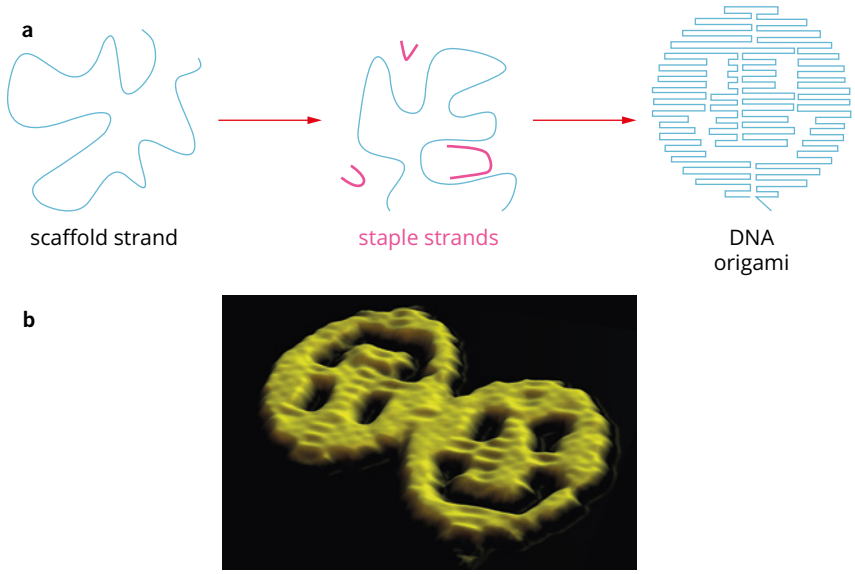


FIGURE 14.1.10 Smiley DNA. Hydrogen bonding between nucleotide base pairs of the scaffold strand and the small staple strands folds and holds the synthetic DNA molecule in a predetermined shape. (a) diagrammatic representation and (b) atomic force microscope image.

As a biomolecule, DNA origami is fully compatible with the human body. Its simplistic name does not capture the complexity of the structures now available, or the extensive possibilities for the use of custom-built DNA structures in medicine. These promising structures can be further manipulated using a range of DNA-modifying enzymes. This makes them even more versatile and useful, even to the level of programming them to move and complete a mechanical task. Examples of these nanorobots are described below.

Protecting groups

A molecule may have more than one functional group that is able to react. A **protecting group** is a molecule or functional group that is reacted with, and attached to, a specific area of a molecular machine to block the reactivity of that area. The role of these reactions and groups is to promote the reaction of a particular functional group in the molecule by preventing other unwanted reactions and products.

In many synthesis reactions, growing structures are attached to a larger molecule or solid support. This strategy serves two purposes. Firstly, the growing chain or molecule is retrievable because it is attached to a large structure, and secondly, the anchored end of the molecule is prevented from reacting. At the completion of the synthetic pathway, the completed structure is chemically removed from the larger structure. The rotaxane example described above uses this strategy (Figure 14.1.4 on page 560).

MOLECULAR MACHINES

Many chemists and biochemists have dreamed of being able to create and use a particular molecule for a particular purpose; however, substantial progress eluded scientists until the 1970s. The 1987 Nobel Prize in Chemistry recognised the importance of synthesised molecules called **crown ethers**, which feature a structure-specific binding site. Figure 14.1.11 on page 564 shows a crown ether. You can see that this is a host–guest system with the doughnut-shaped crown ether 'holding' the host atom (silver) via electrostatic charge interactions.

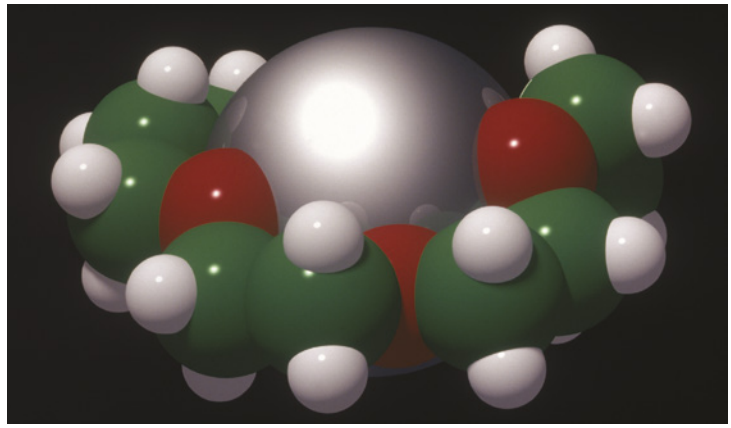


FIGURE 14.1.11 Charge distribution in a crown ether shown by surface potential. Red indicates regions of negative charge, green corresponds to neutral areas, and white indicates regions of positive charge.

Excitement builds with the discovery of each new 'designer' chemical. Some researchers envision medical breakthroughs such as targeted drug delivery, identification and elimination of cancer cells, and molecules roaming the body repairing problems in cells and DNA.

Carbon nanomaterials offer large gains in performance and properties over some materials in current use and have a broad range of potential applications. The carbon–carbon bonds in these structures are very strong. There are no weak points as they are a single layer of graphene or a nanotube.

Carbon nanotubes

Carbon nanotubes (CNTs) are closely related to **graphene**. They are called nanotubes because they have a long, hollow structure with walls formed from graphene. The diameter of these cylinders is very small, around 1 nanometre (10^{-9} metre) wide, while they can be millions of times longer. They can be capped on the end of each cylinder by a half **fullerene** molecule, as shown in Figure 14.1.12. CNTs can be single-walled or multi-walled. A multi-walled nanotube has smaller tubes sitting inside larger tubes. Their strength is derived from the strong carbon–carbon bonds, and they show high thermal and electrical conductivity.

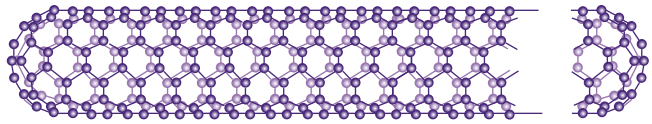


FIGURE 14.1.12 A carbon nanotube can be regarded as a sheet of graphene rolled into a cylinder and capped on the ends by a half fullerene molecule.

Carbon nanotubes can be produced by **chemical vapour deposition**, as shown in Figure 14.1.13. In this process, vaporised hydrocarbon molecules provide carbon atoms that form covalent bonds in the presence of a **metal catalyst**. It involves passing a hydrocarbon and inert carrier gas (such as argon) through a heated chamber (at 600 to 1200°C) containing a solid phase metal catalyst.

After undergoing thermolytic breakdown, carbon atoms are deposited on the metal catalyst and 'grow' upwards (Figure 14.1.13a). While the mechanism of this growth is not fully understood, it is clear that the particle size of the catalyst is important. Changing the dimensions of the catalyst particle changes the diameter of the growing nanotube, implying that carbon atoms initially deposit around the edge of a spherical or dome-shaped catalyst particle. Alkanes, alkenes and alcohols can be used as reactants in this process, and a variety of metal oxides and carbides are used as catalysts.

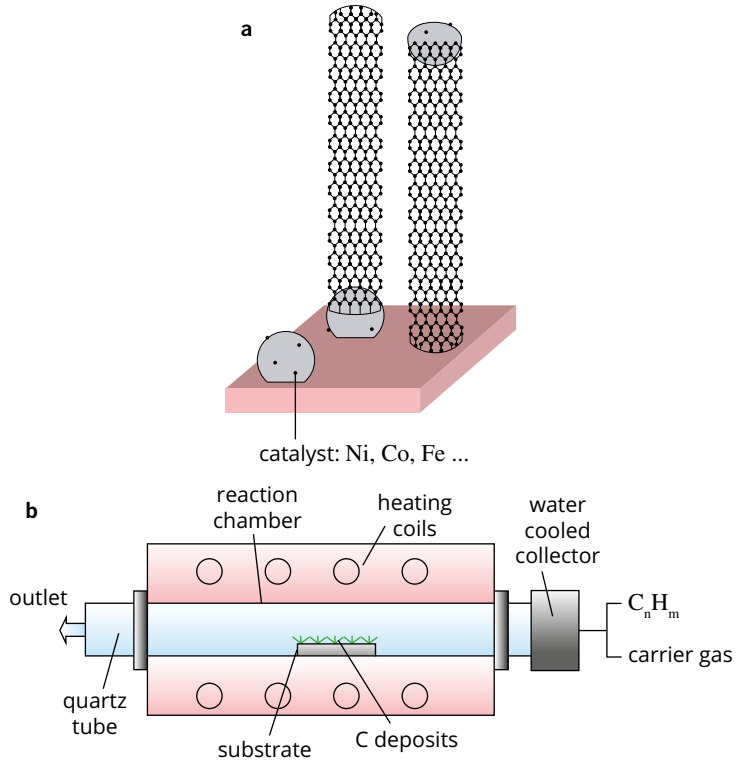


FIGURE 14.1.13 Synthesis of carbon nanotubes using chemical vapour deposition (a) 'Growing' nanotubes attached to catalyst particles, and (b) a diagram of the reaction chamber

Carbon nanotubes are:

- up to 300 times stronger than steel. Rope made from nanotubes with a diameter of 1 cm could support a weight of over 1000 tonnes. Nanotubes are already being used in high-performance sporting equipment
- better conductors of electricity than silver. Since nanotubes are essentially 'wires' that are much narrower in diameter than metal wire, they offer the possibility for extreme miniaturisation of electrical circuits
- better thermal conductors than diamond. Nanotubes could be used to transfer heat away from electrical components
- stronger than Kevlar fibres
- capable of adsorbing more gas or impurities than activated charcoal.

The size, surface area and adsorption properties of carbon nanotubes make them an ideal membrane for filtering toxic chemicals, dissolved salts (during desalination) and biological contaminants from water. A benefit of this technology is in delivering drinking water without the use of chemicals, heat, or power—vital for use in developing countries. The filter removes pathogens and contaminants such as viruses, bacteria, cysts and spores, delivering water that meets or exceeds the US EPA Drinking Water Standards.

Researchers at the University of California have successfully developed carbon nanotubes that can be inserted into both synthetic and natural membranes (Figure 14.1.14), creating artificial pores in cells. They used lipids to refine the structure of the nanotubes, ensuring that they were the right size and composition to penetrate the membrane. As cell membranes consist of a lipid bilayer in which lipid and protein molecules are embedded, the nanotube structure needed to be consistent with this. Nanotubes were coated with lipids, which allowed them to slide into the cell membrane of a cell without causing damage.

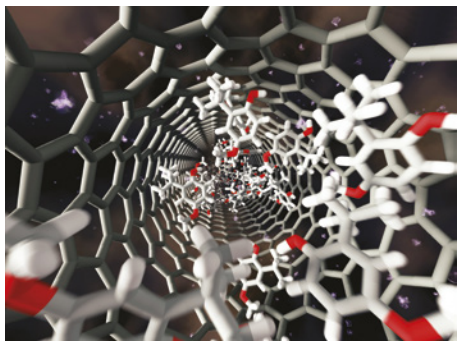


FIGURE 14.1.14 Diagrammatic representation of nanotube drug delivery. Nanotube technology provides the potential for drugs to be delivered to specific tissues and cells.

The researchers also observed the nanotubes opening and closing, just like biological ion channels. They discovered that the charge at the ends of the nanotubes shifted in response to changes in the ion concentration of the surrounding environment. These properties of nanotubes make it possible for scientists to artificially control what enters and exits cells. This provides potential applications in areas such as drug delivery, where the selective transport of molecules could significantly improve the efficacy of treatments.

Nanorobots

Nanorobots are molecules that can automatically carry out nanomechanical tasks. They are sometimes called 'molecular machines' and are usually DNA molecules. DNA structures are 'programmable' using nucleotide sequences. This means that sections of known sequence are synthesised and sequence-specific annealing of two single DNA strands is used to form associations. Other chemical properties such as cleaving the molecule with **restriction enzymes** are also used to change and control the DNA, allowing these molecules to move autonomously in programmed ways. An example of this is the **DNA walker**, shown in Figure 14.1.15, which can move along a 'track' made of a solid surface with annealed **control strands** of DNA. The DNA sequence of the walker is complementary to the control strands and so the 'legs' of the walker are held in place. When a restriction enzyme is employed to digest the control strand of one 'leg', it causes the leg to 'step' forward and reanneal to a new control strand. This action pulls the robot to the new peg and its other foot is freed. This process continues and moves the nanorobot step-by-step across the surface.

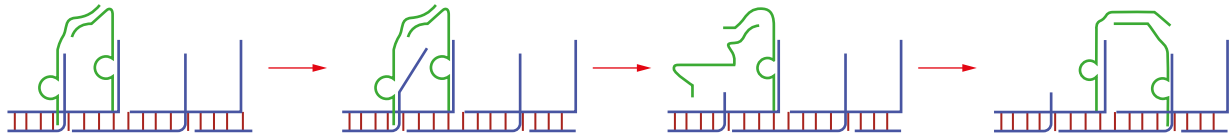


FIGURE 14.1.15 A DNA walker showing annealing of DNA strands to the control strands in the solid phase, followed by removal of the control strand causing one 'leg' to 'step' forward and reanneal to a new control strand

Newer nanorobots have the ability to carry and release a 'load' as they walk. In September 2017, scientists from Caltech published research related to a molecular machine they have developed that can perform such tasks at the nanoscale. This nanorobot, made of a single strand of DNA, can autonomously 'walk' around a surface, pick up certain molecules and drop them off in designated locations. The DNA sequence of the molecule recognises the control strands and carries two types of molecular cargoes to their specific drop-off destinations. These associations are mediated by hydrogen bonds between nucleotide bases.

The **cargo-sorting** of the DNA nanorobots becomes even more spectacular when loads are labelled with fluorescent markers, as shown in Figure 14.1.16. Future applications for these findings may include using DNA robots to sort chemical reactants before synthesis, rearranging circuit components or making programmable RNA able to produce a therapeutic drug in body cells.

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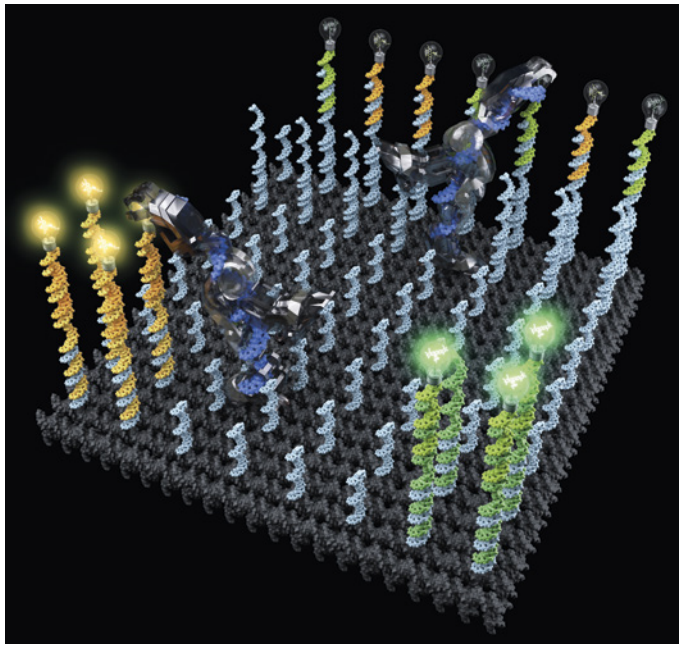


FIGURE 14.1.16 An artist's representation of two of the Caltech robots moving across a surface of control strands (origami surface) with fluorescent molecule 'loads'.

The Wyss Institute at Harvard University has developed an ingenious barrel-shaped DNA device for delivering a chemical load to a target cell (Figure 14.1.17). The barrel resembles a hinged clam shell structure, complete with a DNA double helix 'lock'. This structure will open when the target cell is found and release the chemical inside the barrel.

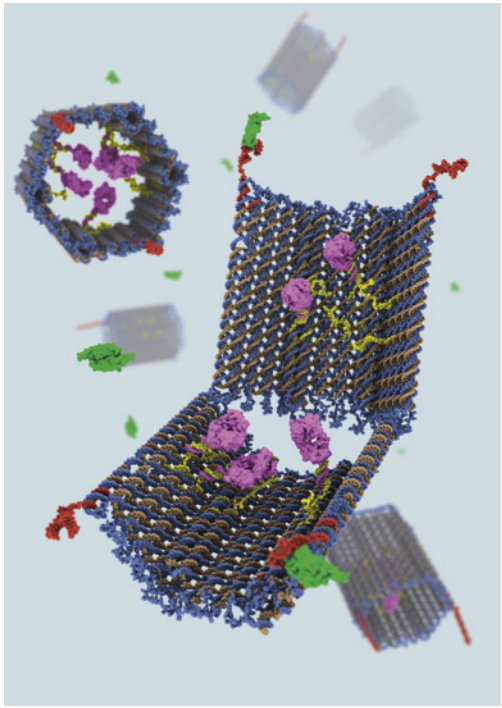


FIGURE 14.1.17 This DNA nanorobot can open when a chemical signal is received.

Nanorobots made from sequence-specific polymers are an exciting opportunity to develop molecules that may be able to synthesise a therapeutic chemical from its constituent parts, sort or repair DNA components and fragments, or deliver a drug in a more controlled or efficient way in the bloodstream or to cells.

In April 2017, scientists from around the world met in Toulouse, France, to race their molecules inside a scanning electron microscope (SEM). In addition to establishing a winner, they were able to share ideas and understand nanorobots further. Figure 14.1.18a shows the six nanocars that raced each other and Figure 14.1.18b provides information about the two winners.

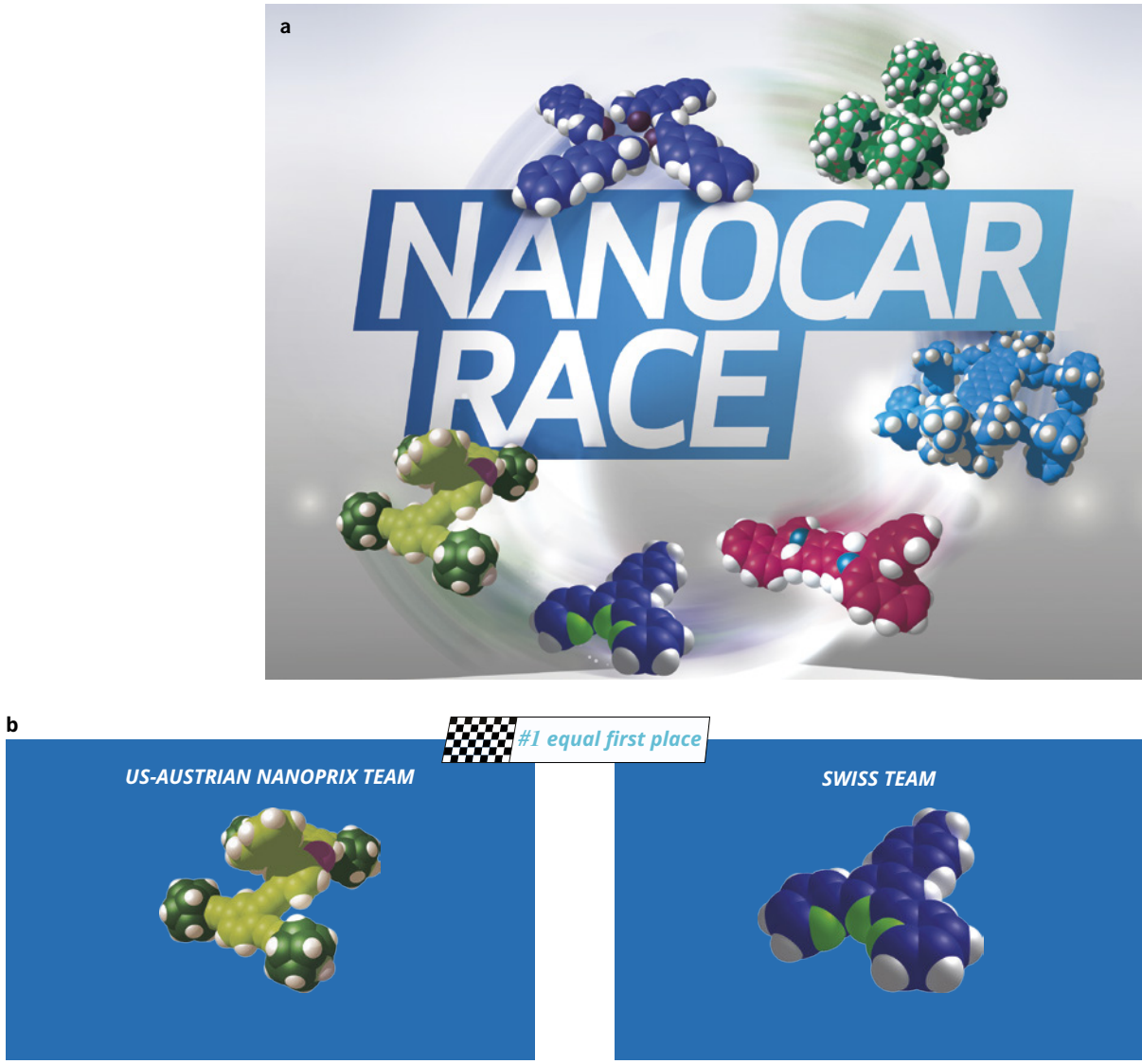


FIGURE 14.1.18 (a) The six nanocars that participated in the NanoCar Race. (b) The US–Austrian team raced their molecule car 1 micron in 29 hours, which constitutes the longest and fastest ever single molecule run. The Swiss team raced their molecule car 133 nm in 6.5 hours. They were declared joint winners of the 2017 NanoCar Race.

Chemical sensors

By utilising the versatililty of DNA molecules and their ability to bind to complementary sequences on a solid support, researchers from Renmin University in China have been able to develop an on-site optical test for detecting mercury (Hg) contamination in water samples.

When mercury binds to thymine in the fluorescence-labelled **DNA probe**, the resulting T-Hg^{2+}-T complexes force the DNA into a hairpin shape. This means that the probe segment will not bind to the solid support and fluoresence will be lost (Figure 14.1.19). This is called a structure-switching change. A decrease in the measured fluoresence of the sample being tested indicates the presence of mercury.

The research group reported that mercury levels down to 1.2 nM can be detected, and that the test can be performed on site in 10 minutes. While current qualitative testing processes are more sensitive than this, they require pre-processing of samples and transport to a laboratory for traditional quantitative methods, such as atomic absorption/emission spectroscopy, inductively coupled plasma mass spectrometry, and cold vapour atomic fluorescence spectrometry. Recommended maximum levels of mercury in water are 30 nM (World Health Organization) or 10 nM (US EPA), and therefore this DNA-based biosensor demonstrates sufficient sensitivity for rapid on-site testing of heavy metals in natural water.

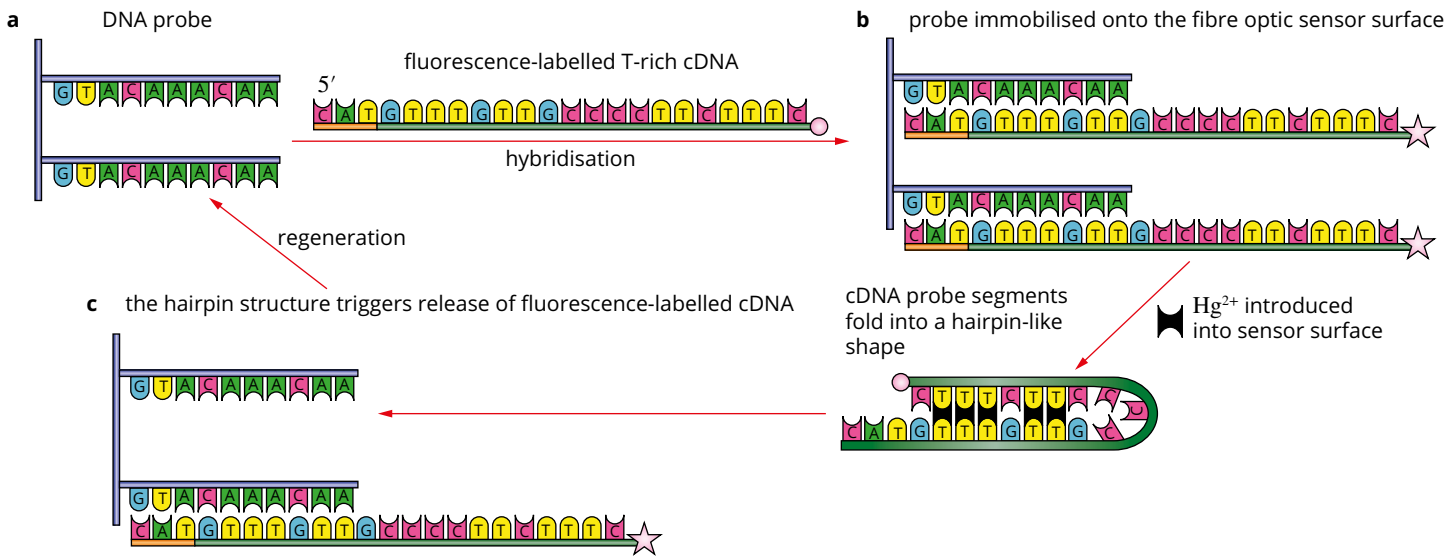


FIGURE 14.1.19 Fluorescence-labelled DNA probe technique used to detect Hg in water samples. (a) Solid support containing DNA probe segments and (b) complementary DNA probe containing fluorescent marker annealed to matching sequences on the solid support. (c) In the presence of Hg the DNA probe becomes folded and detaches from the solid support. The higher the Hg concentration the less fluorescent the solid support appears.

The promise of molecular manufacturing lies in the versatility and capabilities of the molecules themselves, derived directly from interactions between component atoms. Technologies have already begun to harness their power and develop working models. However, synthesis of many of these molecular structures, such as the artificial red blood cell, are hypothetical and beyond current experimental and technological techniques. Insights from computer analysis, and those obtained from understanding the working molecules making up the machinery of living cells, may lead to many more nanomachines that will improve the biological and chemical processes of our world.

Development of molecular manufacturing processes

The world's smallest machines

In 2016 the Nobel Prize in Chemistry was awarded to Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa for their work in developing molecules that can perform a controllable task when energy is added. Their miniature machines were a two-ringed catenane (Figure 14.1.20), a ring-and-dumbbell rotaxane (Figure 14.1.21) and a molecular motor (Figure 14.1.22). Further developments have led to molecular lifts (Figure 14.1.23) and nanocars (Figure 14.1.18 on page 568). The work of these three researchers and their collaborators spans more than three decades.

A common feature of these intriguing molecules is the ability of at least two of their parts to move relative to each other while remaining associated. This is known as a **mechanical bond** and makes these structures analogous to other machines in the macroworld. These projects revealed that, just like the inside workings of your washing machine, small molecules and proteins are physical objects, and many of their most important interactions are accomplished by physical slotting, shifting, ratcheting and rotating.

The molecular motor shown in Figure 14.1.22 is activated by UV light. Each 'rotor blade' consists of three cyclic structures that spin around a central C=C bond. As it rotates, the methyl groups obstruct each other but when heat is applied the methyl groups 'snap' over each other and the rotors continue to spin. By adding molecular 'arms' the molecule acts as a nanostirrer.

Sir J. Fraser Stoddart and collaborators have used their initial discovery of rotaxane machines to build a controllable nanolift or nanoelevator. They descriptively call the moving part of the structure a 'shuttle', which recognises that the macrocycles move up and down relative to the three 'legs' (Figure 14.1.23). The resulting device, which is about 2.5 nm high and roughly 3.5 nm in diameter, is able to develop forces of up to 200 pN.

In the nanolift, the fused macrocycles form a platform that will move up or down in response to changes in pH. When the macrocycle is at the upper level (Figure 14.1.23a), hydrogen bonding involving $–NH_2^+–$ holds the platform in place. Introducing basic conditions causes deprotonation of the $–NH_2^+–$ centres, destroying the hydrogen bonding between the platform rings and the centres so that the platform moves down (Figure 14.1.23b). Adding acid restores the $–NH_2^+–$ centres and moves the platform back up to the higher level. The distance moved is about 0.7 nm.

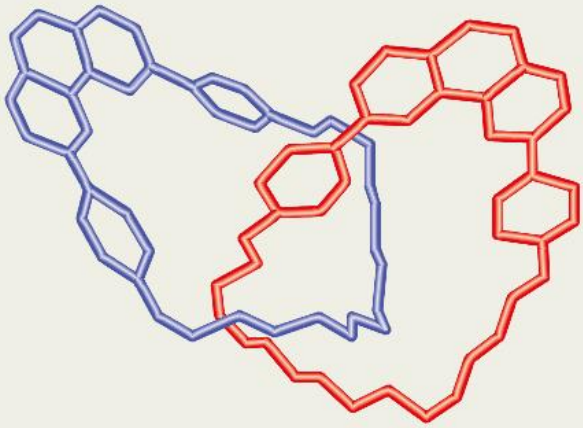


FIGURE 14.1.20 The two interlocking rings of Jean-Pierre Sauvage's catenane

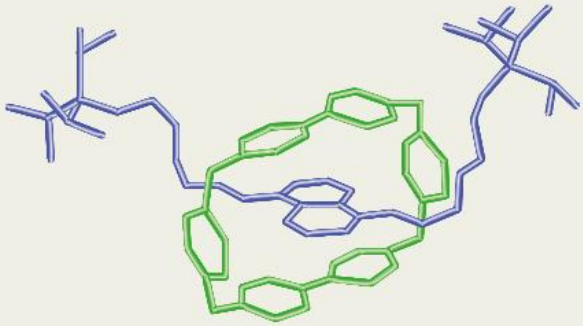


FIGURE 14.1.21 The ring-and-dumbell of Sir J. Fraser Stoddart's rotaxane

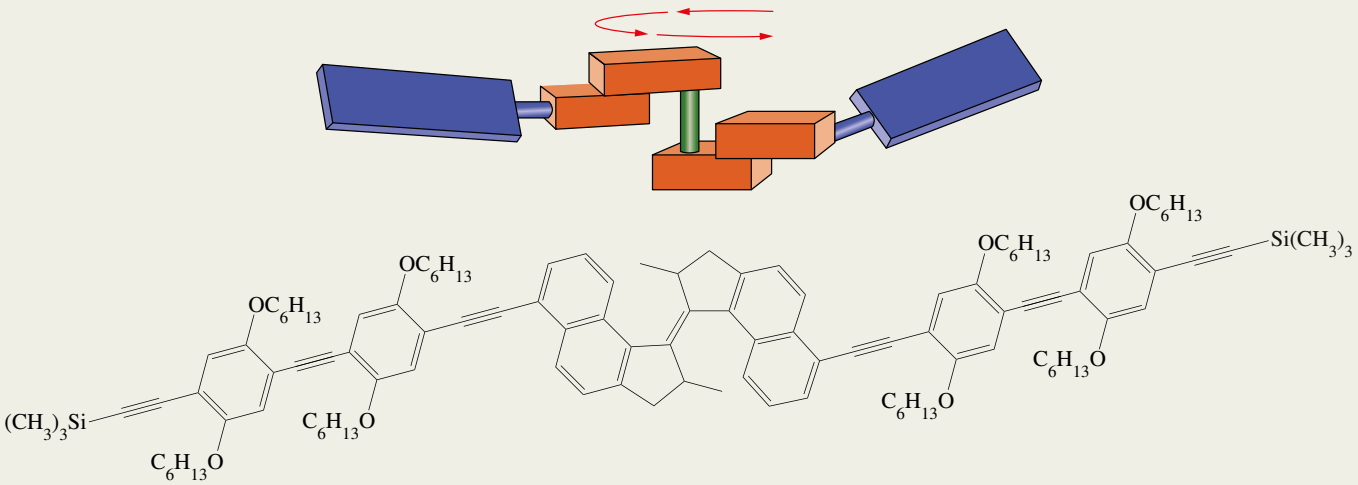


FIGURE 14.1.22 Structure and diagrammatic representation of Bernard L. Feringa's molecular motor with mixer arms attached

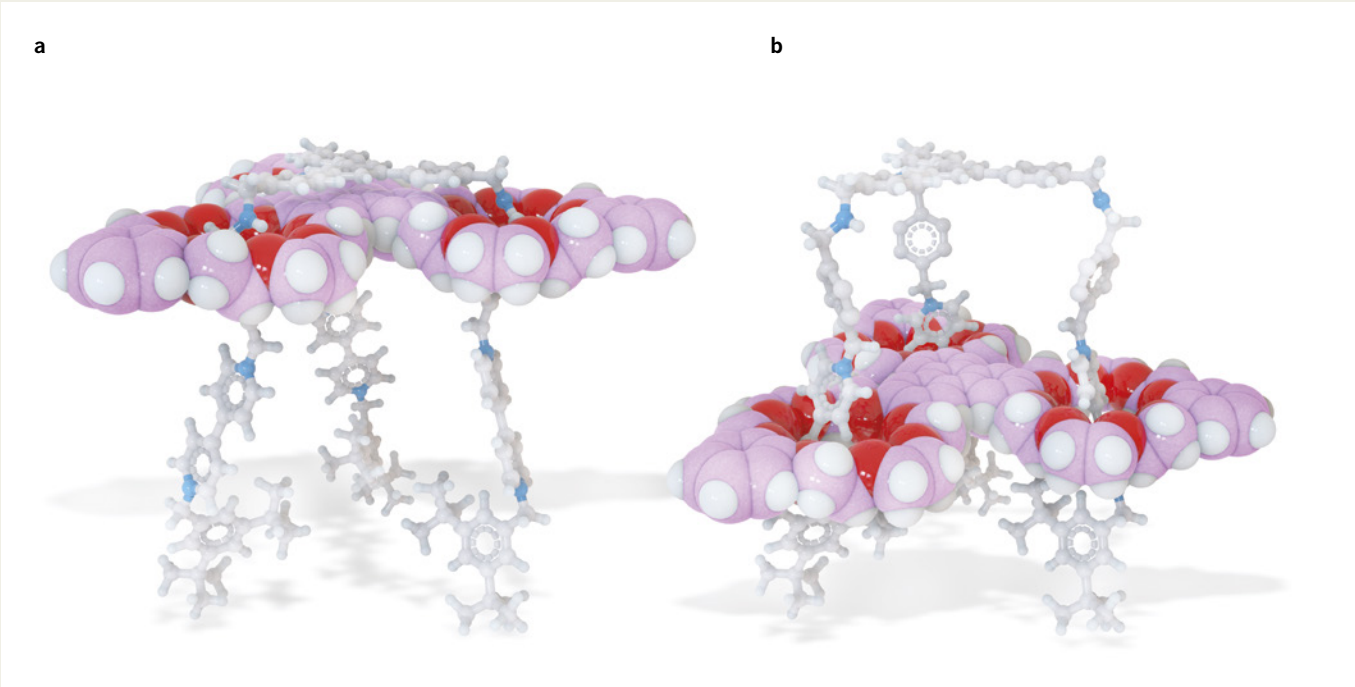


FIGURE 14.1.23 Model of a molecular elevator showing (a) the position of the macrocycle platform in low pH conditions and (b) the position of the macrocycle platform in high pH conditions

Review

1 Describe what the three molecular machines recognised in the 2016 Nobel Prize in Chemistry have in common.

2 Explain the role of hydrogen bonding in the pH-based control of the nanoelevator.

3 Deduce which molecular machine recognised in the 2016 Nobel Prize in Chemistry would be most useful in developing a nanocar with four rotating wheels.

14.1 Review

SUMMARY

- Nanoparticles can be produced from larger substances (top-down approach) or by combining smaller molecules and atoms (bottom-up approach).
- By understanding the shape of molecules and their binding sites, scientists can create a molecule with the required stereospecific bonding.
- The orientation effect describes a situation where physical proximity of two species promotes a reaction.
- Hydrogen bonding between molecules and within molecules can form structures with a particular shape.
- Synthesis of particular DNA sequences allows creation of structures of known shape using nucleotide base pairing.
- During synthesis, unwanted 'side-reactions' can be prevented by temporarily attaching a protecting group, or by temporary attachment to a larger structure.
- Molecular machines have structures that allow them to interact with, and sometimes change, their environment.
- Examples of useful nanoparticles produced by molecular manufacturing are nanotubes, nanorobots and chemical sensors.

KEY QUESTIONS

Retrieval

1 Identify which of the following synthetic processes involve a top-down approach and which involve a bottom-up approach.

a carving a statue
b building a car
c photosynthesis
d translation (the process of synthesising peptides)

Comprehension

2 Explain the orientation effect.

3 Describe the benefits of making molecules with a particular shape.

4 Explain why DNA molecules are useful in molecular manufacturing.

Analysis

5 Molecules are known to change shape (unfold) due to an increase in temperature. Apply your understanding of hydrogen bonding to explain why this occurs.

6 Consider two examples of peptide synthesis described in this chapter. For each type, identify the name of the 'machine' responsible and explain how the orientation effect contributes to their function.

Chapter review

WS 4.2.6 WS 4.2.7

14

KEY TERMS

binding site
bottom-up approach
carbon nanotubes
cargo-sorting
chemical vapour deposition
control strands
crown ethers
deoxyribonucleic acid (DNA)
DNA origami
DNA probe
DNA walker
fullerene
graphene
host–guest system
mechanical bond
metal catalyst
nanoparticle
nanorobot
nucleotide
orientation effect
photosynthesis
protecting group
restriction enzyme
rotaxane
stereospecificity
substrate molecule
top-down approach

KEY QUESTIONS

Retrieval

1 Describe how double-stranded DNA can be separated to form single-stranded DNA.

2 State the key features of a host–guest system.

3 State three physical properties of carbon nanotubes.

Comprehension

4 For a reaction to occur, reactants must collide with sufficient energy to overcome the reaction activation energy. Use this concept to explain how molecular machines use the orientation effect to promote reactions.

5 Describe the origin of hydrogen bonding. Use examples from DNA (Figure 14.1.9 on page 562) in your description.

Analysis

6 Evaluate similarities and differences between the crown ethers (Figure 14.1.11 on page 564) and the metal-binding structures in the mercury test shown in Figure 14.1.19 on page 569.

7 Describe how a rotaxane molecule is similar to a machine in the macroworld.

Knowledge utilisation

8 A recent development in single-walled carbon nanotubes is the development of a carbon nanotube ink for use in displays, sensors and other electronic devices. Potential applications include smartphones with a roll-up screen and a see-through GPS device embedded in the windshield of a car.

Propose potential uses for this technology in other types of displays.

REVIEW QUESTIONS

Structure, synthesis and design

TR 4.1 TR 4.2

Topic 1: Properties and structure of organic materials

Multiple choice

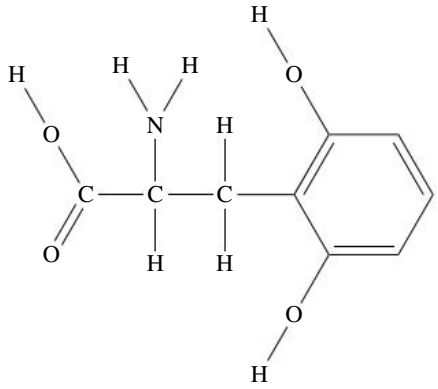
1 Select the homologous series in which the smallest molecule contains two carbon atoms.

A alkanes
B alkenes
C alcohols
D carboxylic acids

2 Select the systematic name for $CH_3CH_2CH_2CH(CH_3)_2$.

A 2-methylpentane
B 2-methylpentene
C 1,1-dimethylbutane
D propyldimethylmethane

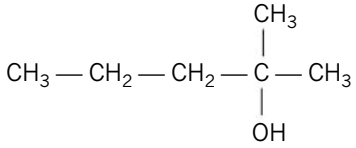
3 The molecule shown below is known as Dopa. It is used in the treatment of Parkinson's disease.



Identify the functional groups in Dopa.

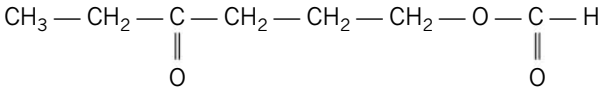
A hydroxyl, amide and ester
B hydroxyl, amine and carboxyl
C hydroxyl, amide and carboxyl
D hydroxyl, carboxyl and amide

4 Select the IUPAC name of the compound represented by the following structural formula.



A 4-methylhexan-4-ol
B 2-methylhexan-2-ol
C 4-methylpentan-4-ol
D 2-methylpentan-2-ol

5 Identify the functional groups that are present in the following compound.



A one ketone and one ester
B one aldehyde and one ester
C one ketone and one carboxylic acid
D one ketone, one aldehyde and one ester

6 Identify the compound with the lowest boiling point.

A $CH_3CH_2CH_3$
B $CH_3CH_2CH_2Cl$
C $CH_3CH_2CH_2OH$
D $CH_3CH_2CH_2CH_3$

7 Select the statements that are true of the homologous series of primary alcohols.

i The members differ by one CH_2 unit.
ii They are all strong bases.
iii They can be oxidised to form carboxylic acids.

A i and ii
B i and iii
C ii and iii
D i, ii and iii

8 Identify the product formed by the reaction of CH_2CH_2 with Br_2.

A CH_2CHBr
B CH_3CH_2Br
C $CHBrCHBr$
D CH_2BrCH_2Br

9 Identify the reaction types that occur in steps I, II and III of the following reaction pathway.

ethene $\xrightarrow{\text{I}}$ chloroethane $\xrightarrow{\text{II}}$ ethanol $\xrightarrow{\text{III}}$ ethanoic acid

A addition, reduction, hydrolysis
B addition, substitution, oxidation
C substitution, addition, hydrolysis
D chlorination, substitution, addition

10 Determine which of the following reactions are substitution reactions.

i $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
ii $C_2H_4 + HCl \rightarrow CH_3CH_2Cl$
iii $CH_2{=}CH_2 + Br_2 \rightarrow CH_2Br{-}CH_2Br$
iv $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$

A i only
B i and ii
C ii and iii
D i and iv

11 The following list gives the formulas of a number of important biochemical molecules.

- **i** $C_6H_{12}O_6$
- **ii** $CO(NH_2)$
- **iii** $C_2H_5NO_2$
- **iv** $C_3H_7NO_2$
- **v** $C_{17}H_{33}COOH$
- **vi** $C_3H_8O_3$
- **vii** CO_2
- **viii** $C_{17}H_{35}COOH$

Identify the two products that might be formed when a saturated fat undergoes hydrolysis.

A i and iii
B ii and viii
C v and vi
D vi and viii

12 The secondary structure of many proteins includes helical regions. Identify the type of chemical bonds responsible for maintaining this shape.

A ionic bonds
B covalent bonds
C hydrogen bonds
D ion–dipole bonds

13 The polysaccharides amylose, amylopectin and cellulose have significantly different properties primarily because:

A each is produced by a different type of organism
B each is formed from a different monosaccharide monomer
C they are composed of different amounts of glucose and fructose
D the monosaccharide monomer from which they are formed is linked together in different ways.

14 Olive oil contains a high proportion of oils made from a fatty acid called oleic acid. The formula of oleic acid is $C_{18}H_{34}O_2$. Select the number of carbon–carbon double covalent bonds in a molecule of oleic acid.

A 0
B 1
C 2
D 3

15 Select the statement that best describes a soap.

A a glycerol triester
B an unsaturated ester
C an ionic salt of a long-chain carboxylic acid
D a substance that does not form a scum in hard water

16 Polyethene is a polymer that can be produced as high density polyethene or low density polyethene. Select the statement that describes high density polyethene as compared to the low-density form.

A It is less branched and has a lower melting temperature.
B It is less branched and has a higher melting temperature.
C It is more branched and has a lower melting temperature.
D It is more branched and has a higher melting temperature.

17 Identify the statement about propan-1-ol and propan-2-ol that is **not** true.

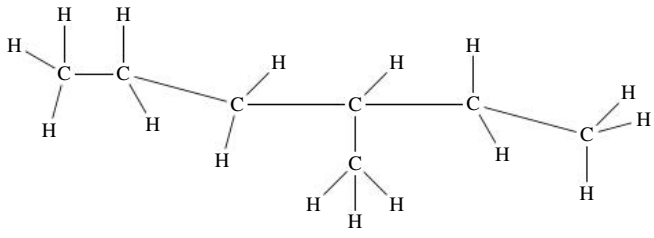
A Neither will react with a solution of sodium carbonate.
B Both will be oxidised by an acidified solution of potassium dichromate.
C The mass spectrum of both will show a peak at a mass-to-charge (*m/z*) ratio of 60.
D The fingerprint region of the IR spectra will be identical for both compounds.

Short answer

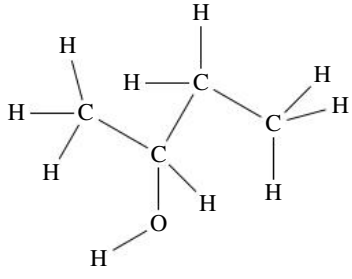
1 For each of the structures below, construct a:

- **i** molecular formula
- **ii** condensed or semistructural formula.

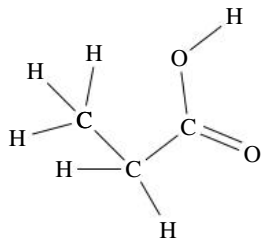
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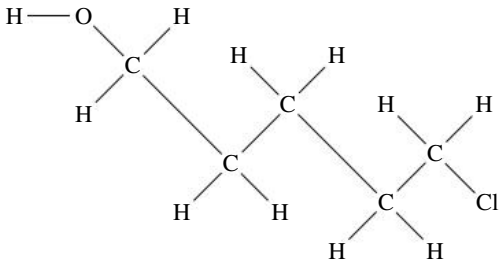
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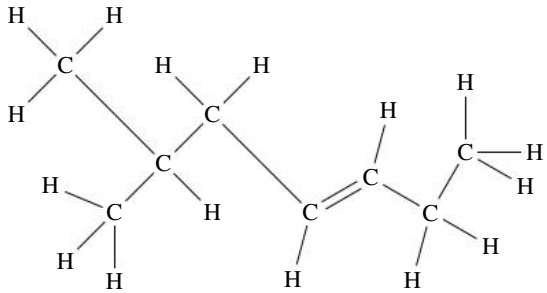
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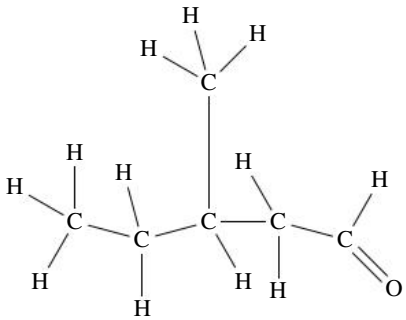
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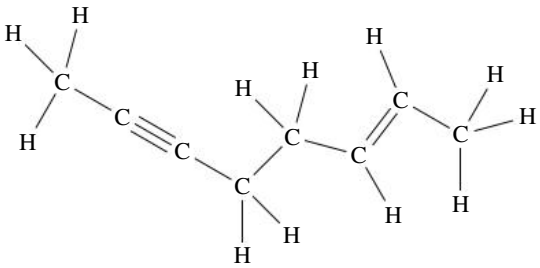
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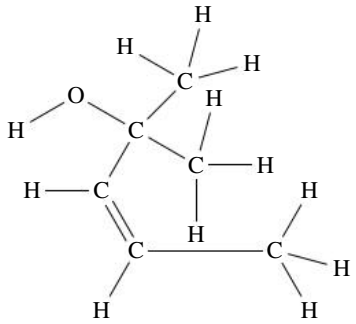
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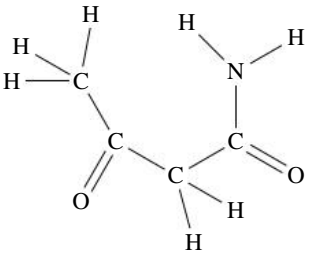
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h



i



2 Give the structural formula and name for a molecule that satisfies each of the following descriptions.

a a carboxylic acid with three carbon atoms
b a tertiary alcohol with five carbon atoms
c a ketone with eight hydrogen atoms
d a nitrile with five hydrogen atoms
e an amine with seven hydrogen atoms
f a chloroalkane with five hydrogen atoms

3 Describe a chemical test you could carry out to distinguish between the two substances in the following pairs. Include the expected results in your answer (equations are not required).

a hexane and hex-1-ene

b hexan-1-ol and hexane

c hexan-2-ol and 2-methylhexan-2-ol

d propanoic acid and propanone

4 The structure of the following amino acids is given in your data booklet: valine, cysteine, aspartic acid, leucine, lysine and threonine. These amino acids constitute part of most enzymes, and the interactions between their side groups contribute to the maintenance of their tertiary structure.

a Identify the strongest interaction that can exist between the side groups of each of the following pairs of amino acids.

Amino acids	Interaction (covalent/ionic/ hydrogen bonds/dipole–dipole interaction/dispersion forces)
threonine and lysine	
cysteine and cysteine	
valine and leucine	
aspartic acid and lysine	

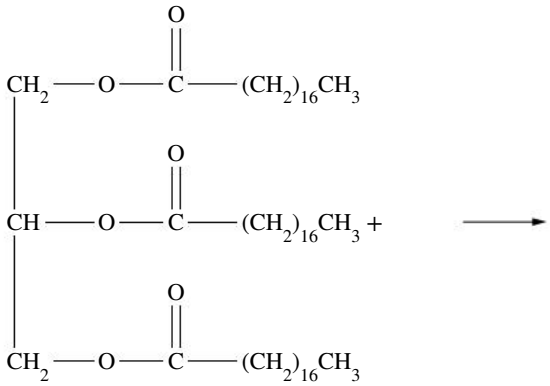
b Explain the effects of high temperature and extremes of pH on the interactions that maintain the tertiary structure of enzymes.

5 Proteins are described as having four structural levels: primary, secondary, tertiary and quaternary. Describe the key features and the nature of the bonding or interactions at each structural level.

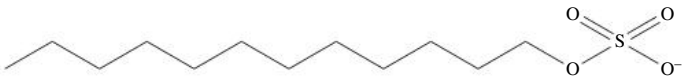
6 Explain why triglycerides composed of saturated fatty acids are solids at room temperature, while triglycerides composed of unsaturated fatty acids are liquids at room temperature.

7 Fats are triglyceride molecules containing three ester groups. They can be used as precursors to produce both soaps and biodiesel. Glycerol is produced as a by-product in both reactions.

a Construct balanced reactions to show how the following triglyceride molecule can be used to produce a soap.



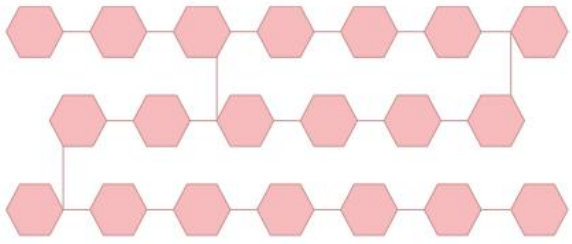
b Detergents and soaps share many structural similarities that enable them to act as cleaning agents. Dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3^-$) is a commonly used detergent and its structure is shown below.



i Discuss the similarities in the structures of soaps and detergents that enable them to remove oil and grease from surfaces.

ii Explain why soaps are less effective than detergents when used in hard water.

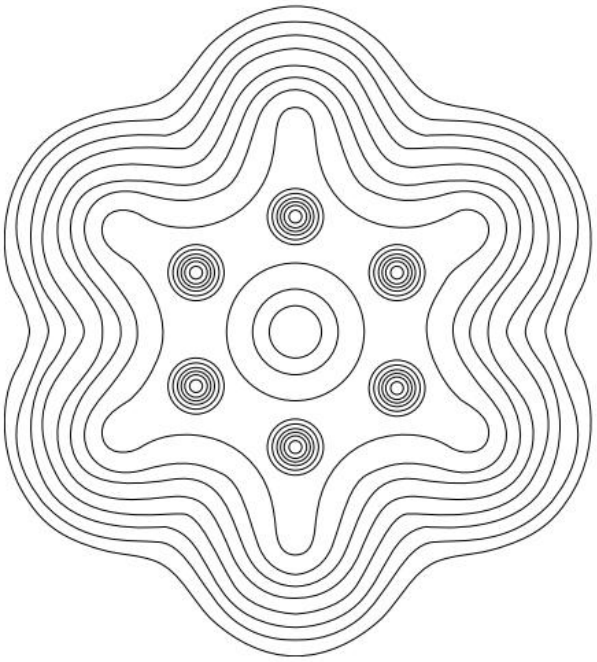
8 In the following diagram the small hexagons represent glucose monomers. Identify three polysaccharides represented in the diagram and state their structural features. Indicate whether the polymer is made up of α-glucose or β-glucose monomers.



9 Briefly describe the information about the structure of a molecule that each of the following analytical techniques provides.

- **a** X-ray crystallography
- **b** mass spectrometry
- **c** infrared spectroscopy

10 The electron density map of benzene (C_6H_6) is provided in the following diagram.



- **a** Briefly describe how this electron density map was obtained.
- **b** Use the information provided in the diagram to deduce the arrangement of carbon atoms in the benzene molecule.

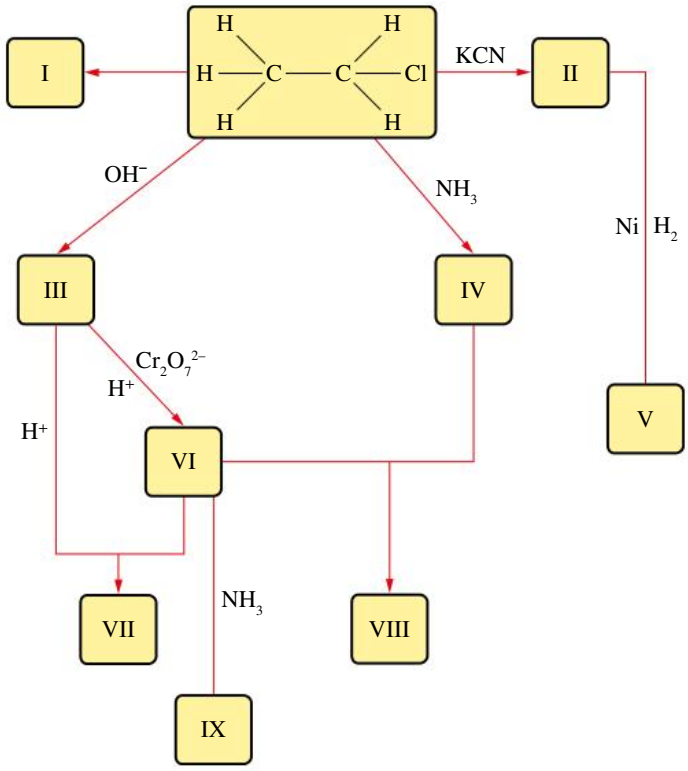
11 Both propanal and propanone have the same molecular formula, C_3H_6O.

- **a** Draw the structures of these two compounds.
- **b** Identify one similarity and one difference you would expect in the IR spectra of propanal and propanone.
- **c** Identify one similarity you would expect in the mass spectra of these two compounds.
- **d** Describe how the mass spectroscopy can be used to distinguish between propanal and propanone.

12 Over 90% of the 10 million known chemicals are organic compounds.

- **a** The formation of isomers is one reason why there are so many carbon compounds. Provide two other reasons why carbon is able to form so many different compounds.
- **b** Distinguish between the terms 'structural isomerism' and 'stereoisomerism'. Draw and name the structural isomers and stereoisomers of butene (C_4H_8) to illustrate your answer.

13 Chloroethane is the base for the synthesis of a number of different compounds, as shown in the flow chart below.

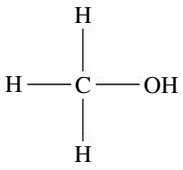
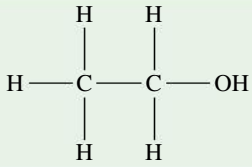
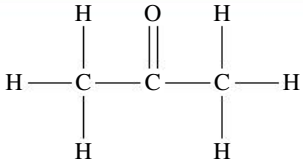
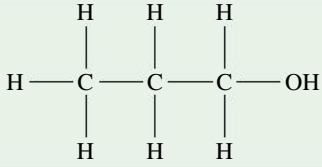
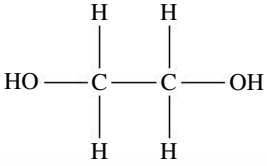
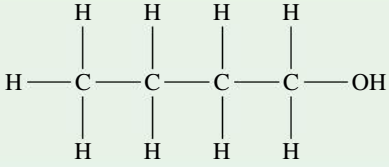
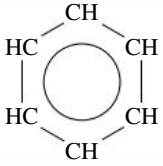
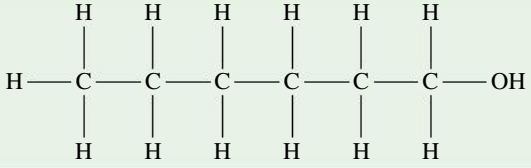


- **a** Identify compounds I to IX.
- **b** Identify the type of reaction involved in the formation of the following compounds and substances.
  - **i** compounds VII, VIII and IX
  - **ii** substance I
  - **iii** compounds II, III and IV
  - **iv** substance VI
  - **v** substance V
- **c** Design synthetic pathways showing all organic intermediates and the reagents/conditions used to prepare the following.
  - **i** propanoic acid from propane
  - **ii** methyl ethanoate from methane and ethene
  - **iii** propyl propanoate from propyl methanoate

14 Identify the type of reaction that occurs between the following reactants.

- **a** The reaction between propanoic acid and sodium hydrogen carbonate.
- **b** The conversion of propan-1-ol to propanoic acid in acidic conditions (redox half-equation).
- **c** The reaction between ethanol and propanoic acid to form ethyl propanoate.
- **d** The reaction between ethanamine and propanoic acid.

15 The following table gives a range of properties for a number of organic compounds arranged in order of increasing molecular mass.

Name	Structure	Molecular mass	Viscosity (relative to methanol)	Boiling point (°C)	Water solubility
methanol		32	1.0	65	miscible
ethanol		46	2.0	78	miscible
propanone		58	0.6	57	miscible
propan-1-ol		60	3.6	98	miscible
ethane-1,2-diol		62	29.6	197	miscible
butan-1-ol		74	4.7	118	73 g L^{-1}
benzene		78	1.1	80	< 2 g L^{-1}
hexan-1-ol		102	8.3	159	~6 g L^{-1}

a Describe what viscosity is a measure of.

b Select compounds from the table that illustrate the trend, and account for the trend in terms of intermolecular bonding for each of the following statements concerning property trends.

i Within any homologous series, viscosity increases as the molecules get larger.

ii Within any homologous series, water solubility decreases as the molecules get larger.

16 A partially completed reaction pathway for the synthesis of butanone is provided below. Compound A has the formula C_4H_8 and does not show *cis-trans* isomerism.

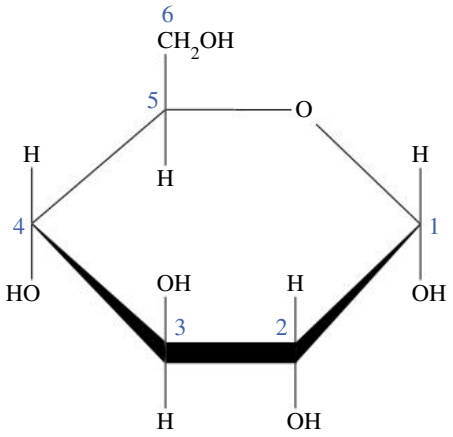
Compound A $\xrightarrow[HCl]{\text{step 1}}$ 2-chlorobutane $\xrightarrow{\text{step 2}}$ Compound B $\xrightarrow{\text{step 3}}$ butanone

- **a** Draw the structural formula of butanone.
- **b** Name compound A.
- **c** Write the condensed structural formula of compound B.
- **d** Identify which step involves a substitution reaction.
- **e** Determine the overall yield of the production of butanone if the yield for each of steps 1, 2 and 3 is 90%.

17 Give explanations for the following facts relating to protein structure and function.

- **a** Formation of the primary structure of proteins produces water as a by-product but formation of the secondary, tertiary and quarternary structures do not.
- **b** Despite having unique and very different amino acid sequences, virtually all proteins are able to form α-helical and β-pleated regions.
- **c** The secondary and tertiary structures of proteins are generally much more easily disrupted than the primary structure.
- **d** The tertiary structures of some proteins are more easily disrupted by an increase in temperature than are those of others.
- **e** All proteins are denatured by extreme pH changes, but some enzymes can lose their activity as a result of relatively small pH changes without being fully denatured.

18 The structure of α-glucose is provided below.



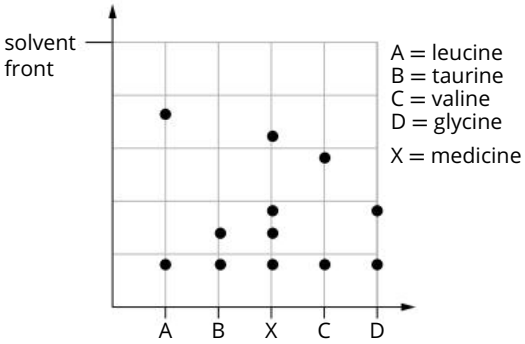
α-glucose

- **a** Draw the structure of β-glucose and describe the structural features that enable a distinction to be made between the two forms of glucose.
- **b** Starch and cellulose are different polymers formed from glucose molecules. Discuss the formation of these polymers and identify:
  - which form of glucose is found in each polysaccharide
  - the type of reaction that occurs between glucose molecules
  - the name of the bond that links the glucose molecules.
- **c** Starch can be broken down into glucose by enzymes in the human body. These enzymes cannot break down cellulose into glucose. Briefly explain why.
- **d** Amylose and amylopectin are different forms of starch. Describe and account for their structural differences.
- **e** Explain in terms of the structural differences between amylose and amylopectin why amylose is a less soluble form of starch than amylopectin.
- **f** Classify glucose as either an aldose or ketose. Explain your answer.

19 A pure sample of an unknown compound, which has a fruity smell, was analysed and found to have the empirical formula C_2H_4O. The compound was also analysed using a variety of spectroscopic techniques.

- **a** Show the molecular formula of the unknown compound.
- **b** The sweet smell suggests that the compound is an ester and not a carboxylic acid. Explain how the IR spectrum confirms this.
- **c** Draw structural formulas of the possible esters that have the molecular formula determined in part **a**.
- **d** Explain how infrared spectra and mass spectrographs can be used to identify a specific ester.

20 a The following diagram shows a thin-layer chromatogram of amino acids in a medicine.



i Identify the amino acids in the medicine.

ii Amino acids are colourless. Describe a technique that could be used to visualise the amino acid spots.

iii Calculate the R_f value of taurine.

iv Identify the amino acid that is least strongly bonded to the mobile phase.

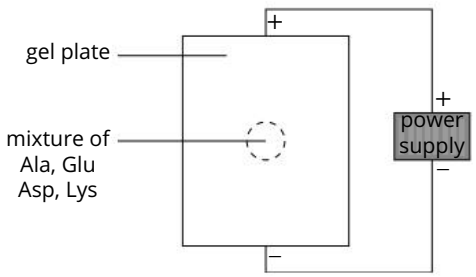
b Amino acids and protein fragments can also be separated using electrophoresis.

i The isoelectric point of glycine is 6.06. Draw the formula of the predominant forms of glycine at pH 1, pH 6 and pH 12.

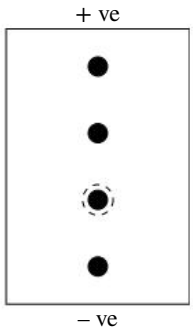
ii Some information about alanine, glutamic acid, aspartic acid and lysine is provided in the following table.

Amino acid	Isoelectric point	Molar mass ($g\ mol\ L^{-1}$)
alanine (Ala)	6.10	89.11
aspartic acid (Asp)	2.95	133.12
glutamic acid (Glu)	3.22	147.15
lysine (Lys)	9.72	146.22

Electrophoresis is used to separate a mixture of the four amino acids in a buffer solution that has pH = 6.10. The amino acid mixture is placed at the centre of an electrophoresis gel as shown in the diagram below.



A voltage was applied for a short period of time. The electrophoresis plate was then sprayed with a coloured dye. The location of coloured spots on the plate is shown in the following diagram.



Identify the amino acid responsible for each spot and provide an explanation for the location of each amino acid.

Topic 2: Chemical synthesis and design

Multiple choice

1 Identify which one of the following molecules could be a major component of biodiesel.

A $C_{17}H_{35}COOH$
B $C_{17}H_{35}COONa$
C $C_{17}H_{35}COOCH_3$
D $CH_2(OH)CH(OH)CH_2(OH)$

2 Identify the correct statement about the properties of biodiesel and petrodiesel.

A Biodiesel is more stable than petrodiesel.
B Both biodiesel and petrodiesel are hygroscopic.
C Biodiesel and petrodiesel are composed of long-chain alkanes.
D At low temperatures biodiesel is more viscous than petrodiesel.

Questions 3 and 4 refer to the following reaction, which forms part of the contact process.

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

3 If, at constant temperature and pressure, 8.2 kL of SO_2 is mixed with 6 kL of O_2, 3.8 kL of SO_3 is produced. Select the correct percentage calculation of efficiency of the process.

A 92.7%
B 73.2%
C 63.3%
D 46.3%

4 Sulfur dioxide and oxygen are usually mixed together in a 1:1 molar ratio, despite their 2:1 stoichiometric ratio in the equation. Determine which of the following statements is the best explanation for this choice.

A An excess of oxygen is required as it also reacts with other impurities in the reaction vessel.
B Sulfur dioxide is heavier than oxygen, so its molecules have a lower velocity than the molecules of oxygen gas.
C An excess of oxygen is used to drive the equilibrium position to the right, favouring the formation of sulfur trioxide.
D Although the frequency of collisions between oxygen and sulfur dioxide remains constant, using an excess of oxygen increases the proportion of collisions that are successful.

5 Ammonia can be produced according to the following equation:

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

The reaction as written is exothermic.
Identify which of the following changes will increase the amount of ammonia at equilibrium.

i adding a finely divided catalyst
ii increasing the partial pressure of the gases
iii increasing the temperature in the reaction vessel

A i only
B ii only
C i and ii only
D ii and iii only

6 A newly developed drug, X, is prepared in a difficult three-step reaction sequence. The percentage yield for each step of the sequence is shown below.

	A	→	B	→	C	→	drug X
% yield	18%		70%		10%		

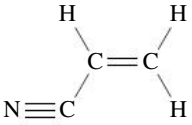
The overall percentage yield for the conversion of A to drug X is:

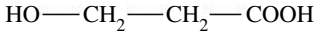
A 1%
B 10%
C 33%
D 98%

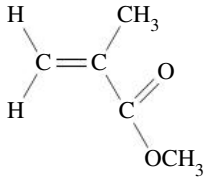
7 Select the statement that correctly compares fuels cells with secondary cells.

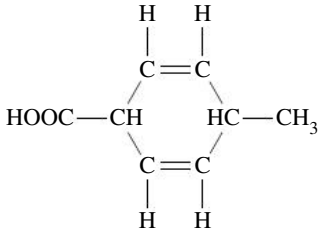
A Both fuel cells and secondary cells convert electrical energy to chemical energy.
B Fuel cells use only gaseous reactants, while secondary cells use gaseous, solid and aqueous reactants.
C Fuel cells must be continuously supplied with reactants, while secondary cells contain a fixed quantity of reactants.
D In both fuel cells and secondary cells the electrodes have a catalytic function as well as being the site of reactions.

8 Identify the molecule that could be a monomer for the formation of a condensation polymer.

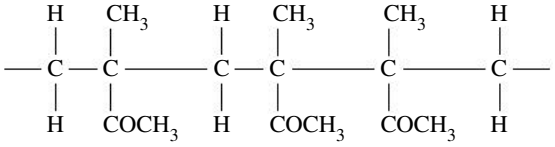
A


B


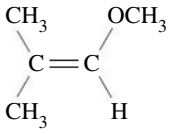
C


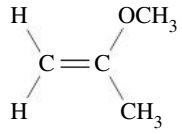
D


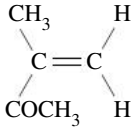
9 The following structural formula represents a section of a polymethyl methacrylate (Perspex®) polymer.

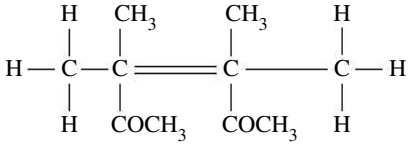


Identify the alternative that gives the formula of the monomer that forms the Perspex®.

A


B


C


D


10 The following list gives the formulas of a number of important biochemical molecules.

i $C_6H_{12}O_6$
ii $CO(NH_2)$
iii NH_2CH_2COOH
iv $NH_2CH(CH_3)COOH$
v $C_{17}H_{33}COOH$
vi $C_3H_8O_3$
vii CO_2
viii $C_{17}H_{35}COOH$

Identify two molecules that would react together to form a dipeptide.

A iv and ii
B ii and iii
C iii and iv
D iv and vi

11 Proteins such as insulin are formed by a condensation reaction. Identify the option that best describes what this reaction involves.

A two hydroxy functional groups
B a carboxy functional group and an amino functional group
C a hydroxy functional group and a carboxy functional group
D a hydroxy functional group and an amino functional group

12 Determine in which one of the following groups of biologically important polymers peptide links join the constituent parts.

A vitamins
B proteins
C triglycerides
D carbohydrates

13 Identify the term by which the linkages of monosaccharides to disaccharides and polysaccharides are known.

A ester links
B peptide links
C glycosidic links
D carbohydrate links

14 Starch is formed from glucose. Select the statement that best describes this reaction.

A A condensation reaction between two hydroxy functional groups.
B An addition reaction between a carboxy functional group and an amino functional group.
C An addition reaction between a hydroxy functional group and an amino functional group.
D A condensation reaction between a hydroxy functional group and a carboxy functional group.

Short answer

1 In the contact process, sulfuric acid is manufactured in stages from sulfur dioxide. The overall process can be summarised as follows:

Step 1: Sulfur dioxide is produced from the combustion of sulfur.
Step 2: Sulfur dioxide is oxidised by oxygen to form sulfur trioxide.
Step 3: Sulfur trioxide dissolves in sulfuric acid to form oleum ($H_2S_2O_7$).
Step 4: Oleum is mixed with water to form sulfuric acid.

a Construct equations to represent each of the reactions described above.
b The reaction described in step 2 is an equilibrium step, with an ΔH value of –197 kJ. In practice, this reaction is carried out at a moderate temperature of 400–500°C and at atmospheric pressure. Explain why these conditions are used, with reference to both rate and yield and relevant chemical theories.

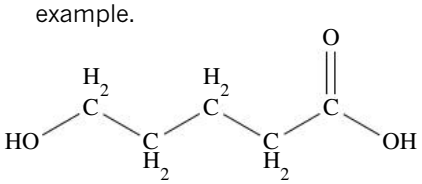
2 Ethanol is produced industrially by the reaction between ethene, a by-product from the distillation of crude oil, and steam. The reaction is carried out at 300°C and 60 atm pressure in a continuous process.

A large amount of ethanol is also produced by the fermentation of glucose at room temperature and pressure.

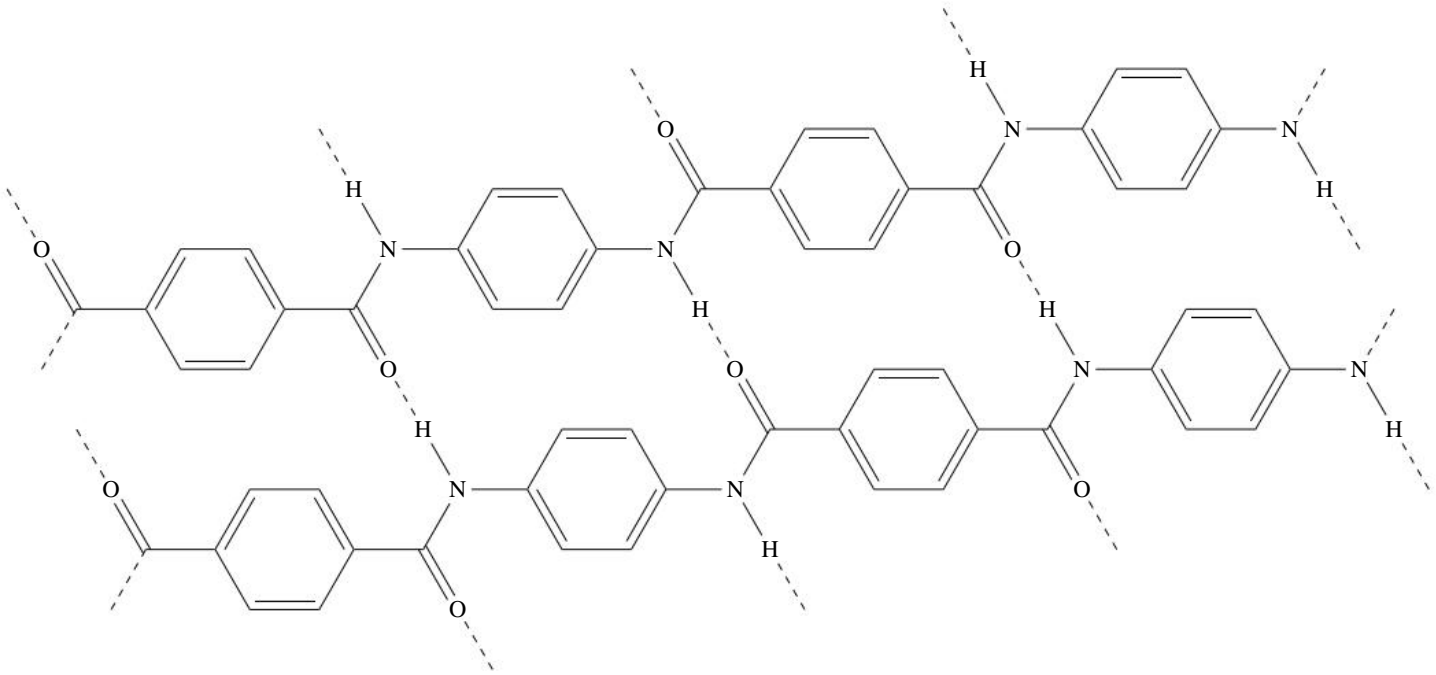
a Show equations for the synthesis of ethanol via these two processes.
b Calculate the atom economy of the production of ethanol from ethene and glucose.
c The synthesis of ethanol from ethene is catalysed by phosphoric acid. Identify the type of catalyst used in the fermentation process.
d Compare the environmental impact of producing ethanol from ethene and glucose.

3 The following molecule ($M = 118.15\,g\,mol^{-1}$) can be used to produce a polymer when it is heated under acidic conditions.

a Draw the structure of the polymer, showing two repeating units.
b Define the type of polymer of which this is an example.

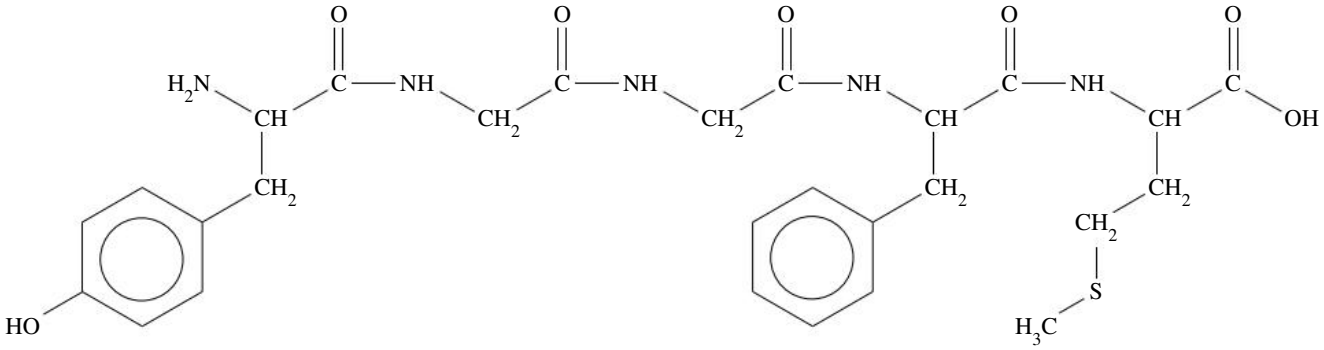


4 Kevlar is a polymer with a high melting point and is used in the manufacture of bulletproof clothing and Formula One car tyres. The diagram below shows two parallel polymer chains.



a Name the class of polymers to which Kevlar belongs.
b Explain the meaning of the dashed lines in the diagram.
c Draw the full structures of the monomer(s) from which Kevlar is made.

5 Enkephalins are short polypeptides involved in the nervous system's detection of pain and harm. The structure of met-enkephalin, so-called because it contains a methionine amino acid, is shown. Another important example is leu-enkephalin, which has a leucine (side chain $CH_2CH(CH_3)_2$) residue in place of methionine.

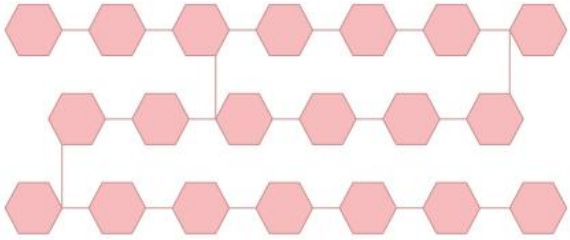


a Draw the structure of leu-enkephalin.
b Label the following on your structure circle.
  i peptide linkages
  ii terminal carboxy and amino groups
c Name the other amino acids present in leu-enkephalin, after referring to a table of amino acids.

6 The amino acid sequence in a tripetide consisting of aspartic acid, glutamic acid and lysine is Asp-Lys-Glu.
a Draw the structural formula of this tripeptide.
b Show the amino acid sequence of all the other possible tripeptides that contain these three amino acids.

7 The following diagrams are simplified representations of the structure of some important polysaccharides in which the glucose monomers are represented by small hexagons.

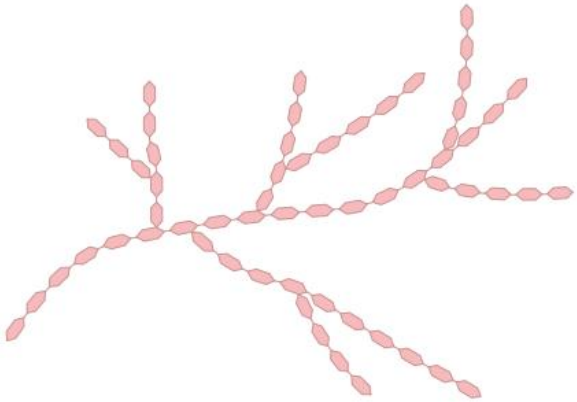
I



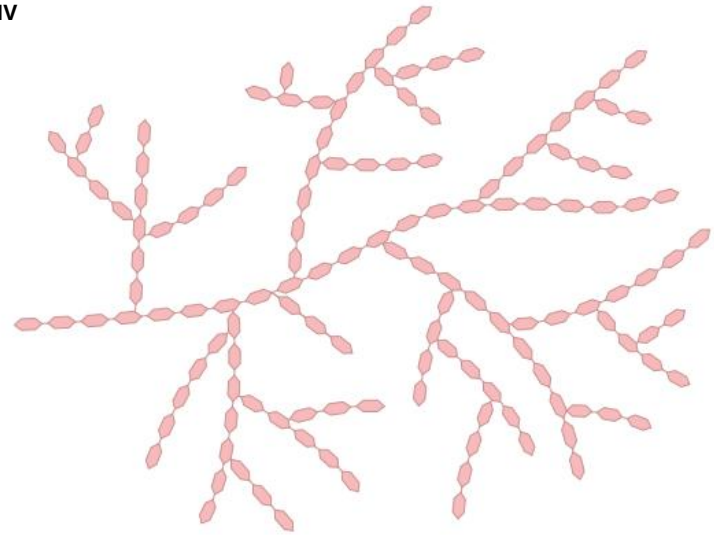
III



II



IV



Identify the polysaccharides represented in the diagram.

8 You need to synthesise to create a product that meets the following criteria.

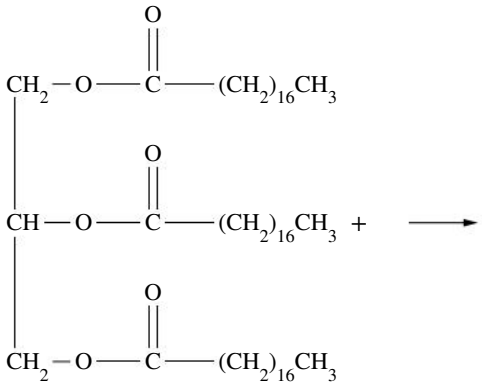
- a volatile liquid
- has a pleasant odour
- reasonably soluble in water
- has a molar mass of approximately 60 g mol^{-1}.

Explain how the product of your synthesis meets the listed criteria.

9 **a** Describe three differences between the base-catalysed and the lipase-catalysed methods for the production of biodiesel.

b Explain why the lipase-catalysed method is considered to be more environmentally friendly than the base-catalysed method.

c Show balanced reactions to demonstrate how the triglyceride molecule below can be used to produce biodiesel.



d Identify the type of reactions involved in the conversion of triglycerides to biodiesel.

10 **a** Draw a labelled diagram of an alkaline hydrogen fuel cell showing the reactants used, the anode and cathode, the polarity of the electrode and the nature of the electrolyte.

i Using appropriate equations, describe the reactions that occur at the anode and cathode in an alkaline hydrogen fuel cell.

ii Using appropriate equations, describe the reactions that occur at the anode and cathode in a phosphoric acid fuel cell.

b Much of the research advancing fuel cell technology aims at improving the catalytic effect of the electrode materials. Explain why this is important.

c Hydrogen fuel cells are potential candidates to power electric cars. State two advantages and two disadvantages of using hydrogen fuel cells to power electric cars, as compared to rechargeable battery technologies such as lead–acid cells or lithium batteries.

d Using appropriate equations, describe how hydrogen is produced on an industrial scale.

e The overall equation for the reactions that occur in the direct methanol fuel cell is:

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

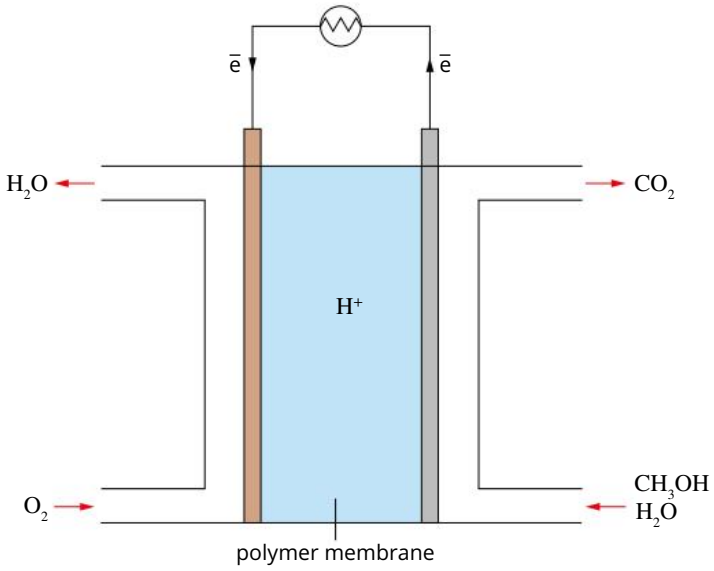
The reaction that occurs at one of the electrodes is represented by the following equation:

$$CH_3OH(l) + 2H_2O(l) \rightarrow 6H^+(aq) + CO_2(g) + 6e^-$$

i Construct an equation for the reaction that occurs at the other electrode.

ii A simplified representation of the direct methanol fuel cell is shown below. Indicate on the diagram the:

- anode and cathode
- direction in which H^+ ions move through the polymer membrane.



iii Explain one advantage and one disadvantage of the methanol fuel cell compared to the hydrogen fuel cell.

11 Polyethene is produced in large quantities by addition polymerisation of ethene.

a Show an equation for the polymerisation of ethene.

b Describe what is meant by the term 'addition polymerisation'.

c One particular strand of polyethene has a molar mass of $45\,000\,g\,mol^{-1}$. Calculate the number of monomer molecules polymerised to form that chain.

d The use of polymers has many advantages but also some disadvantages. State one advantage and one disadvantage of the use of polymeric materials.

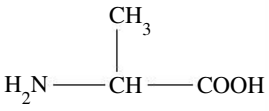
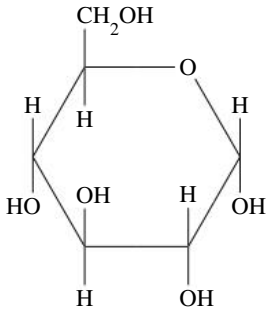
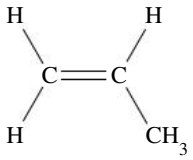
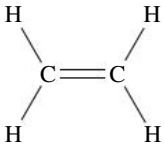
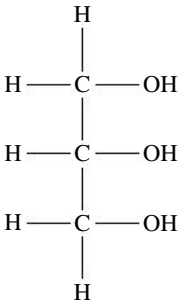
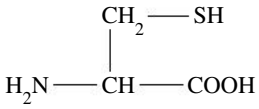
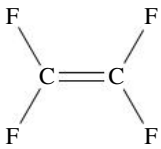
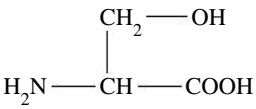
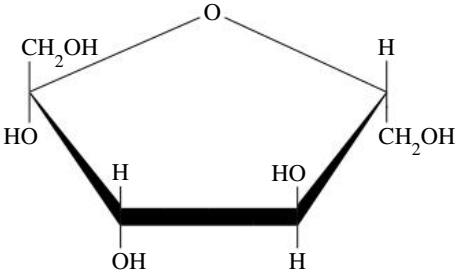
e Construct an equation for the synthesis of polytetrafluoroethylene.

12 a Describe how molecular manufacturing or molecular assembly has the potential to produce complex molecular structures that serve a specific purpose. In your answer you should include:

- an explanation of what is meant by the term 'molecular manufacturing'
- an outline of chemical understandings that are applied to the process
- an explanation of how unwanted side reactions are prevented from occurring
- a brief discussion of the potential applications of molecular manufacturing.

b Complex molecules such as drugs produced by the pharmaceutical industry are currently synthesised using reaction pathways that involve a large number of separate reactions. Suggest some possible benefits of using molecular assembly to synthesise pharmaceuticals.

13 The structural formulas of some monomers used to make natural and synthetic polymers are provided in the table below.

A 	**B** 	**C** 	**D** $C_{17}H_{35}COOH$
E 	**F** $H_2N—CH_2—COOH$	**G** 	**H** 
I $C_{17}H_{35}COOH$	**J** 	**K** 	**L** 

a Distinguish between an addition polymerisation and a condensation polymerisation reaction.

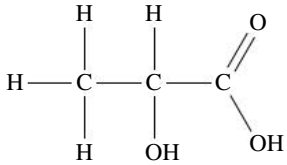
b Select the monomers that will form each of the following polymers. Construct an equation for the polymerisation reaction. Identify the reaction as either an addition polymerisation reaction or a condensation polymerisation reaction.

i polypropylene

ii polytetrafluoroethene

iii polyethene

c The structural formula of lactic acid is provided below.



Write an equation using the structural formula for the formation of polylactic acid. Identify the type of polymerisation reaction.

d Identify the monomers in the dipeptide represented by the notation Gly-Ala. Use structural formulas to write an equation for the synthesis of Gly-Ala. Name the bond type that links the monomers in Gly-Ala and identify the type of reaction that occurs between the monomers.

e Identify the molecules that will react to form a triglyceride in which all the fatty acid residues are saturated. Construct an equation for the formation of this triglyceride and identify the type of reaction.

f Identify the molecules that will form sucrose and construct an equation for this reaction. Identify the bond type between reactant molecules and name the type of reaction that occurs between them.

g Identify the molecule that is the monomer in starch and cellulose. Using appropriate diagrams, describe the differences between the structures of the starch and cellulose polymers.

APPENDIX A Symbols, units and fundamental constants

TABLE 1 Units and symbols based on the SI system*

Quantity	Symbol for physical quantity	Corresponding SI unit	Symbol for SI unit	Definition of SI unit
Mechanics				
length	l	metre	m	fundamental unit
area	A	square metre	m^2	
volume	V	cubic metre	m^3	
mass	m	kilogram	kg	fundamental unit
density	d	–	$kg\,m^{-3}$	
time	t	second	s	fundamental unit
force	F	newton	N	$kg\,m\,s^{-2}$
pressure	P	pascal	Pa	$N\,m^{-2}$
energy	E	joule	J	N m
Electricity				
electric current	I	ampere	A	fundamental unit
electric charge	Q	coulomb	C	A s
electric potential difference	V	volt	V	$J\,A^{-1}\,s^{-1}$
Nuclear and chemical quantities				
atomic number	Z	–	–	–
neutron number	N	–	–	–
mass number	A	–	–	$Z + N$
number of moles of a substance	n	mole	mol	fundamental unit
relative atomic mass	A_r	–	–	amu
relative molecular mass	M_r	–	–	amu
molar mass	M	–	–	$g\,mol^{-1}$
molar volume	V_m	–	–	$m^3\,mol^{-1}$
concentration	c	–	–	$mol\,L^{-1}$ or $mol\,dm^{-3}$
Thermal quantities				
temperature	T	kelvin	K	fundamental unit
specific heat capacity	c	–	–	$J\,K^{-1}\,kg^{-1}$

*Units listed in red are the arbitrarily defined fundamental units of the SI system.

TABLE 2 SI prefixes, symbols and values

SI prefix	Symbol	Value		
tera	T	10^{12}	trillion	1 000 000 000 000
giga	G	10^{9}	billion	1 000 000 000
mega	M	10^{6}	million	1 000 000
kilo	k	10^{3}	thousand	1 000
hecto	h	10^{2}	hundred	100
deca	da	10^{1}	ten	10
–	–	1	unit	1
deci	d	10^{-1}	tenth	0.1
centi	c	10^{-2}	hundredth	0.01
milli	m	10^{-3}	thousandth	0.001
micro	μ	10^{-6}	millionth	0.000 001
nano	n	10^{-9}	billionth	0.000 000 001
pico	p	10^{-12}	trillionth	0.000 000 000 001
femto	f	10^{-15}	quadrillionth	0.000 000 000 000 001
atto	a	10^{-18}	quintillionth	0.000 000 000 000 000 001

TABLE 3 Physical constants and values

Description	Symbol	Value
Avogadro's constant	N_A	$6.02 \times 10^{23}\,mol^{-1}$
neutron mass	m_n	$1.674\,927\,5 \times 10^{-27}\,kg$
proton mass	m_p	$1.672\,621\,9 \times 10^{-27}\,kg$
electron mass	m_e	$9.109\,383\,5 \times 10^{-31}\,kg$
gas constant	R	$8.31\,J\,mol^{-1}\,K^{-1}$
ionic product for water	K_w	1.00×10^{-14} at 25°C
molar volume of an ideal gas (at STP)	V_m	$2.27 \times 10^{-2}\,m^3\,mol^{-1}$; $22.7\,dm^3\,mol^{-1}$
specific heat capacity of water	c_w	$4.18\,J\,g^{-1}\,K^{-1}$
density of water	d	$1.00\,g\,mL^{-1}$ at 298 K
temperature in kelvin	T_K	T°C + 273
standard temperature and pressure	STP	273 K and 100 kPa

APPENDIX B Table of relative atomic masses*

Element name	Symbol	Atomic number	Relative atomic mass	Element name	Symbol	Atomic number	Relative atomic mass	Element name	Symbol	Atomic number	Relative atomic mass
actinium	Ac	89	(227.0)	hafnium	Hf	72	178.49	praseodymium	Pr	59	140.91
aluminium	Al	13	26.98	hassium	Hs	108	(265.1)	proactinium	Pa	91	231.0
americium	Am	95	(241.1)	helium	He	2	4.00	promethium	Pm	61	(146.9)
antimony	Sb	51	121.76	holmium	Ho	67	164.93	protactinium	Pa	91	231.0
argon	Ar	18	39.95	hydrogen	H	1	1.01	radium	Ra	88	(226.1)
arsenic	As	33	74.92	indium	In	49	114.82	radon	Rn	86	(222.0)
astatine	At	85	210.0	iodine	I	53	126.90	rhenium	Re	75	186.21
barium	Ba	56	137.33	iridium	Ir	77	192.22	rhodium	Rh	45	102.91
berkelium	Bk	97	(249.1)	iron	Fe	26	55.85	roentgenium	Rg	111	(272)
beryllium	Be	4	9.01	krypton	Kr	36	83.80	rubidium	Rb	37	85.47
bismuth	Bi	83	208.98	lanthanum	La	57	138.91	ruthenium	Ru	44	101.07
bohrium	Bh	107	(264.1)	lawrencium	Lr	103	(262.1)	rutherfordium	Rf	104	(261.1)
boron	B	5	10.81	lead	Pb	82	207.20	samarium	Sm	62	150.36
bromine	Br	35	79.90	lithium	Li	3	6.94	scandium	Sc	21	44.96
cadmium	Cd	48	112.41	livermorium	Lv	116	(293)	seaborgium	Sg	106	(263.1)
caesium	Cs	55	132.91	lutetium	Lu	71	174.97	selenium	Se	34	78.97
calcium	Ca	20	40.08	magnesium	Mg	12	24.31	silicon	Si	14	28.09
californium	Cf	98	(252.1)	manganese	Mn	25	54.94	silver	Ag	47	107.87
carbon	C	6	12.01	meitnerium	Mt	109	(268)	sodium	Na	11	22.99
cerium	Ce	58	140.12	mendelevium	Md	101	(258.1)	strontium	Sr	38	87.62
chlorine	Cl	17	35.45	mercury	Hg	80	200.59	sulfur	S	16	32.06
chromium	Cr	24	52.00	molybdenum	Mo	42	95.95	tantalum	Ta	73	180.95
cobalt	Co	27	58.93	moscovium	Mc	115	(288)	technetium	Tc	43	(98.91)
copernicium	Cn	112	(285)	neodymium	Nd	60	144.24	tellurium	Te	52	127.60
copper	Cu	29	63.55	neon	Ne	10	20.18	tennessine	Ts	117	(294)
curium	Cm	96	(244.1)	neptunium	Np	93	(237.0)	terbium	Tb	65	158.93
darmstadtium	Ds	110	(281)	nickel	Ni	28	58.69	thallium	Tl	81	204.38
dubnium	Db	105	(262.1)	nihonium	Nh	113	(284)	thorium	Th	90	232.0
dysprosium	Dy	66	162.50	niobium	Nb	41	92.91	thulium	Tm	69	168.93
einsteinium	Es	99	(252.1)	nitrogen	N	7	14.01	tin	Sn	50	118.71
erbium	Er	68	167.26	nobelium	No	102	(259.1)	titanium	Ti	22	47.87
europium	Eu	63	151.96	oganesson	Og	118	(294)	tungsten	W	74	183.84
fermium	Fm	100	(252.1)	osmium	Os	76	190.23	uranium	U	92	238.0
flerovium	Fl	114	(289)	oxygen	O	8	16.00	vanadium	V	23	50.94
fluorine	F	9	19.00	palladium	Pd	46	106.42	xenon	Xe	54	131.29
francium	Fr	87	223.0	phosphorus	P	15	30.97	ytterbium	Yb	70	173.05
gadolinium	Gd	64	157.25	platinum	Pt	78	195.08	yttrium	Y	39	88.91
gallium	Ga	31	69.72	plutonium	Pu	94	(239.1)	zinc	Zn	30	65.38
germanium	Ge	32	72.63	polonium	Po	84	(210.0)	zirconium	Zr	40	91.22
gold	Au	79	196.97	potassium	K	19	39.10				

*Based on the atomic mass of $^{12}C = 12$.
Values in brackets are for the isotope with the longest half-life.

APPENDIX C Electronegativities and first ionisation energy of selected elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 2.2 1318																	2 **He** 2379
3 **Li** 1.0 526	4 **Be** 1.6 906											5 **B** 2.0 807	6 **C** 2.6 1093	7 **N** 3.0 1407	8 **O** 3.4 1320	9 **F** 4.0 1687	10 **Ne** 2087
11 **Na** 0.9 502	12 **Mg** 1.3 744											13 **Al** 1.6 584	14 **Si** 1.9 793	15 **P** 2.2 1018	16 **S** 2.6 1006	17 **Cl** 3.2 1257	18 **Ar** 1527
19 **K** 0.8 425	20 **Ca** 1.0 596	21 **Sc** 1.4 637	22 **Ti** 1.5 664	23 **V** 1.6 656	24 **Cr** 1.7 659	25 **Mn** 1.6 724	26 **Fe** 1.8 766	27 **Co** 1.9 765	28 **Ni** 1.9 743	29 **Cu** 1.9 752	30 **Zn** 1.7 913	31 **Ga** 1.8 585	32 **Ge** 2.0 768	33 **As** 2.2 953	34 **Se** 2.6 947	35 **Br** 3.0 1146	36 **Kr** 2.9 1357
37 **Rb** 0.8 409	38 **Sr** 1.0 556	39 **Y** 1.2 606	40 **Zr** 1.3 666	41 **Nb** 1.6 670	42 **Mo** 2.2 691	43 **Tc** 1.9 708	44 **Ru** 2.2 717	45 **Rh** 2.3 726	46 **Pd** 2.2 811	47 **Ag** 1.9 737	48 **Cd** 1.7 874	49 **In** 1.8 565	50 **Sn** 2.0 715	51 **Sb** 2.1 840	52 **Te** 2.1 876	53 **I** 2.7 1015	54 **Xe** 2.6 1177
55 **Cs** 0.8 382	56 **Ba** 0.9 509																

Atomic number

Symbol
electronegativity
first ionisation energy ($kJ\,mol^{-1}$)

Groups in accordance with IUPAC numbering.

Atomic radius ($\times 10^{-12}$ m)
Symbol
Ionic radius (r_{ion})

32 **H**																	37 **He**
130 **Li** 76 (1+)	99 **Be** 45 (2+)											84 **B** 27 (3+)	75 **C** 16 (4+)	71 **N** 146 (3–)	64 **O** 140 (2–)	60 **F** 133 (1–)	62 **Ne**
160 **Na** 102 (1+)	140 **Mg** 72 (2+)											124 **Al** 53 (3+)	114 **Si** 40 (4+)	109 **P** 38 (5+)	104 **S** 184 (2–)	100 **Cl** 181 (1–)	101 **Ar**
200 **K** 138 (1+)	174 **Ca** 100 (2+)	159 **Sc** 75 (3+)	148 **Ti** 86 (2+) 61 (4+)	144 **V** 79 (2+) 54 (5+)	130 **Cr** 62 (3+) 44 (6+)	129 **Mn** 83 (2+) 64 (3+)	124 **Fe** 78 (2+) 64 (3+)	118 **Co** 74 (2+) 61 (3+)	117 **Ni** 69 (2+) 60 (3+)	122 **Cu** 77 (1+) 73 (2+)	120 **Zn** 74 (2+)	123 **Ga** 62 (3+)	120 **Ge** 53 (4+) 272 (4–)	120 **As** 58 (3+) 46 (5+)	118 **Se** 198 (2–)	117 **Br** 196 (1–)	116 **Kr**
215 **Rb** 152 (1+)	190 **Sr** 118 (2+)	176 **Y** 90 (3+)	164 **Zr** 72 (4+)	156 **Nb** 64 (5+)	148 **Mo** 65 (4+)	138 **Tc** 65 (4+)	136 **Ru** 62 (4+)	134 **Rh** 67 (3+)	130 **Pd** 86 (2+)	136 **Ag** 115 (1+)	140 **Cd** 95 (2+)	142 **In** 80 (3+)	140 **Sn** 69 (4+)	140 **Sb** 76 (3+)	137 **Te** 221 (2–)	136 **I** 220 (1–)	136 **Xe**
238 **Cs** 167 (1+)	206 **Ba** 135 (2+)																

APPENDIX E Activity and electrochemical series

TABLE 1 The activity series of metals with their half-equations

Order of reactivity of the metal	Half-equation representing loss of electrons
increasing metal reactivity ↑	$K(s) \rightarrow K^+(aq) + e^-$
	$Na(s) \rightarrow Na^+(aq) + e^-$
	$Li(s) \rightarrow Li^+(aq) + e^-$
	$Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$
	$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$
	$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$
	$Mn(s) \rightarrow Mn^{2+}(aq) + 2e^-$
	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
	$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-$
	$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
	$Co(s) \rightarrow Co^{2+}(aq) + 2e^-$
	$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$
	$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$
	$Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$
	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
	$Ag(s) \rightarrow Ag^+(aq) + e^-$

TABLE 2 Electrochemical series

	Oxidised species ⇌ reduced species	E° (V)	
Increasing oxidising strength ↓	$Li^+(aq) + e^- \rightleftharpoons Li(s)$	–3.04	↑ Increasing reducing strength
	$K^+(aq) + e^- \rightleftharpoons K(s)$	–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	
	$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.15	
	$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+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	
	$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68	
	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+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	
	$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77	
	$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.89	

APPENDIX F Formula and charges for polyatomic ions

Positive ions (cations)						Negative ions (anions)			
+1		+2		+3		−1		−2	
caesium	Cs^+	barium	Ba^{2+}	aluminium	Al^{3+}	bromide	Br^-	carbonate	CO_3^{2-}
copper(I)	Cu^+	cadmium(II)	Cd^{2+}	chromium(III)	Cr^{3+}	chloride	Cl^-	chromate	CrO_4^{2-}
gold(I)	Au^+	calcium	Ca^{2+}	gold(III)	Au^{3+}	cyanide	CN^-	dichromate	$Cr_2O_7^{2-}$
lithium	Li^+	cobalt(II)	Co^{2+}	iron(III)	Fe^{3+}	chlorite	ClO_2^-	hydrogen phosphate	HPO_4^{2-}
potassium	K^+	copper(II)	Cu^{2+}			chlorate	ClO_3^-	oxalate	$C_2O_4^{2-}$
rubidium	Rb^+	iron(II)	Fe^{2+}	+4		dihydrogen phosphate	$H_2PO_4^-$	oxide	O^{2-}
silver	Ag^+	lead(II)	Pb^{2+}	lead(IV)	Pb^{4+}	ethanoate(acetate)	CH_3COO^-	peroxide	O_2^{2-}
sodium	Na^+	magnesium	Mg^{2+}	tin(IV)	Sn^{4+}	fluoride	F^-	sulfide	S^{2-}
		manganese(II)	Mn^{2+}			hydrogen carbonate	HCO_3^-	sulfite	SO_3^{2-}
		mercury(II)	Hg^{2+}			hydrogen sulfate	HSO_4^-	sulfate	SO_4^{2-}
		nickel	Ni^{2+}			hydrogen sulfide	HS^-	thiosulfate	$S_2O_3^{2-}$
		strontium	Sr^{2+}			hydrogen sulfite	HSO_3^-	−3	
		tin(II)	Sn^{2+}			hydroxide	OH^-	citrate	$C_6H_5O_7^{3-}$
		zinc	Zn^{2+}			hypochlorite	ClO^-	nitride	N^{3-}
						iodide	I^-	phosphate	PO_4^{3-}
						nitrate	NO_3^-		
						nitrite	NO_2^-		
						perchlorate	ClO_4^-		
						permanganate	MnO_4^-		

APPENDIX G Solubility of selected compounds at 298 K

	bromide	carbonate	chloride	hydroxide	iodide	nitrate	oxide	phosphate	sulfate
aluminium	s	–	s	i	s	s	i	i	s
ammonium	s	s	s	s	s	s	–	s	s
barium	s	i	s	s	s	s	s	i	i
calcium	s	i	s	p	s	s	p	i	p
cobalt(II)	s	i	s	i	s	s	i	i	s
copper(II)	s	–	s	i	i	s	i	i	s
iron(II)	s	i	s	i	s	s	i	i	s
iron(III)	s	–	s	i	s	s	i	i	s
lead(II)	p	i	s	i	i	s	i	i	i
lithium	s	s	s	s	s	s	s	–	s
magnesium	s	i	s	i	s	s	i	p	s
manganese(II)	s	i	s	i	s	s	i	p	s
potassium	s	s	s	s	s	s	s	s	s
silver	i	i	i	i	i	s	i	i	p
sodium	s	s	s	s	s	s	s	s	s
zinc	s	i	s	i	s	s	i	i	s

Key:

Abbreviation	Explanation
s	soluble in water (solubility greater than 10 g L^{-1})
p	partially soluble in water (solubility between 1 and 10 g L^{-1})
i	insoluble in water (solubility less than 1 g L^{-1})
–	no data

APPENDIX H Average bond enthalpies at 298 K

Single bonds (kJ mol^{-1})							
C–H	414	N–H	391	O–H	463	F–F	159
C–C	346	N–N	158	O–O	144		
C–N	286	N–O	214	O–F	191	Cl–F	255
C–O	358	N–F	278	O–Cl	206	Cl–Cl	242
C–F	492	N–Cl	192	O–I	201		
C–Cl	324	N–Br	243			Br–F	249
C–Br	285			S–H	364	Br–Cl	219
C–I	228	H–H	436	S–F	327	Br–Br	193
C–S	289	H–F	567	S–Cl	271		
		H–Cl	431	S–Br	218	I–Cl	211
		H–Br	366	S–S	266	I–Br	178
		H–I	298			I–I	151
				O–Br	201		
				F–I	280		
Multiple bonds (kJ mol^{-1})							
C=C	614	N=N	470	O=O	498		
C≡C	839	N≡N	945				
C=N	615			S=O	523		
C≡N	890			S=S	429		
C=O	804						

APPENDIX I Standard enthalpies of formation and combustion

TABLE 1 Standard enthalpies of formation and standard entropies

Substance	Formula	ΔH°_f (kJ mol^{-1})
ammonia	$NH_3(g)$	–45.9
butane	$C_4H_{10}(g)$	–126
carbon dioxide	$CO_2(g)$	–393.5
carbon monoxide	$CO(g)$	–110.5
ethane	$C_2H_6(g)$	–84.0
ethanol	$C_2H_5OH(l)$	–278
ethene	$C_2H_4(g)$	+52.0
ethyne (acetylene)	$C_2H_2(g)$	+228
glucose	$C_6H_{12}O_6(s)$	–1271
hydrogen	$H_2(g)$	0
hydrogen bromide	$HBr(g)$	–36.3
hydrogen chloride	$HCl(g)$	–92.3
hydrogen fluoride	$HF(g)$	–273.3
hydrogen iodide	$HI(g)$	+26.5
methane	$CH_4(g)$	–74.8
nitrogen	$N_2(g)$	0
nitrogen dioxide	$NO_2(g)$	+33.1
nitrogen monoxide	$NO(g)$	+90.2
octane	$C_8H_{18}(l)$	–250.3
oxygen	$O_2(g)$	0
propane	$C_3H_8(g)$	–105
water(g)	$H_2O(g)$	–241.8
water(l)	$H_2O(l)$	–285.8

TABLE 2 Enthalpies of combustion*

Substance	Formula	ΔH°_c (kJ mol^{-1})
butane	$C_4H_{10}(g)$	–2886
carbon (graphite)	$C(s)$	–394
ethane	$C_2H_6(g)$	–1560
ethene	$C_2H_4(g)$	–1411
ethanol	$C_2H_5OH(l)$	–1367
glucose	$C_6H_{12}O_6(s)$	–2803
hydrogen	$H_2(g)$	–286
methane	$CH_4(g)$	–890
methanol	$CH_3OH(l)$	–725
octane	$C_8H_{18}(l)$	–5450
propane	$C_3H_8(g)$	–2220

*The values for the molar enthalpy of combustion are measured at standard state conditions (298 K, 1 bar).

APPENDIX J Indicators and their pH range and pK_a value

Indicator	pH range	pK_a
methyl violet	0.0–1.6	–
thymol blue	1.2–2.8	1.7
methyl orange	3.1–4.4	3.7
bromophenol blue	3.0–4.6	3.8
bromocresol green	3.8–5.4	4.7
methyl red	4.4–6.2	5.1
bromothymol blue	6.0–7.6	7.0
phenol red	6.8–8.4	7.9
phenolphthalein	8.3–10.0	9.6
alizarin yellow	10.1–12.0	11.2

APPENDIX K Infrared data

Bond	Organic molecules	Wavelength (cm^{-1})
C–I	iodoalkanes	490–620
C–Br	bromoalkanes	500–600
C–Cl	chloroalkanes	600–800
C–F	fluoroalkanes	1000–1400
C–O	alcohol, ester	1050–1410
C=C	alkenes	1620–1680
C=O	aldehydes, carboxylic acid, esters, ketones	1700–1750
C≡C	alkynes	2100–2260
O–H	carboxylic acids (hydrogen-bonded)	2500–3000
C–H	alkanes, alkenes, alkynes, aldehydes, amides	2720–3100
O–H	alcohol (hydrogen-bonded)	3200–3600
N–H	amines	3300–3500

APPENDIX L Straight-chain and α-ring forms of glucose and fructose

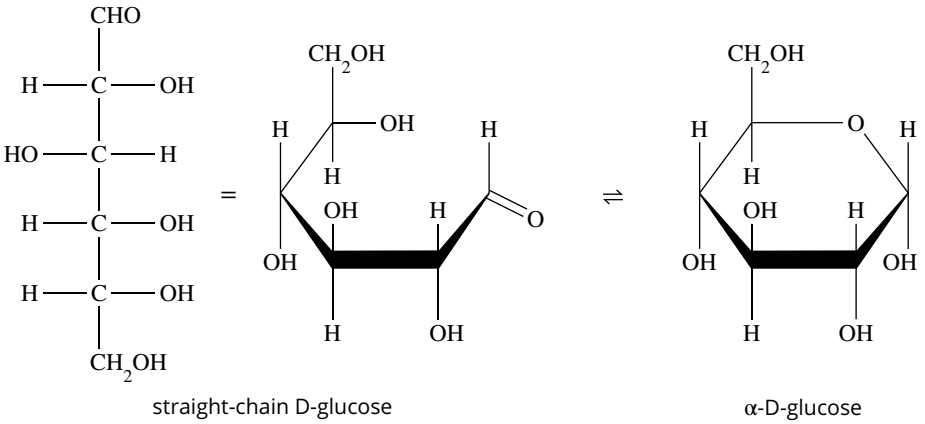


FIGURE 1 Glucose exists in solution in equilibrium between these isomers. Note the aldehyde in the straight-chain form.

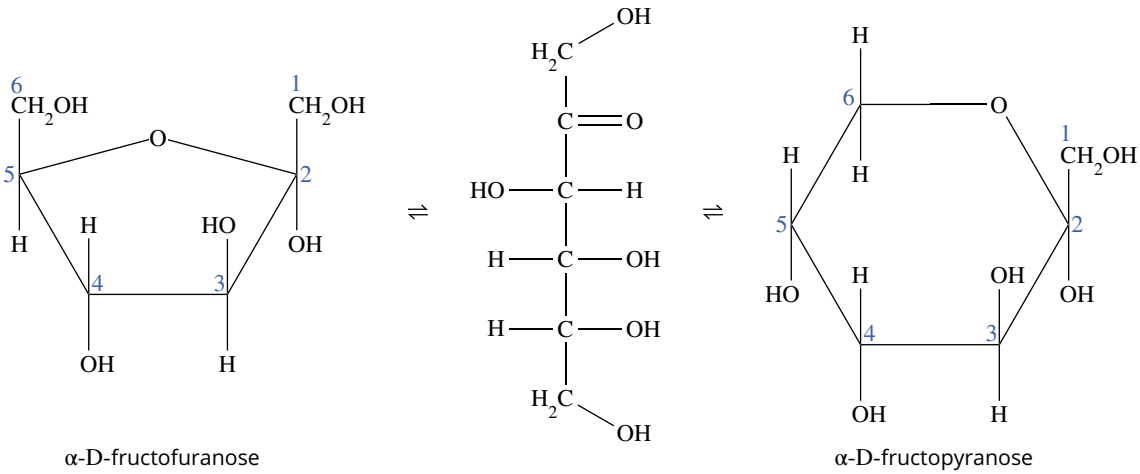
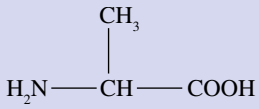
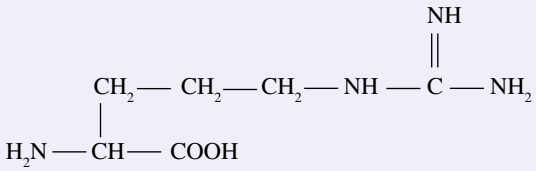
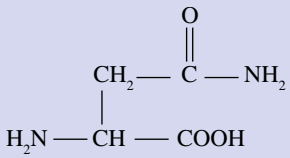
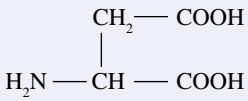
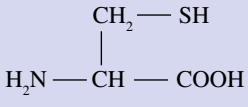
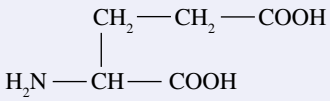
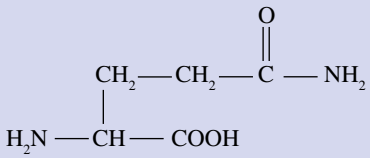
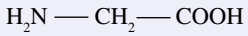
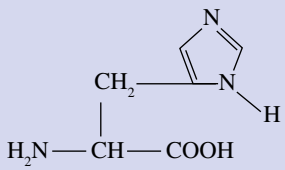
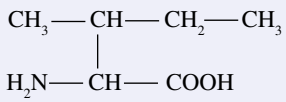
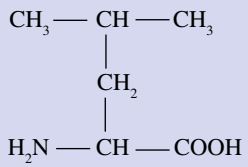
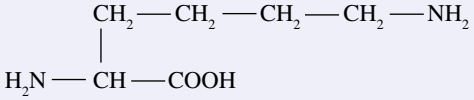
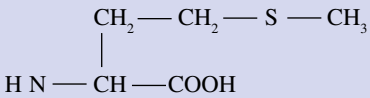
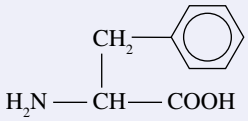
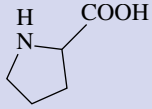
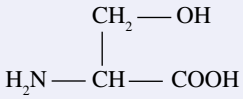
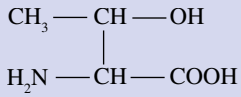
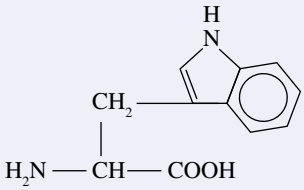
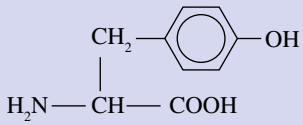
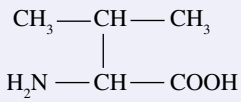


FIGURE 2 Fructose exists in solution in equilibrium between a number of isomers, three of which are shown here. Note the ketone in the straight-chain form.

APPENDIX M Common name, symbol, structural formula and pH of isoelectric point for amino acids

Name	Symbol	Structural formula	pH of isoelectric point
alanine	Ala		6.1
arginine	Arg		10.7
asparagine	Asn		5.4
aspartic acid	Asp		3.0
cysteine	Cys		5.1
glutamic acid	Glu		3.2
glutamine	Gln		5.7
glycine	Gly		6.1
histidine	His		7.6
isoleucine	Ile		6.0
leucine	Leu		6.0
lysine	Lys		9.7
methionine	Met		5.7

APPENDIX M Common name, symbol, structural formula and pH of isoelectric point for amino acids (*continued*)

Name	Symbol	Structural formula	pH of isoelectric point
phenylalanine	Phe		5.7
proline	Pro		6.3
serine	Ser		5.7
threonine	Thr		5.6
tryptophan	Trp		5.9
tyrosine	Tyr		5.7
valine	Val		6.0

Answers

All answers are given to the least number of significant figures given in the question. See page e35 for more details.

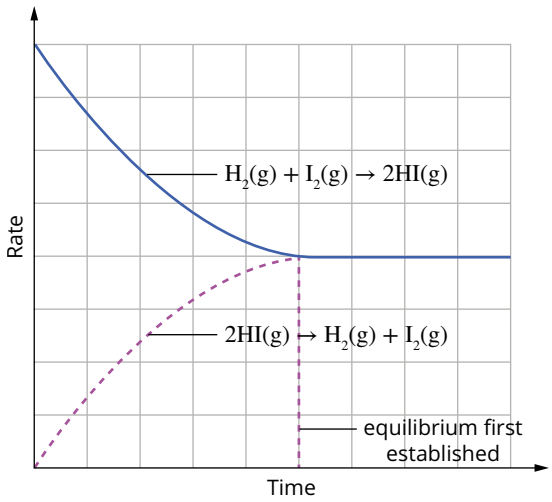
Chapter 2 Chemical equilibrium

2.1 Dynamic equilibrium

1 **a** open **b** closed **c** dynamic **d** different

2 **a** false **b** false **c** true **d** false

3



4 closed, decreases, less, reverse, increases, equal

5 **a** open; both energy and matter are exchanged with the surroundings
b closed; only energy can be exchanged with the surroundings
c open; both energy and matter are exchanged with the surroundings

6 B and F

7 $130\,kJ\,mol^{-1}$

8 **a** Chemical equilibrium is 'dynamic' because both forward and reverse reactions occur at the same rate.
b When the bag is opened, water vapour escapes and the rate of evaporation exceeds the rate of condensation. The system is not in equilibrium and the clothes dry.

9 **a** $0.07\,mol\,L^{-1}$ **b** $0\,mol\,L^{-1}$ **c** $0.03\,mol\,L^{-1}$
d $0.08\,mol\,L^{-1}$ **e** 0.04 mol
f no change in concentration of NO_2 or N_2O_4: equilibrium **g** 6 s
h The intensity of the brown colour will increase as the concentration of NO_2 increases until equilibrium is reached.

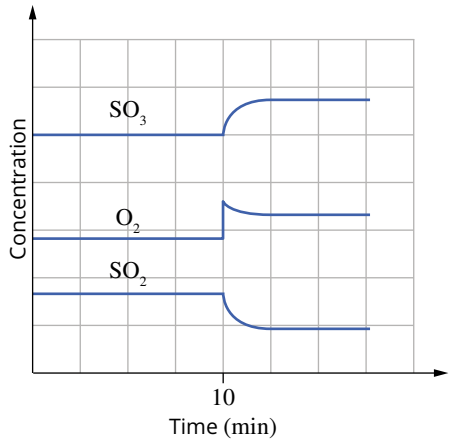
2.2 Factors that affect equilibrium

TY 2.2.1 A net reverse reaction will occur.

1 If an equilibrium system is subjected to a change, the position of equilibrium will shift to partially oppose the effect of the change.

2 greater, decreases, increases, decreases, increases

3



4 **a** net forward reaction (shift to the right)
b net reverse reaction (shift to the left)
c net forward reaction (shift to the right)

5 **a** net reverse reaction (shift to the left)
b net forward reaction (shift to the right)

2.3 Applying Le Châtelier's principle and collision theory to equilibria

TY 2.3.1 shift to the left; increase in Cl_2

TY 2.3.2 net reverse reaction (shift to the left); higher concentrations of CO_2 and H_2, lower concentrations of CH_4 and H_2O

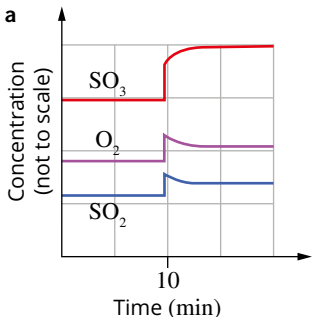
1 **a** true **b** false **c** false **d** true

2 lowers, equally, does not, will increase

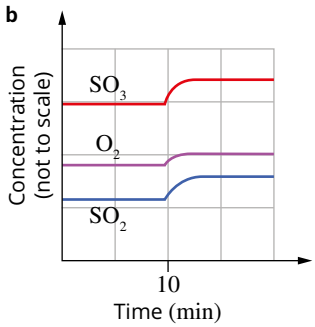
3 shifts to the right, shifts in the direction of the least particles, no change, shifts to the right, shifts to the right, shifts in the direction of the most particles

4 Reducing the volume of the system increases the total pressure of the gas mixture. The particles will collide more frequently and the rates of both the forward and reverse reactions will increase. However, the rate of the forward reaction will increase more than the rate of the reverse reaction because there are two particles on the left side of the equation compared with one on the right. As the forward reactions proceeds, there is a decrease in the rate of the forward reaction and an increase in the rate of the reverse reaction. The rates of the forward and reverse reactions become equal again and equilibrium is re-established but, overall, there is a net forward reaction.

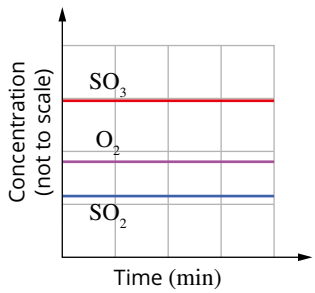
5 **a**



b



c



6 **a** net forward reaction **b** net reverse reaction **c** no effect

7 **a** net forward reaction **b** no effect **c** net forward reaction

8 **a** concentration of NO_2 will decrease
b mass of NO_2 will be higher

9 **a** decrease; since the reaction is endothermic, the equilibrium will shift to the left as temperature decreases and more H_2 will be consumed
b decrease; since the reaction is exothermic, the equilibrium will shift to the right as temperature decreases and more H_2 will be consumed

2.4 Equilibrium constants

TY 2.4.1 $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$ **TY 2.4.2** 0.694 **TY 2.4.3** $0.17\,mol\,L^{-1}$

TY 2.4.4 0.0248 **TY 2.4.5** $Y = 8.1 \times 10^{-5}\,mol\,L^{-1}$

1 **a** A system in which all the species are in the same state.
b Q_c is equal to K_c at equilibrium.
c The ratio of the equilibrium concentrations of the products over the equilibrium concentrations of the reactants raised to the power of their coefficients.

2 $Q_c = \frac{[HCl]^2}{[H_2][Cl_2]}$

3 **a** $K_c = \frac{[HI]^2}{[H_2][I_2]}$ **b** $K_c = \frac{[N_2]^2[O_2]}{[N_2O]^2}$ **c** $K_c = \frac{[NO_2]}{[NO][O_2]^{\frac{1}{2}}}$
d $K_c = \frac{[N_2]^2[H_2O]^6}{[NH_3]^4[O_2]^3}$

4 B

5 The reaction will shift to the right to establish equilibrium.

6 $Q_c = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4}$

7 **a** $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$ **b** 0.01 **c** $K_c = \frac{[N_2]^{\frac{1}{2}}[H_2]^{\frac{3}{2}}}{[NH_3]}$ **d** 10
e **i** the value of the equilibrium constant is the reciprocal of the original constant
ii the new equilibrium constant has a value equal to the square root of the original constant

8 **a** 0.020 **b** 50

9 **a** 8.35 **b** 0.767 **c** 1.30 **d** 0.346

10 **a** increased **b** decreased **c** increased **d** decreased

11 0.10

12 1.1×10^2

13 $0.127\,mol\,L^{-1}$

14 0.033

15 2.41×10^{-3}

16 **a** $0.011\,mol\,L^{-1}$ **b** 0.020
c the system is not at equilibrium; a net reverse reaction will occur

17 557

18 $1.05 \times 10^{-4}\,mol\,dm^{-3}$

Chapter 3 Equilibrium in acid and base chemistry

3.1 The Brønsted–Lowry model of acids and bases

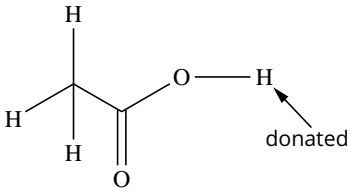
1 H_2SO_4/HSO_4^- and $H_2NO_3^+/HNO_3$

2 **a** H_2O **b** H_3O^+ **c** CH_3NH_2

3 The HCl loses a proton to the base: $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$. The ionic equation provides a clearer way (by eliminating spectator ions) of noting the reaction between the H^+ and OH^- ions neutralising to form water: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$.

4 **a** NH_4^+ **b** CH_3COOH **c** $H_2PO_4^-$ **d** HCO_3^-

5



6 In a diprotic substance each molecule can donate two protons to a base. An amphiprotic substance can act as either an acid or a base.

7 Acting as an acid:
a $HCO_3^-(aq) + H_2O(l) \rightarrow CO_3^{2-}(aq) + H_3O^+(aq)$
b $HPO_4^{2-}(aq) + H_2O(l) \rightarrow PO_4^{3-}(aq) + H_3O^+(aq)$
c $HSO_4^-(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + H_3O^+(aq)$
d $H_2O(l) + H_2O(l) \rightarrow OH^-(aq) + H_3O^+(aq)$

Acting as a base:
a $HCO_3^-(aq) + H_2O(l) \rightarrow H_2CO_3^{2-}(aq) + OH^-(aq)$
b $HPO_4^{2-}(aq) + H_2O(l) \rightarrow H_2PO_4^-(aq) + OH^-(aq)$
c $HSO_4^-(aq) + H_2O(l) \rightarrow H_2SO_4(aq) + OH^-(aq)$
d $H_2O + H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq)$

8 H_2SO_4 is a diprotic acid as it is able to donate two protons. Each proton is donated in two dissociation steps, and therefore, the first conjugate base formed is HSO_4^-. This HSO_4^- is therefore able to accept a proton and act as a base, or dissociate further and donate the remaining proton and therefore act as an acid.

9 When water acts as an acid it donates a proton to form OH^- ions. When it acts as a base, H_3O^+ ions are formed as it accepts a proton.

10 The advantage of the Brønsted–Lowry model is that a reaction between two gases could be considered an acid–base reaction.

3.2 Strength of acids and bases

1 **a** $HClO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO_4^-(aq)$
b $HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$
c $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

2 Reaction B is a reaction of a strong acid as the reaction arrow indicates the nitric acid completely ionises in water to form H_3O^+ ions and NO_3^- ions. In reaction A, HF acts as a weak acid as it only partially dissociates, as shown by the double equilibrium arrows.

3 Stage 1: $H_3AsO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2AsO_4^-(aq)$
Stage 2: $H_2AsO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HAsO_4^{2-}(aq)$
Stage 3: $HAsO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + AsO_4^{3-}(aq)$

4 As perchloric acid is stronger, more hydrogen ions would be present in solution than in a solution of ethanoic acid, making it a better conductor of electricity.

5 $H_2PO_4^-$ would be a stronger acid as it is diprotic and the first stage dissociates to a greater extent than the second stage.

3.3 Acidity of solutions

TY 3.3.1 $1.8 \times 10^{-9}\,mol\,L^{-1}$ **TY 3.3.2** 8.2 **TY 3.3.3** 12.3
TY 3.3.4 12.25 **TY 3.3.5** $4 \times 10^{-11}\,mol\,L^{-1}$ **TY 3.3.6** 1.5
TY 3.3.7 11.7

1 basic

2 by a factor of 100

3 1.3

4 1.00×10^{-11}

5 $1.0 \times 10^{-9}\,mol\,L^{-1}$

6 1.0×10^{-6} (or 0.000001) $mol\,L^{-1}$

3.4 Buffers

1 A solution that will resist pH change even upon the addition of extra acid or base.

2 The NaOH will fully dissociate forming OH^- ions. These ions will react with the NH_4^+ ions to form ammonia (NH_3), increasing the amount of undissociated NH_3 in solution.

3 Hydrochloric acid is a strong acid and fully dissociates in water.

4 The equilibrium position will shift to the left at first; however, the addition of H^+ ions will cause the pH to drop.

3.5 Dissociation constants

TY 3.5.1 $0.00592\,mol\,L^{-1}$ **TY 3.5.2** 11.5

1 $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

2 H_3PO_4 is the strongest acid.

3 9.14

4 HSO_4^- is the strongest acid.

3.6 Indicators

1 $HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$

2 **a** yellow **b** colourless
c intermediate between blue and yellow

3 Universal indicator is a mixture of several indicators and therefore changes through a range of colours.

4 **a** yellow
b The equilibrium will shift to the left and the solution will have a yellow colour.

5 8.3 and very pale pink

6 According to Le Châtelier's principle, in reactions with weak acids and their conjugate bases, the addition of the base will cause the system to move the equilibrium position towards the reactants. This causes the colour of the indicator to appear as it would in acidic solution.

7 **a** Cgr^{-}, H_3O^{+}
b **i** purple **ii** red **iii** blue **iv** red

Chapter 4 Volumetric analysis

4.1 Principles of volumetric analysis

TY 4.1.1 4.00 mol L^{-1} **TY 4.1.2** 10 mL **TY 4.1.3** 0.523 g

1 Weigh the solid primary standard on an electronic balance. Transfer the solid into the volumetric flask using a clean, dry funnel. Rinse any remaining solid particles into the flask using deionised water. Half fill the flask with deionised water and swirl vigorously to dissolve the solid. Fill the flask with deionised water to just below the calibration mark. Add deionised water drop-by-drop up to the calibration line on the flask until the bottom of the meniscus touches the line. Stopper and shake the solution to ensure an even concentration throughout.

2 The equivalence point is the point in the reaction at which equivalent amounts of acid and base have been mixed according to the ratio given in the chemical equation. The end point is the point in the titration at which the indicator changes colour.

3 Selecting the indicator based on the expected equivalence point enables for a sharp end point to be seen.

4 15.0 mL

5 NaOH readily absorbs moisture from the air and can therefore not be accurately weighed and used as a primary standard as its concentration cannot be accurately determined from its mass.

6 $n = \frac{m}{M} = \frac{2.042}{204.23} = 0.01000\,\text{mol}$

$c = \frac{n}{V} = \frac{0.01000}{0.050000} = 0.2000\,\text{mol L}^{-1}$

7 13.3 g

8 **a** $H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$
b 15.0 mL

9 **a** $2HNO_3(aq) + Ca(OH)_2(aq) \rightarrow Ca(NO_3)_2(aq) + 2H_2O(l)$
b 0.133 mol L^{-1}

10 phenolpthalein for titration 1; methyl orange for titration 2

11 **a** phenolpthalein **b** decreasing
c pH will be greater than 7 as NaOH is a stronger base than the ethanoic acid

4.2 Performing volumetric analysis

TY 4.2.1 0.108 mol L^{-1} **TY 4.2.2** 12.88 mol L^{-1}

1 **a** potassium hydrogen phthalate
b **i** vinegar **ii** deionised water **iii** sodium hydroxide

2 16.22 mL, 16.26 mL and 16.18 mL

3 **a** A burette delivers a precise variable volume of solution.
b A pipette delivers a precise known volume of solution.
c A standard flask is used to prepare a solution of known concentration.

4 25.42 mL

5 0.770 mol L^{-1}

6 **a** $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$
b 0.02145 mol **c** 0.02145 mol **d** 0.858 mol L^{-1}

7 10.45 mol L^{-1}

Chapter 5 Redox reactions

5.1 Introducing redox reactions

TY 5.1.1 oxidation half-equation: $Na(s) \rightarrow Na^{+}(s) + e^{-}$
reduction half-equation: $Cl_2(g) + 2e^{-} \rightarrow 2Cl^{-}(s)$

TY 5.1.2 Cu(s) is being oxidised, $Ag^{+}(aq)$ is being reduced

TY 5.1.3 $4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

TY 5.1.4 $2Ag^{+}(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$

1 **a** The process by which a chemical species (i.e. atom, molecule or ion) gains electrons.
b The process by which a chemical species (i.e. atom, molecule or ion) loses electrons.
c A reaction in which there is an electron transfer from one chemical species to another.

2 **a** A substance that causes the oxidation of another substance, and is reduced in the process.
b A substances that causes the reduction of another substance, and is oxidised in the process.

3 Ag, Cu, Sn, Ni, Mg, Li

4 Dry corrosion refers to the oxidation of a metal by oxygen gas. Wet corrosion involves both oxygen gas and water.

5 **a** oxidation **b** reduction **c** reduction **d** oxidation

6 I_2, loses, oxidised, gains, reduced, I^{-}

7 Salts dissolved in aerosol water droplets in air are good electrolytes and therefore accelerate the rusting process.

8 The water contains impurities that increase the rate of corrosion. The shallow depth of water allows a relatively high concentration of dissolved oxygen, so the reaction proceeds at a faster rate just below the surface. Dry corrosion is a relatively slow process, so the steel pillar above the water will corrode more slowly.

9 **a** magnesium is oxidised, copper is reduced
b $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^{-}$
c $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$
d $Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$
e the oxidising agent is Cu^{2+}; the reducing agent is Mg
f The solution loses some of its blue colour due to the loss of the $Cu^{2+}(aq)$, which reacts to form Cu(s).

10 **a** no **b** no **c** yes **d** yes **e** yes **f** yes **g** no

11 **a** $3Cu^{2+}(aq) + 2Al(s) \rightarrow 3Cu(s) + 2Al^{3+}(aq)$ **b** no reaction
c $2Ag^{+}(aq) + Zn(s) \rightarrow 2Ag(s) + Zn^{2+}(aq)$

12 **a** $Fe(s) \rightarrow Fe^{3+}(aq) + 3e^{-}$ (oxidation)
b $K(s) \rightarrow K^{+}(aq) + e^{-}$ (oxidation)
c $F_2(g) + 2e^{-} \rightarrow 2F^{-}(aq)$ (reduction)
d $O_2(g) + 4e^{-} \rightarrow 2O^{2-}(aq)$ (reduction)

5.2 Identifying redox reactions

TY 5.2.1 $\overset{+1}{Na}\overset{+5}{N}\overset{-2}{O_3}$

TY 5.2.2 The hydrogen has been identified as the reducing agent (it caused the reduction of Cu from CuO to Cu). The copper in the CuO is identified as the oxidising agent (it caused the H_2 gas to be oxidised to H_2O).

1 The actual charge on the atom if it exists as an element or monatomic ion, or a hypothetical charge assigned to the atom in the substance governed by simple rules.

2 **a** zero **b** the charge on the ion

3 **a** increases **b** decreases

4 **a** +1 **b** +3 **c** +3

5 K_2MnO_4, Mn = +6

6 **a** Ca: +2; O: –2 **b** Ca: +2; Cl: –1 **c** H: +1; S: +6; O: –2
d Mn: +7; O: –2 **e** F: 0 **f** S: +4; O: –2
g Na: +1; N: +5; O: –2 **h** K: +1; Cr: +6; O: –2

7

Redox reaction	Conjugate redox pair (oxidation process)	Conjugate redox pair (reduction process)
$Na(s) + Ag^{+}(aq) \rightarrow Na^{+}(aq) + Ag(s)$	$Na(s)/Na^{+}(aq)$	$Ag^{+}(aq)/Ag(s)$
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$	$Zn(s)/Zn^{2+}(aq)$	$Cu^{2+}(aq)/Cu(s)$
$2K(s) + Cl_2(g) \rightarrow 2K^{+}(s) + 2Cl^{-}(s)$	$K(s)/K^{+}(s)$	$Cl_2(g)/Cl^{-}(s)$

8 **a** +2 **b** +4 **c** –4 **d** 0 **e** +4

9 **a** oxidising agent is Cl_2; reducing agent is Mg
b oxidising agent is O_2; reducing agent is SO_2
c oxidising agent is Fe_2O_3; reducing agent is CO
d oxidising agent is H_2O_2; reducing agent is Fe^{2+}

10 **a** charges are not balanced: $Ag(s) \rightarrow Ag^{+}(aq) + e^{-}$
b electrons appear on both sides of the equation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$
c state symbols are incorrect: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$
d atoms are not balanced: $I_2(aq) + 2e^{-} \rightarrow 2I^{-}(aq)$
e electrons are being subtracted: $Na^{+}(aq) + e^{-} \rightarrow Na(s)$

11 V, V^{2+}, V^{3+}, VO_2^{+} and VO_2^{+}

5.3 Balancing complex redox reactions using half-equations

TY 5.3.1 $3C_2H_6O(l) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3C_2H_4O_2(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$

1 **a** right-hand **b** left-hand

2 (1) balance all atoms except oxygen and hydrogen; (2) balance the oxygen atoms by adding H_2O molecules to one side of the half-equation; (3) balance the hydrogen atoms by adding H^+ ions to one side of the equation; (4) balance the charge on both sides of the half-equation by adding electrons (e^-) to the side with the greater positive charge; (5) indicate whether each substance exists as a dissolved solute or as a solid, liquid or gas by inserting the appropriate label.

3 **a** $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$
b $MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$
c $SO_4^{2-}(aq) + 10H^+(aq) + 8e^- \rightarrow H_2S(g) + 4H_2O(l)$
d $SO_2(g) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$
e $H_2S(g) \rightarrow S(s) + 2H^+(aq) + 2e^-$
f $SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$

4 **a** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
b $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
c $3Zn(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 3Zn^{2+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

5 **a** $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$
b $SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
$5SO_3^{2-}(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$
c $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$
$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
$MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Cl_2(g)$

6 **a** redox **b** not redox **c** not redox **d** redox **e** not redox

7 **a** **i** +3 **ii** +2 **iii** +4
b $S_2O_4^{2-}(aq) + 2H_2O(l) \rightarrow 2HSO_3^-(aq) + 2H^+(aq) + 2e^-$
$S_2O_4^{2-}(aq) + 2H^+(aq) + 2e^- \rightarrow S_2O_3^{2-}(aq) + H_2O(l)$

Chapter 6 Galvanic cells as a source of energy

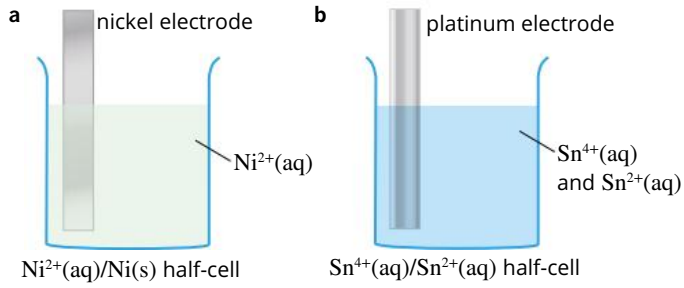
6.1 Galvanic cells

1 **a** a type of electrochemical cell that converts chemical energy into electrical energy
b a device that converts chemical energy into electrical energy, or vice versa
c an electrical connection between two half-cells in a galvanic cell
d a combination of cells connected in series

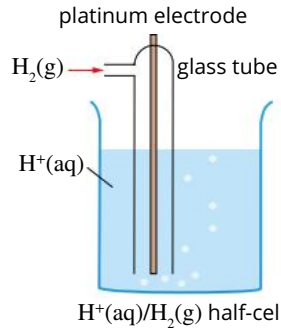
2 A galvanic cell is composed of two half-cells connected by a salt bridge. Each half-cell contains an electrode in contact with a solution. The species present in each half-cell form a conjugate redox pair. The salt bridge is made from an absorbent material such as filter paper saturated in an electrolyte solution.

3 negative, positive, cathode, anode

4

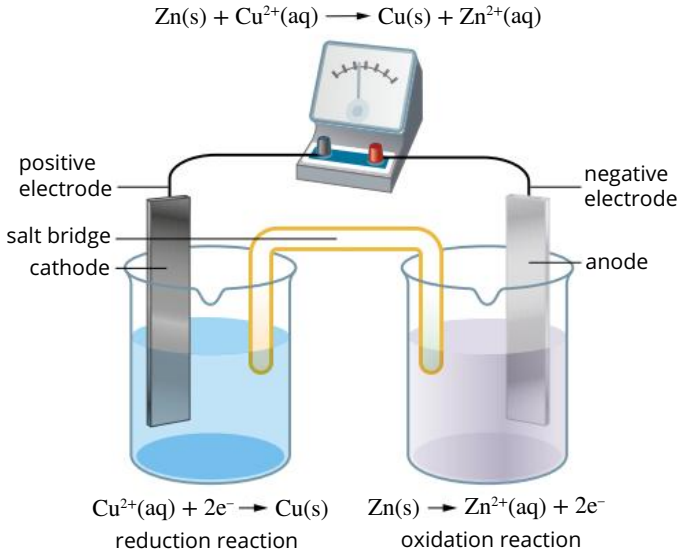


c



5 **a** Mg **b** Pt or C (graphite)
c Pt, C (graphite) or other inert conducting material

6

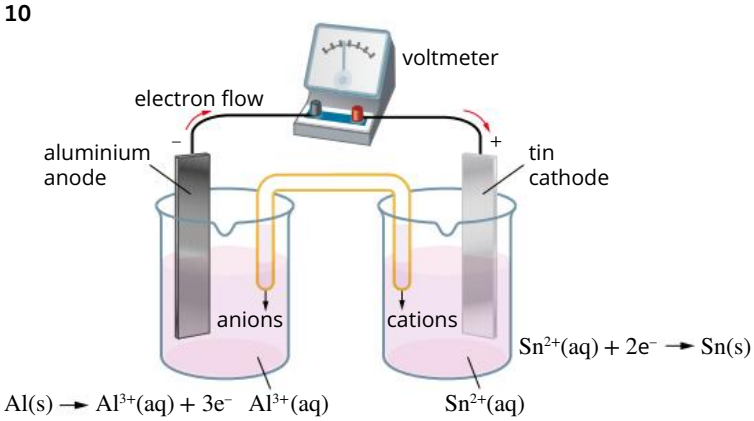


7 The ions in the salt bridge move to balance charges formed in the half-cells. Oxidation occurs at the anode so electrons leave this electrode via the external circuit. Anions therefore need to move towards this electrode to balance the positive charge that is formed as the electrons leave. Similarly, reduction occurs at the cathode as electrons react at this electrode. Cations therefore need to move towards this electrode to balance the negative charge that is formed.

8 **a** Place a lead rod in a solution containing Pb^{2+} ions.
b Place an inert electrode in an acidified solution containing $Cr_2O_7^{2-}$ and $Cr^{3+}(aq)$ ions.

9 **a** $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ **b** $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

10



11 **a** **i** $Mg^{2+}(aq)/Mg(s)$ **ii** $Cl_2(g)/Cl^-(aq)$

b In the cell, the chemical energy of magnesium and chlorine is converted to electrical energy. When magnesium and chlorine react directly, chemical energy is converted into thermal energy.

12 **a** $H^+(aq)/H_2(g)$

b Cations in the salt bridge move towards the cathode of the cell, which is positive. They therefore move towards the $Sn^{4+}(aq)/Sn^{2+}(aq)$ half-cell.

c $Sn^{4+}(aq) + H_2(g) \rightarrow Sn^{2+}(aq) + 2H^+(aq)$

6.2 The electrochemical series

TY 6.2.1 Electrons flow from the negative electrode (anode) to the positive electrode (cathode).

TY 6.2.2 0.28 V

1 **a** Potential difference measures the tendency to push electrons into the external circuit; it is the electromotive force between two points in a circuit.

b Reference conditions used to compare measurements. Gas pressure is 1 bar (100 kPa) and the concentration of dissolved species is 1 mol L^{-1}. Temperatures are usually measured at 25°C.

c The voltage measured when a half-cell, at standard conditions, is connected to a standard hydrogen half-cell.

2 negative, anode, positive, cathode

3 The half-cell should be constructed at standard conditions. The cell is connected to a standard hydrogen electrode to form a galvanic cell and the potential difference of the cell is measured with a voltmeter. This value is the standard electrode potential ($E°$). If the terminal of the half-cell has a positive polarity, the $E°$ of the cell is given a positive value, and vice versa.

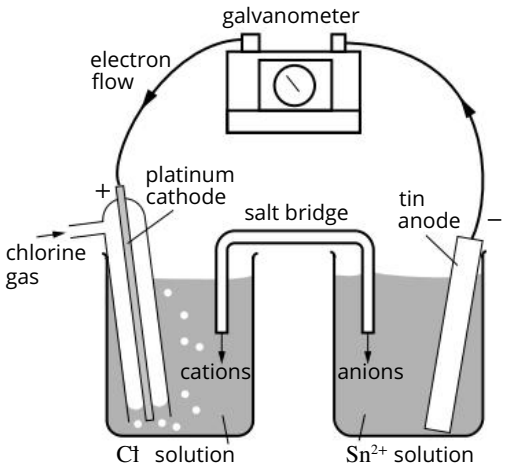
4 **a** reduction: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$
oxidation: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

b Multiply the Pb^{2+}/Pb half-equation by three and the Al^{3+}/Al half-equation by two so that the number of electrons in each half-equation is equal, and then add the two equations together:

$$[Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)] \times 3$$
$$[Al(s) \rightarrow Al^{3+}(aq) + 3e^-] \times 2$$
$$3Pb^{2+}(aq) + 2Al(s) \rightarrow 3Pb(s) + 2Al^{3+}(aq)$$

c The lead electrode will be the cathode and the aluminium electrode will be the anode.

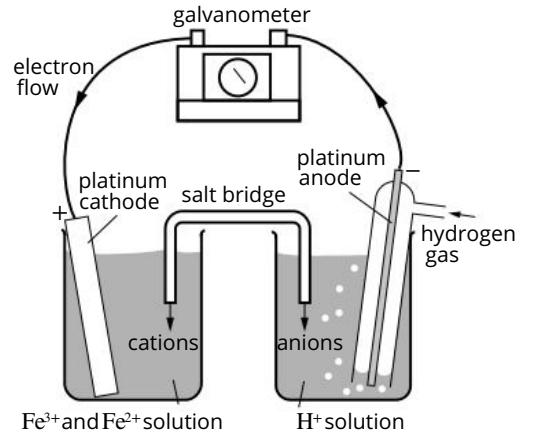
5



$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$ $Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$

Overall reaction: $Cl_2(g) + Sn(s) \longrightarrow 2Cl^-(aq) + Sn(s)$

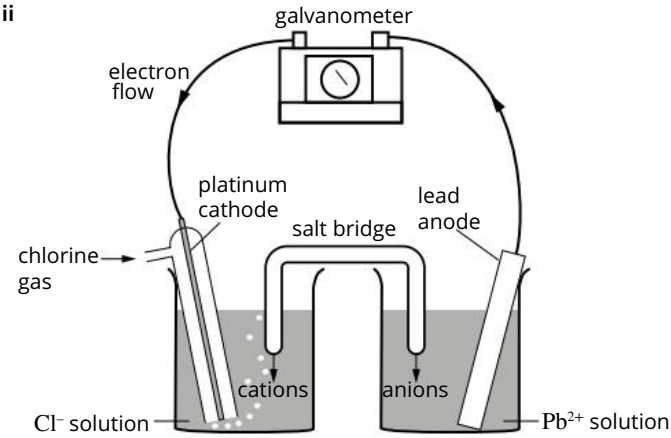
6 **i**



$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$ $H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

Overall reaction: $2Fe^{3+}(aq) + H_2(g) \longrightarrow 2Fe^{2+}(aq) + 2H^+(aq)$

ii



$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$ $Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$

Overall reaction: $Cl_2(g) + Pb(s) \longrightarrow Pb^{2+}(aq) + 2Cl^-(aq)$

7 **a** 0.80 V **b** 1.52 V

8 –0.40 V **9** –0.38 V

10 **a** $Fe^{3+}(aq)$ **b** Ni(s)

c Cations in the salt bridge flow towards the cathode and anions flow towards the anode. The $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell has the higher $E°$ and will be the cathode (positive). Therefore cations flow towards the $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell and anions flow towards the $Ni^{2+}(aq)/Ni(s)$ half-cell.

11 From highest to lowest:
$Fe^{2+}(aq)/Fe(s)$ and $Cl_2(g)/Cl^-(aq)$ = 1.80 V
$Fe^{2+}(aq)/Fe(s)$ and $Ag^+(aq)/Ag(s)$ = 1.24 V
$Ag^+(aq)/Ag(s)$ and $Cl_2(g)/Cl^-(aq)$ = 0.56 V

6.3 Predicting direct redox reactions

TY 6.3.1 **a** No reaction occurs because both I_2 and Pb^{2+} are oxidising agents.

b No reaction occurs because the oxidising agent, I_2, is below the reducing agent, Cl^-, in the electrochemical series.

c No reaction occurs because both Cl^- and Pb are reducing agents.

1 An oxidising agent (which is located on the left-hand of the electrochemical series) must react with a reducing agent (on the right-hand side) that is lower in the electrochemical series.

2 **a** $Zn(s) + 2Ag^{2+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$

b Chemical energy transformed into heat energy.

3 There are two possible reasons.

- When conditions are not standard conditions, the order of half-reactions in the electrochemical series may be different.
- The rate of the reaction may be slow.

4 **a** Lithium is a stronger reducing agent.
b $Fe^{2+}(aq)$ is a stronger oxidising agent.
c $Sn^{2+}(aq)$ can act as either an oxidising agent and a reducing agent in different reactions.

5 **a** reaction **b** no reaction **c** no reaction **d** reaction

6 **a** $Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br(l)$
b $Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(s)$
c no reaction **d** $Br_2(l) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(s)$

7 $CuSO_4$ and $Pb(NO_3)_2$

6.4 Everyday sources of power

1 Secondary cells can be recharged, whereas primary cells cannot.

2 **a** secondary **b** primary **c** secondary **d** primary

3 **a** $Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$
b $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$

4 **a** false **b** true **c** false **d** true

5 **a** $Pb(s)$ **b** $PbO_2(s)$
c $2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)$
d electrical energy to chemical energy

Chapter 7 Production of chemicals by electrolysis

7.1 Electrolytic cells

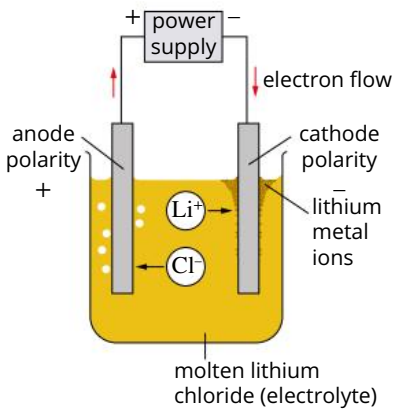
TY 7.1.1 $Zn^{2+}(aq) + Cu(s) \rightarrow Zn(s) + Cu^{2+}(aq)$

1 **a** the electrode at which oxidation occurs
b a conducting fluid; contains ions that are free to move
c an electrode that does not react
d a type of electrochemical cell in which electrolysis occurs
e a device that converts chemical energy into electrical energy, or vice versa

2 non-spontaneous, electrical, chemical, positive, negative, oxidation, reduction, reducing

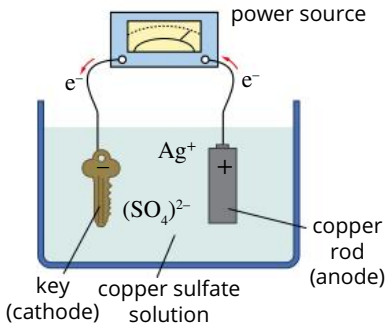
3 electroplating, electrorefining of metals, electrocoagulation for waste and water treatment

4 **a, b**



c anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
cathode: $Li^+(l) + e^- \rightarrow Li(l)$

5 **a**

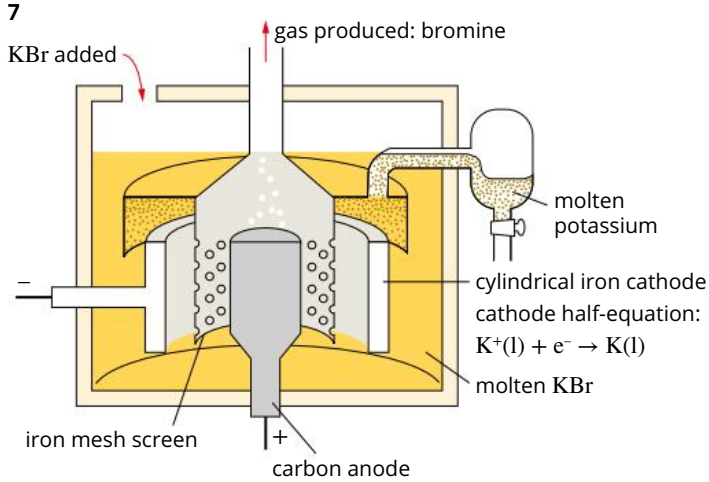


b The electrolyte should be a soluble copper(II) salt, such as copper(II) sulfate or copper(II) nitrate.

c The concentration of Cu^{2+} ions in the electrolyte stays constant because these ions are formed at the anode and consumed at the cathode.

6 **a** true **b** false **c** false **d** true

7



8 **a** the nickel rod
b carbon rod (positive): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
nickel rod (negative): $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
c $2H_2O(l) + 2Ni^{2+}(aq) \rightarrow O_2(g) + 4H^+(aq) + 2Ni(s)$

9 **a**

$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	–2.36 V
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH(aq)$	–0.83 V
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	–0.44 V
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	–0.13 V
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23 V

b anode: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$. Pb(s) is oxidised instead of Fe(s), even though Fe(s) is the stronger reducing agent, because Fe(s) is at the cathode where there is a continuous supply of electrons.
cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$. As water is a stronger oxidising agent than Mg^{2+}, water will be reduced in preference to the Mg^{2+}.
c $Pb(s) + 2H_2O(l) \rightarrow Pb(OH)_2(s) + H_2(g)$

10 **a** anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$. Cu(s) is oxidised instead of $H_2O(l)$ because Cu(s) is a stronger reducing agent. Although NO_3^- ions are attracted to the anode, they cannot be ionised because nitrogen is already in its highest oxidation state (+5).
cathode: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$. $Zn^{2+}(aq)$ is a stronger oxidising agent than $H_2O(l)$.
b $Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$

11 **a** anode: $2I^-(l) \rightarrow I_2(g) + 2e^-$ (I_2 is a gas at the temperature needed to melt CaI_2)
cathode: $Ca^{2+}(aq) + 2e^- \rightarrow Ca(l)$ (Ca is a liquid at the temperature needed to melt CaI_2)
b anode: $2Br^-(l) \rightarrow Br_2(g) + 2e^-$ (Br_2 is a gas at the temperature needed to melt NaBr)
cathode: $Na^+(aq) + 2e^- \rightarrow Na(l)$ (Na is a liquid at the temperature needed to melt NaBr)
c anode: $2I^-(aq) \rightarrow I_2(aq) + 2e^-$
cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
d anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

12 **a** Zinc ions are a stronger oxidising agent than water, so the zinc ions are preferentially reduced at the cathode. It is also cheaper than the molten electrolyte.
b oxygen gas

13 **a** Chlorine can be produced by the electrolysis of either concentrated sodium chloride solution or molten sodium chloride. The cost of supplying energy to melt sodium chloride means that it is more economical to use an aqueous electrolyte.
b Fluorine is a powerful oxidising agent and is not found as a pure element on Earth. A non-spontaneous reaction that occurs in an electrolysis cell, driven by electrical energy, is needed to produce the element from its compounds.
c Zn^{2+} ions are weaker oxidising agents than Cu^{2+} ions and so Cu^{2+} ions are preferentially deposited at the cathode.

14 The following two half-equations appear in the electrochemical series:
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$ −1.68 V
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH(aq)$ −0.83 V
The extraction of a metal from its salts involves reduction, which occurs at the cathode of an electrolytic cell. When several reactions are possible at the cathode of a particular cell, generally the strongest oxidising agent undergoes reduction. Half-reactions with more positive E° values involve stronger oxidising agents and are more likely to occur as reduction reactions. Since the oxidising strength of $H_2O(l)$ is greater than that of $Al^{3+}(aq)$, if water is present in an electrolysis cell it reacts preferentially at the cathode and electrolysis of aqueous aluminium salts does not yield aluminium metal.

15 **a** The anode is positive and the cathode is negative in an electrolytic cell, whereas the anode is negative and the cathode is positive in a galvanic cell.
Electrical energy is converted into chemical energy in an electrolytic cell, whereas chemical energy is converted into electrical energy in a galvanic cell.
A non-spontaneous reaction occurs in an electrolytic cell, whereas a spontaneous reaction occurs in a galvanic cell.
b Both types of cell involve interconversion between chemical and electrical energy.
Oxidation occurs at the anode and reduction occurs at the cathode in both cells.
Anions in the electrolyte move towards the anode and cations move towards the cathode in both cells.

Chapter 8 Structure and physical properties of organic compounds

8.1 Diversity of organic compounds

1 **a** a molecule that contains only single carbon–carbon bonds
b an atom or a group of atoms that gives a characteristic set of chemical properties to a molecule containing those atoms

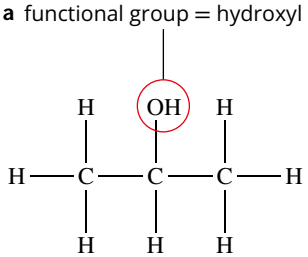
2 **a** triple bond **b** carbonyl **c** carboxylate

3 **a** 2,4 or $1s^2 2s^2 2p^2$ **b** 4 **c** 4

4 **a** it is a compound made up of carbon and hydrogen
b Each carbon atom needs four electrons to complete its outer shell. Each hydrogen atom needs one electron to complete its outer shell. Because both atoms need electrons, they will share electrons; that is, form covalent bonds. It will take four hydrogen atoms to provide the four electrons required by each carbon atom.

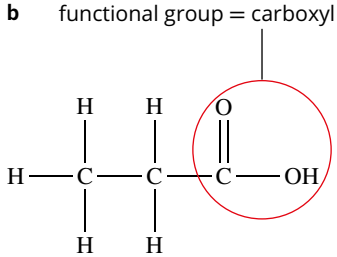
5

a functional group = hydroxyl



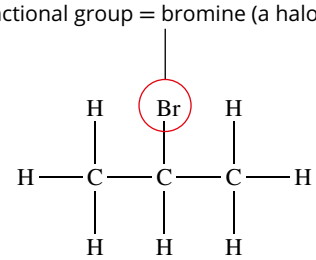
class = alcohol

b functional group = carboxyl



class = carboxylic acid

c functional group = bromine (a halogen)



class = haloalkane

6 Carbon has a valence of 4, which means it can form four covalent bonds with up to four other carbon atoms, each of which can also bond with up to four other carbon atoms. This means that carbon atoms can bond with each other to make branched chains of various lengths and rings of different sizes.
Single, double or triple bonds can be formed between two carbon atoms. All of these bonds are relatively strong, but carbon–carbon triple bonds are generally stronger than carbon–carbon double bonds which are, in turn, generally stronger than carbon–carbon single bonds.
In its compounds, carbon is almost always associated with hydrogen, which gives organic molecules a hydrocarbon skeleton. However, in addition to bonding with hydrogen, carbon can also bond with other non-metallic elements such as oxygen, nitrogen and chlorine.

8.2 Hydrocarbons

TY 8.2.1 octane; C_8H_{18} **TY 8.2.2** 2,2-dimethylpropane
TY 8.2.3 2,3-dimethylbut-1-ene

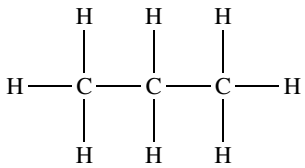
1 **a** C_nH_{2n+2} **b** C_nH_{2n} **c** C_nH_{2n} **d** C_nH_{2n-2}

2 **a** a hydrocarbon that consists of single covalent bonds
b a hydrocarbon that contains at least one carbon–carbon double bond
c a hydrocarbon that contains at least one carbon–carbon triple bond

3 **a** alkene **b** alkane **c** alkyne

4 **a** pentane **b** pentane **c** 2-methylbutane

5 **a**

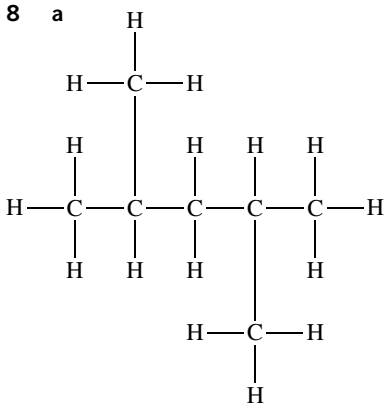


b propane **c** $CH_3CH_2CH_3$

6 ethene (two carbons), prop-1-ene (three carbons), pent-1-ene (five carbons), oct-1-ene (eight carbons), non-1-ene (nine carbons)

7 **a** hex-3-yne **b** 2-mehtlyprop-1-ene c 5-methylhept-3-ene

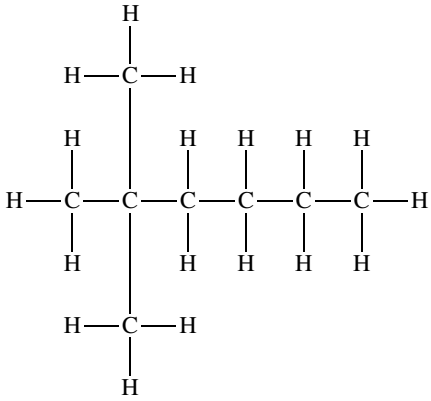
8 **a**



$CH_3CH(CH_3)CH_2CH(CH_3)CH_3$
condensed structural formula

extended structural formula

b

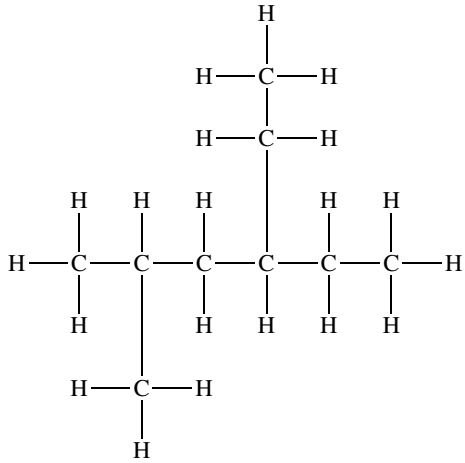


$CH_3C(CH_3)_2CH_2CH_2CH_2CH_3$

condensed structural formula

extended structural formula

c

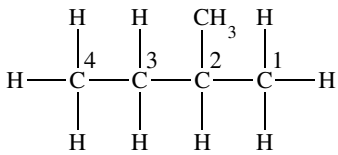


$CH_3CH(CH_3)CH_2CH(CH_2CH_3)CH_2CH_3$

condensed structural formula

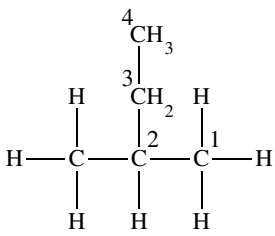
extended structural formula

9 a



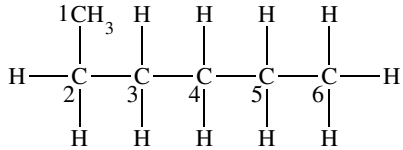
3-methylbutane is incorrect because the methyl side chain has been numbered as the third carbon rather than the second. The correct name is 2-methylbutane.

b



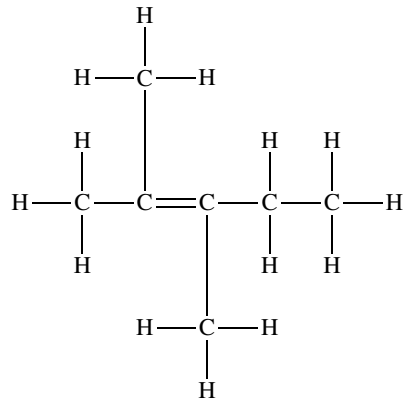
2-ethylpropane is incorrect because the longest continuous carbon chain contains four carbon atoms, not three. The parent alkane is butane, not propane. The correct name is 2-methylbutane.

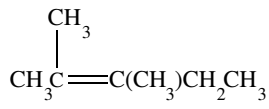
c



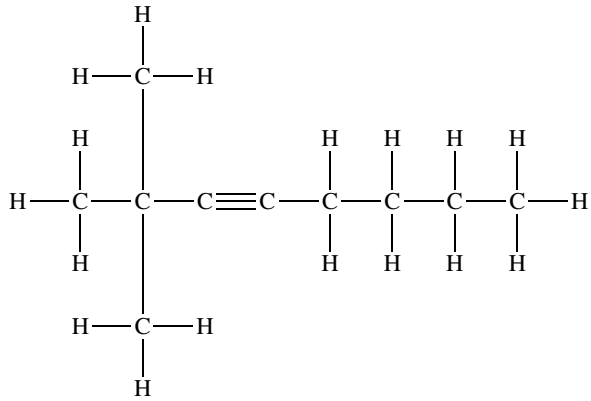
An alkyl side chain can never be added to the first carbon atom; doing this will just extend the length of the parent alkane. In this case, the added methyl group extends the parent alkane by one carbon. The correct name of this compound is hexane.

10 a



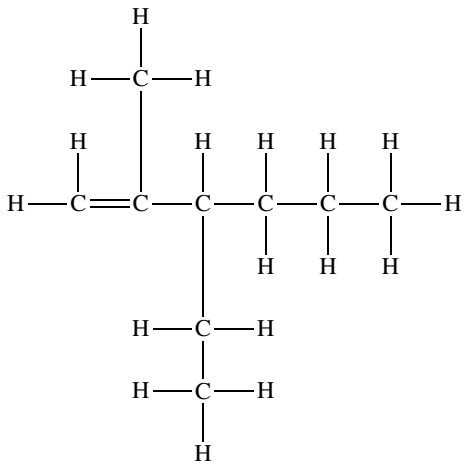


b



$CH_3C(CH_3)_2C{\equiv}CCH_2CH_2CH_2CH_3$

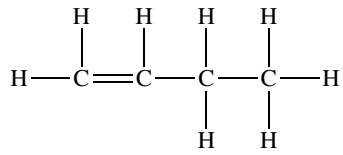
c

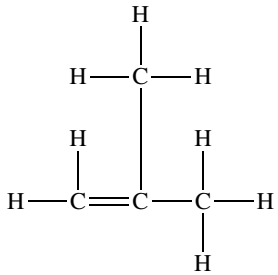


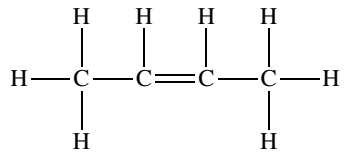
$H_2C{=}C(CH_3)CH(CH_2CH_3)CH_2CH_2CH_3$

8.3 Isomerism

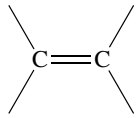
TY 8.3.1

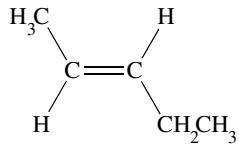




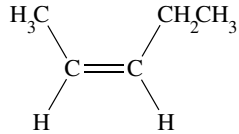


TY 8.3.2





trans-isomer



cis-isomer

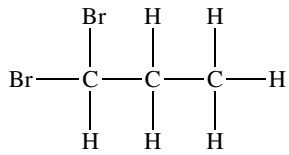
1 molecules that have the same molecular formula but a different arrangement of atoms

2 **a** chain and positional isomers
b geometric and optical isomers

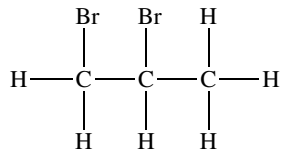
3 Chain isomers are molecules that have a different branching sequence on the main carbon chain. Positional isomers are molecules whose functional group is in a different position on the carbon chain.

4 In alkanes, the carbon–carbon single bonds freely rotate. However, in alkenes, the double bond prevents this rotation. The groups situated on the carbon atoms on either side of the double bond are in fixed positions and geometric isomers are therefore possible.

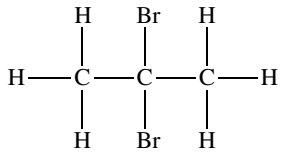
5



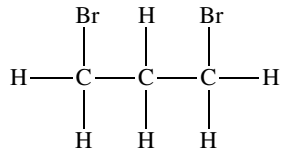
1,1-dibromopropane



1,2-dibromopropane

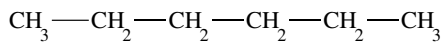


2,2-dibromopropane

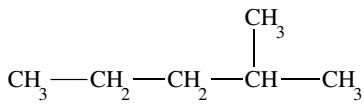


1,3-dibromopropane

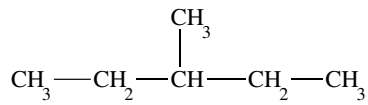
6



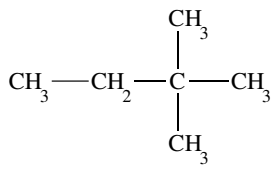
hexane



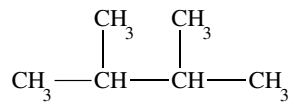
2-methylpentane



3-methylpentane



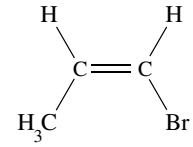
2,2-dimethylbutane



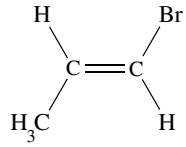
2,3-dimethylbutane

7 **a** 1-bromoprop-1-ene

b



cis-1-bromoprop-1-ene

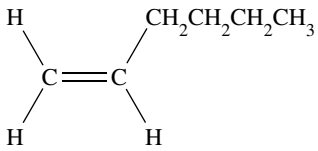


trans-1-bromoprop-1-ene

c *Cis-trans* isomers are only possible if both of the carbon atoms in the double bond are attached to two different groups. One of the double bond carbon atoms in prop-1-ene is attached to two identical groups (two hydrogen atoms). Therefore, *cis-trans* isomerism is not possible.

8 $H_2C{=}CHCH_2CH_2CH_2CH_3$

hex-1-ene



Hex-1-ene cannot have *cis*- and *trans*-isomers because the groups coming off the first carbon in the double bond are identical (both are hydrogen atoms).

9 **a** two carbon atoms
b four carbon atoms

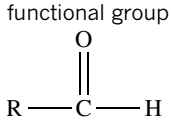
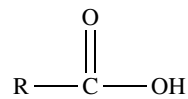
8.4 Hydrocarbon derivatives

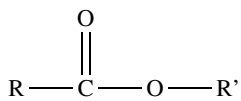
TY 8.4.1 propan-2-ol **TY 8.4.2** 2,4-dimethylpentan-3-ol
TY 8.4.3 there is a hydroxyl group present; the compound is an alcohol; 4-methylpentan-2-ol **TY 8.4.4** methyl butanoate

1 **a** a group of atoms consisting of a carbon atom doubly bonded to an oxygen atom
b aldehydes, ketones, carboxylic acids, esters and amides

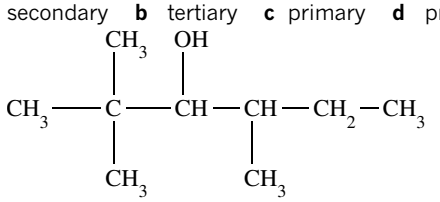
2 **a** ketone **b** alcohol **c** ester

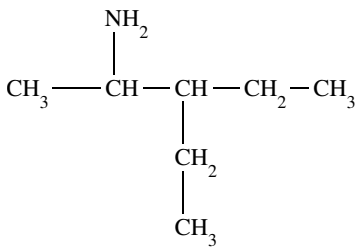
3 **a** derived from an alkane in which one or more hydrogen atoms have been replaced with a halogen functional group
b derived from an alkane and contains a hydroxyl (–OH) functional group attached to a saturated carbon atom

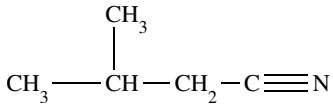
4 **a**  **b** 

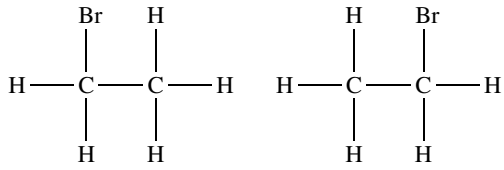
c 

5 **a** secondary **b** tertiary **c** primary **d** primary **e** tertiary

6 **a** 

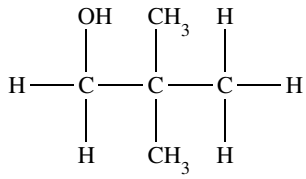
b 

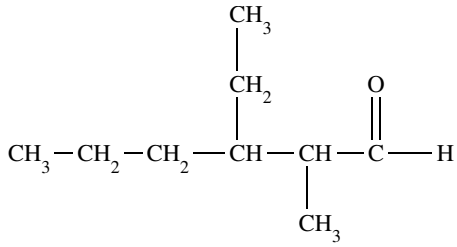
c 

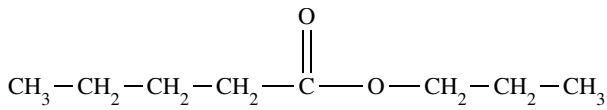
7 **a** 

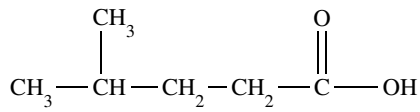
identical structures

b insufficient information

c 

8 **a** 

b 

c 

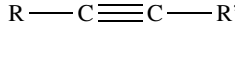
9 **a** When naming alcohols, the hydroxyl functional group takes priority over any alkyl side chains when numbering the carbon atoms in the main chain. The correct name is 3-methylbutan-2-ol.
b When naming amines, the amino functional group takes priority over any alkyl side chains when numbering the carbon atoms in the main chain. The correct name is 4-ethylhexan-3-amine.

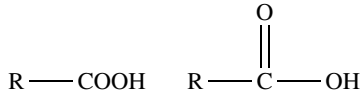
10 **a** The '-one' ending of the name of this compound implies that it is a ketone. However, the carbonyl group on a ketone can never be on carbon number 1. (If the carbonyl group is on the first carbon atom then the compound would be an aldehyde and named as 2-methylbutanal.)
b The '-al' ending of the name of this compound implies that it is an aldehyde. However, the carbonyl group in an aldehyde is always on the terminal (or end) carbon atom. (If the carbonyl group is on carbon number 3, then the compound would be a ketone and named as pentan-3-one.)
c The carbon atom of the carboxyl functional group in a carboxylic acid is always on carbon number 1. The methyl group cannot also be on this carbon atom because that carbon atom would then have five bonds.

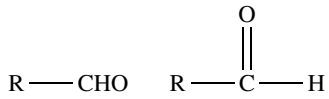
8.5 An overview of IUPAC nomenclature

TY 8.5.1 6-chlorohexanamine

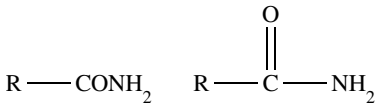
1 **a** International Union of Pure and Applied Chemists
b the set of rules developed by IUPAC so that chemists can name a given compound

2 **a** 

b 

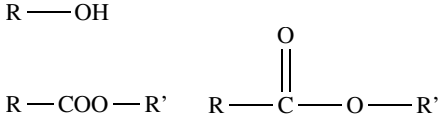
c 

d



e R—OH

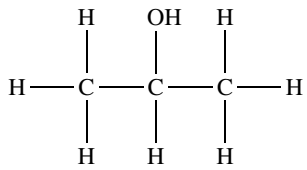
f



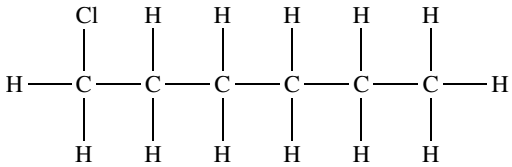
3 **a** pentan-3-one **b** propanoic acid **c** 2-methylpropanoic acid
d pent-2-ene

4 **a** 3-hydroxybutanoic acid **b** 3-methylpentan-2-amine
c 4-chloro-3-ethylpentan-2-ol **d** 5-fluoropent-2-yne

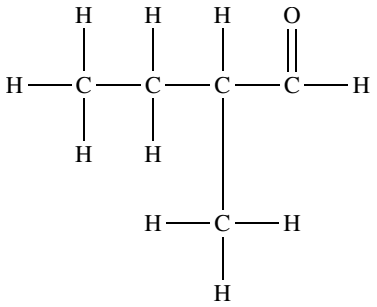
5 **a**



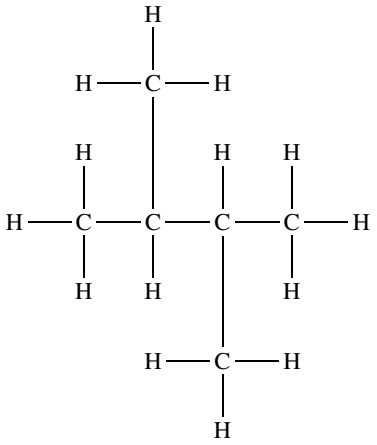
b



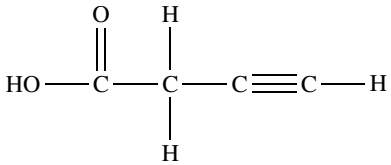
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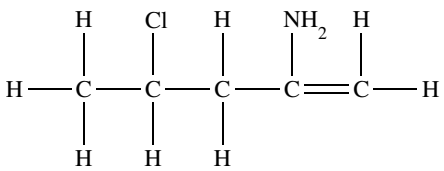
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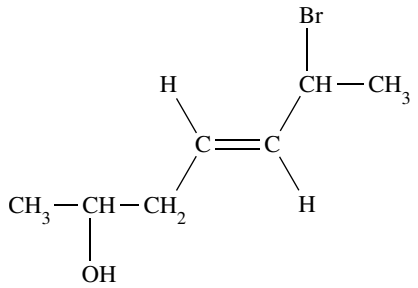
6 **a**



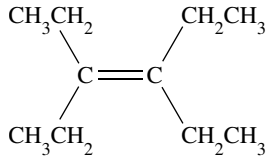
b



c



d



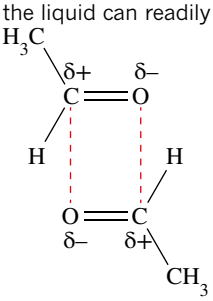
8.6 Boiling point change and volatility of organic compounds

TY 8.6.1 **a** decane **b** ethanoic acid

1 dispersion forces

2 the liquid can readily evaporate

3



4 Pentane only contains relatively weak dispersion forces holding its molecules together in the liquid state. These dispersion forces are easily overcome so pentane can readily evaporate.

5 2,2-dimethylpropane < 2-methylbutane < pentane

6 ethylbenzene < benzaldehyde < benzylamine

7 butan-1-ol < butanal < pentane

8 decane < octane < hexane

9 **a** Boiling point within a homologous series increases as the carbon chain length increases. The boiling points of alcohols are higher than the boiling points of aldehydes with a similar molecular mass.

b The boiling point of pentanoic acid ($CH_3(CH_2)_3COOH$) in experiment 3 is much lower than expected. The experimental data shows it has a similar boiling point to hexan-1-ol ($CH_3(CH_2)_4CH_2OH$) but this is an anomaly in the trend. As can be seen from the data in experiments 1 and 2, carboxylic acids have higher boiling points than aldehydes and alcohols of a comparable molecular mass.

c Boiling points within a homologous series increase as the carbon chain length increases because the dispersion forces between neighbouring molecules become stronger. The boiling points of alcohols are greater than the boiling points of aldehydes. Carboxylic acids have a higher boiling point than alcohols.

10 **a** methyl methanoate **b** butyl ethanoate
c butyl ethanoate

11 **a** D < C < B < A

b A = ethane
B = butane
C = pentane
D = heptane

All the compounds listed are alkanes. Alkanes are held together in the liquid state with dispersion forces. The smaller alkanes will have weaker dispersion forces so their molecules will be less tightly held together. These smaller alkanes are therefore more volatile than alkanes with longer carbon chains because they are able to evaporate more easily.

c The compounds listed in the table are all alkanes. Ethanol would be much less volatile than these alkanes. This is because its molecules are held together in the liquid state with hydrogen bonds. Hydrogen bonding is the strongest intermolecular force and its effects far outweigh the effect of the dispersion forces in the alkanes.

d Because the volatility of ethanol is much lower than the volatility of the alkanes, its vapour pressure would also be lower.

12 **a** –32°C

b The increase in melting point is related to the strength of the intermolecular forces and the ability of the molecules to pack together. As the number of carbon atoms increases, the strength of the intermolecular force increases due to a greater number of dispersion forces.

8.7 Solubility of organic compounds

TY 8.7.1 hexan-1-ol < butan-1-ol < ethanol

1 The type of functional group present in the compound and the length of the carbon chain.

2 Because hydrocarbons are non-polar, they can only form weak dispersion forces with water molecules that are not strong enough to break the hydrogen bonds between the water molecules. However, solvent molecules in non-polar solvents are only held together by dispersion forces. The energy required to break these intermolecular forces is low and is compensated for by the similar amount of energy that is released when the hydrocarbons dissolve and form dispersion forces with the solvent molecules.

3 **a** miscible **b** immiscible **c** miscible

4 **a** chloromethane < propan-1-ol < ethanoic acid

b ethanoic acid < propan-1-ol < chloromethane

5 Ethanol and pentan-1-ol both contain a hydroxyl functional group that can hydrogen bond with water molecules. However, the non-polar hydrocarbon portion of the molecule is longer in pentan-1-ol; this can get in the way and prevent some of the pentan-1-ol molecules from forming hydrogen bonds with water. Hexane is a non-polar solvent. Pentan-1-ol is more soluble in hexane than ethanol because its longer non-polar hydrocarbon portion of the carbon chain can form stronger dispersion forces with the non-polar solvent.

6 Butan-1-ol is an alcohol, whereas butanoic acid is a carboxylic acid. Both compounds would be soluble in water to some degree because they can both form hydrogen bonds with the water molecules. However, while the first four members of the homologous series of carboxylic acids are highly soluble, only the first two members of the homologous series of alcohols are highly soluble. Carboxylic acids are generally more soluble than alcohols because they can hydrogen bond to water with their carbonyl group as well as with their hydroxyl group. Alcohols, on the other hand, can only form hydrogen bonds with their hydroxyl group. As a result, butanoic acid would be more soluble than butan-1-ol.

7 **a** Pentan-3-one is much less soluble in water than propanone because it has a longer carbon chain. In general, ketones become less soluble in water as the length of their carbon chain increases. While the carbonyl group of the ketone molecules can form hydrogen bonds with water, the non-polar hydrocarbon part of the molecule cannot. Therefore, as chain length increases and the hydrocarbon part of the molecule gets bigger, ketones become less soluble in water.

b The solubility of 3-methylbutan-2-one would be greater than that of pentan-2-one. 3-methylbutan-2-one is a branched isomer of pentan-2-one; consequently, it would have weaker dispersion forces between its molecules in the pure liquid. Because of these weaker dispersion forces, when 3-methylbutan-2-one is added to water, its molecules would be able to separate from each other more easily and mix with the water molecules.

Chapter 9 Chemical properties and reaction pathways

9.1 Understanding the reactivity of organic compounds

1 **a** 6 **b** 3 **c** 1

2 Ethylamine because amines act as bases in solution, whereas carboxylic acids act as acids in solution.

3 Student answers will vary.

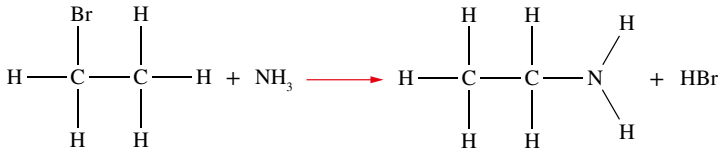
4 The test tube containing the separated liquids must contain decanol in water as it has a large non-polar 'tail' giving the molecule insufficient polarity to dissolve in water.

5 Two tests could be performed on each sample:
1 pH test, e.g. universal indicator or litmus. This will show that (a) has a low pH and is a carboxylic acid
2 Add acidified potassium dichromate (or potassium permanganate) and heat. This will give a dark green colour for indicating a 1° or 2° alcohol.

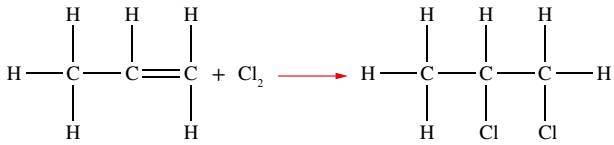
6 Test tube A: coconut oil. Test tube B: olive oil

9.2 Chemical reactions of alkanes, haloalkanes and alkenes

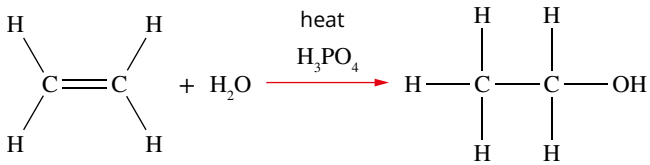
TY 9.2.1 $CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$



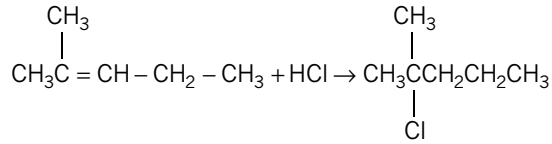
TY 9.2.2 $CH_2CHCH_2CH_3 + I_2 \rightarrow CH_2ICHICH_2CH_3$



TY 9.2.3



TY 9.2.4



TY 9.2.5 water and NaBr

1 $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$

2 **a** chloroethane **b** 1,2-dichloroethane **c** ethanol
d ethane

3 **a** ethanamine **b** butan-2-ol **c** pentan-2-ol

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

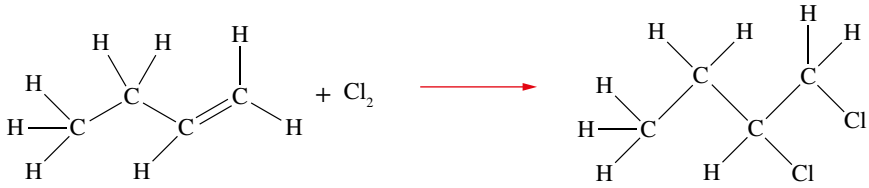
b $2C_6H_{14}(l) + 19O_2(g) \rightarrow 12CO_2(g) + 14H_2O(g)$

5 **a** $C_3H_6(g) + Br_2(aq) \rightarrow C_3H_6Br_2$

b $C_4H_8(g) + H_2O(g) \rightarrow C_4H_9OH(l)$

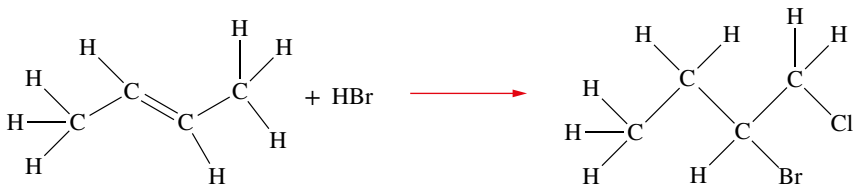
6 $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$
$CH_3Cl(g) + Cl_2(g) \rightarrow CH_2Cl_2(g) + HCl(g)$
$CH_2Cl_2(g) + Cl_2(g) \rightarrow CHCl_3(g) + HCl(g)$
$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$

7 **a**



but-1-ene 1,2-dichlorobutane

b

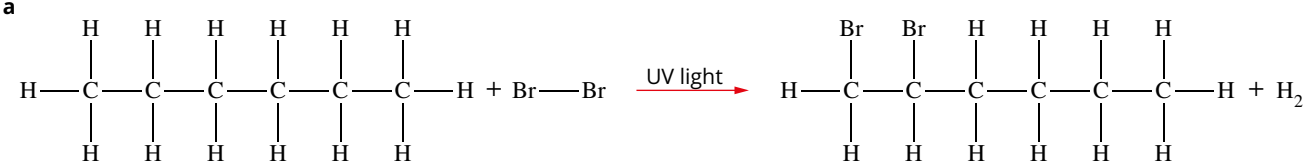


but-2-ene 2-bromobutane

8 Alkenes will react with bromine water because they contain at least one double bond. The electrons of this bond are available to bond with bromine atoms which are then 'added' into the molecule. This causes the bromine solution to change colour. Saturated molecules (alkanes) do not react because bonding electrons are not available.

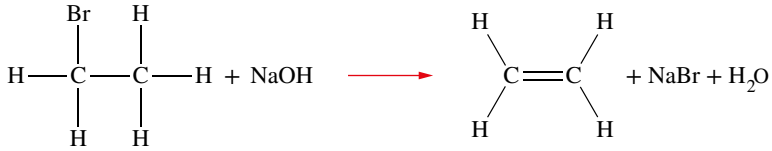
9 Two possible reaction products are butan-1-ol and butan-2-ol. The most common reaction product is butan-2-ol. This follows Markovnikov's rule, which states that when a water molecule is added to a double bond, the H group will add to the carbon with the most H atoms attached and the OH group will add to the carbon with the least H groups attached.

10 **a**



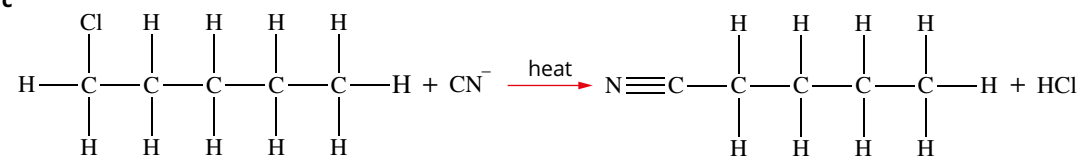
product is 1, 2-dibromohexane

b



product is ethene

c

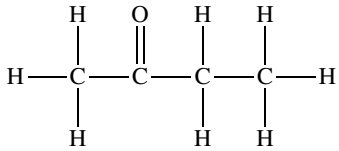


product is pentanitrile

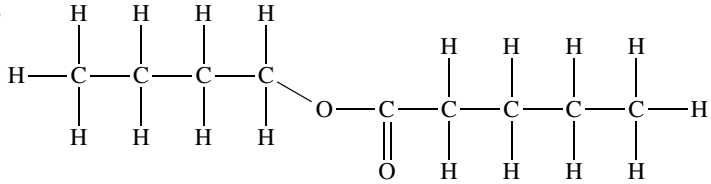
11 **A** ethene **B** dibromoethane **C** chloroethane **D** polyethene

9.3 Reaction of compounds containing oxygen and nitrogen atoms

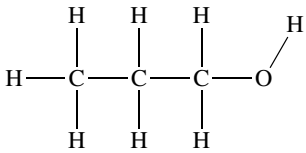
TY 9.3.1 2° butanol is oxidised to butanone



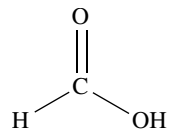
TY 9.3.2 butyl pentanoate



TY 9.3.3 propanol



methanoic acid

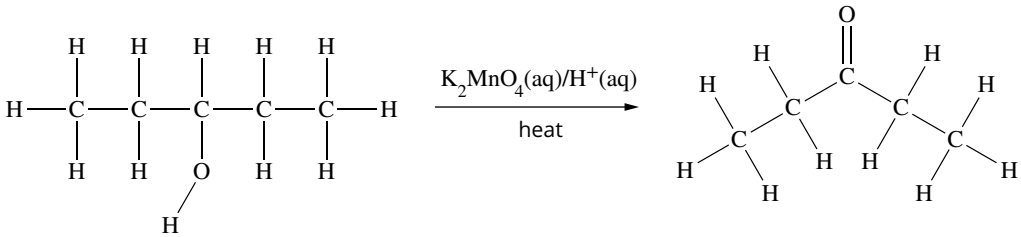


1 **a** tertiary **b** secondary **c** primary

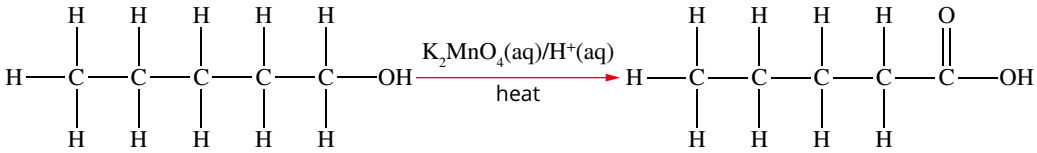
2 **a** $2C_5H_{12}O(g) + 15O_2(g) \rightarrow 10CO_2(g) + 12H_2O(g)$

b pentan-3-ol, secondary; 2-methylbutan-2-ol, tertiary; pentan-1-ol, primary

c Pentan-3-ol will oxidise to pentan-3-one. The solution will change from deep purple to colourless as the reaction proceeds.



2-Methylbutan-2-ol is a tertiary alcohol so will not react under the conditions described. No colour change will be observed; the solution will remain deep purple. Pentan-1-ol will oxidise to the carboxylic acid. The solution will change from purple to colourless as the reaction proceeds.



3

Compound	IUPAC name	Product
A	butan-1-ol	butanoic acid
B	pentan-2-ol	pentanone
C	2-methylpentan-2-ol	no reaction
D	propan-2-ol	propanone

4 **a** Water must be present as a reagent and the reaction requires an alkali or dilute acid catalyst.

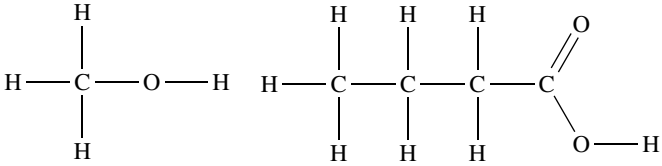
b **i** methanol and pentanoic acid

ii propan-1-ol and ethanoic acid

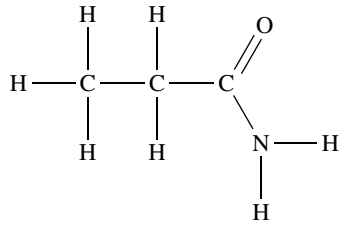
iii hexanol and propanoic acid

5 amide, water, condensation

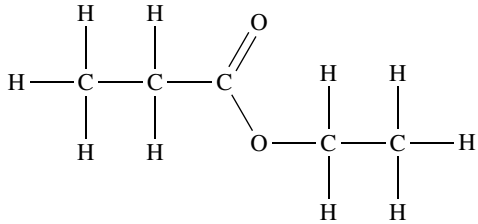
6 **a** methanol and butanoic acid



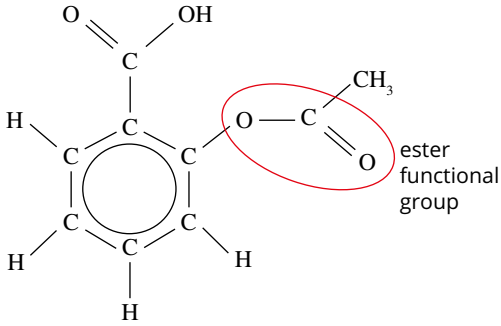
b propanamide



c ethyl propanoate

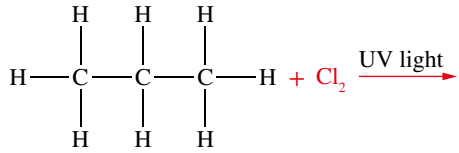


7 Ethanoic acid is one reactant used to produce aspirin because the C=O is part of a two-carbon chain.

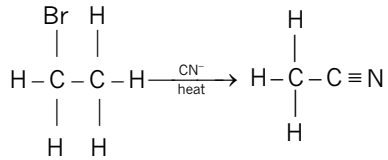


9.4 Designing reaction pathways

TY 9.4.1



TY 9.4.2



TY 9.4.3 $CH_3CH_2CH_3 + Cl_2 \xrightarrow{\text{UV light}} CH_3CH_2CH_2Cl + NH_3 \rightarrow CH_3CH_2CH_2NH_2$

1 C

2 **a** propanal **b** $Cr_2O_7^{2+}H^+$ **c** propanoic acid
d $Cr_2O_7^{2+}H^+$/heat **e** condensation H_2O

3 **a** 1-chloroethane $\xrightarrow{NH_3}$ ethylamine

b butane $\xrightarrow{Cl_2/UV\ light}$ 1-chlorobutane $\xrightarrow{OH^-}$ butan-1-ol

c 1-chloropentane $\xrightarrow{OH^-}$ 1-pentanol $\xrightarrow{K_2Cr_2O_7/H^+/heat}$ pentanoic acid

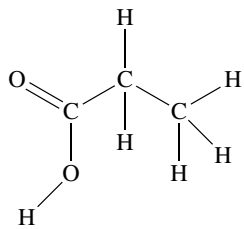
4 This synthesis is carried out in three parts: (1) synthesis of 1-butanol, (2) synthesis of ethanoic acid and (3) synthesis of butyl ethanoate.

butane $\xrightarrow{Cl_2/UV\ light}$ 1-chlorobutane $\xrightarrow{OH^-}$ butan-1-ol

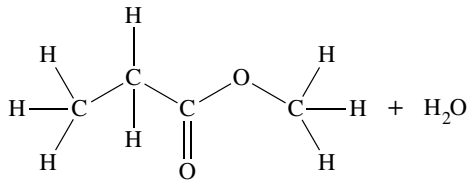
ethene $\xrightarrow{H_2PO_4/H_2O/heat}$ ethanol $\xrightarrow{Cr_2O_7^{2+}/H^+/heat}$ ethanoic acid

ethanoic acid + butan-1-ol $\xrightarrow{H_2SO_4}$ butyl ethanoate + water

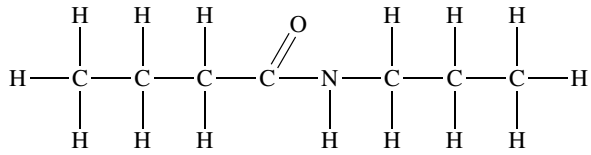
5 **a**



b



6 **a** substitution and condensation
b amide



7 D

Chapter 10 Organic materials: structure and function

10.1 Amino acids

1 **a** asparagine **b** tyrosine **c** aspartic acid **d** methionine

2 Nine out of the 20 amino acids required by the body cannot be manufactured in the body. They must be provided by the food we eat.

3 Animal protein provides all the essential amino acids required by the human body. Vegetable protein is often deficient in one or more essential amino acids.

4 **a** pH greater than 7 **b** $H_2N–CH(R)–COO^-$

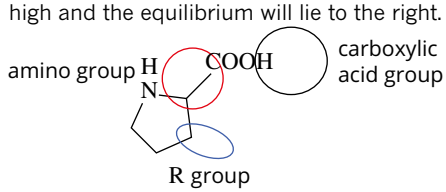
5 The carboxyl group is carbon number 1. Therefore, the amino group is not attached to carbon number 2, rather it is attached to carbon number 3.

6

Structure of R group	Is the R group polar or non-polar?	Is the R group acidic, basic or neutral?
$–CH(CH_3)_2$	non-polar	neutral
$–CH_2COOH$	polar	acidic
$–CH_2C_6H_5$	non-polar	neutral
$–(CH_2)_4NH_2$	polar	basic

7 $^+H_3N–CH(CH_2SH)–COO^-(aq) + H_3O^+(aq) \rightleftharpoons {}^+H_3N–CH(CH_2SH)–COOH(aq) + H_2O(l)$
For cysteine to form a cation it needs to be in a solution with pH lower than 7. In such a solution, the concentration of H_3O^+ ions is high and the equilibrium will lie to the right.

8



The R group is non-polar.

9 Glutamic acid has a carboxylic acid in its R group, which will be protonated at pH 6 and so it is likely to be neutral. Lysine has an amino group in its R group, which will be protonated at pH 6 so it will be positively charged. Thus, the lysine will be attracted to the negative charge of the resin's side chain slowing its movement through the column.

10.2 The formation of proteins

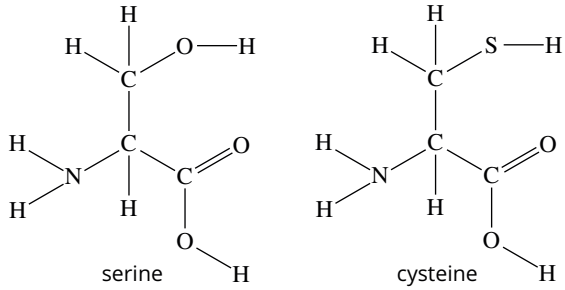
1 tripeptide: three amino acids joined by peptide links in a polypeptide chain
R group: variable part of an amino acid
polypeptide: several amino acids that are joined by peptide links
amino group: functional group present in all amino acids
water: by-product of the reaction that produces polypeptides

2 **a** hydrolysis **b** A is H_2O; B is $H_2NCH(CH_3)COOH$; C is $H_2NCH(CH(CH_3)_2)COOH$

3 **a** A—amino group; B—peptide or amide link or bond or group; C—R group; D—carboxyl group
b alanine, serine, leucine

4 2-amino acids contain both an amino functional group and a carboxyl functional group, thus they can undergo condensation reactions with each other that link them in a chain.

5 **a**

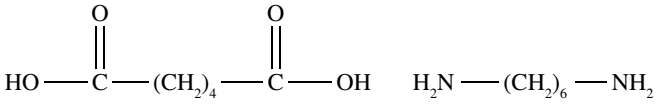


b $H_2NCH(CH_2OH)CONHCH(CH_2SH)COOH$ and $H_2NCH(CH_2SH)CONHCH(CH_2OH)COOH$

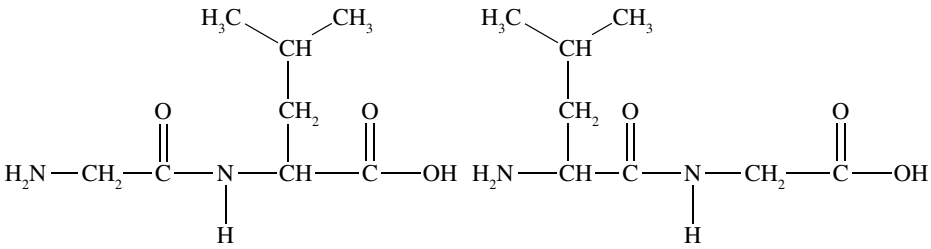
c $H_2NCH(CH_2OH)COOH + H_2NCH(CH_2SH)COOH \rightarrow H_2NCH(CH_2OH)CONHCH(CH_2SH)COOH + H_2O$. It is called a condensation reaction.

6 **a** six **b** five

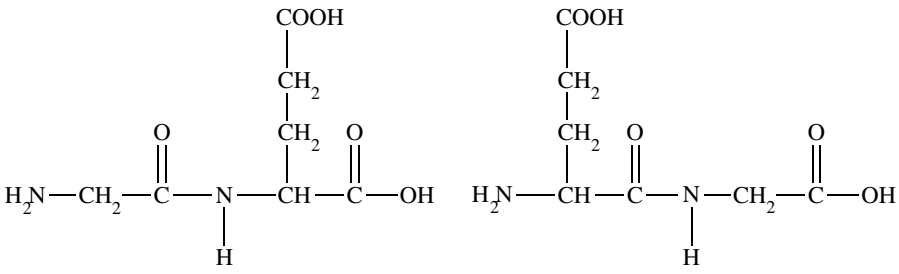
7 amide (peptide) group

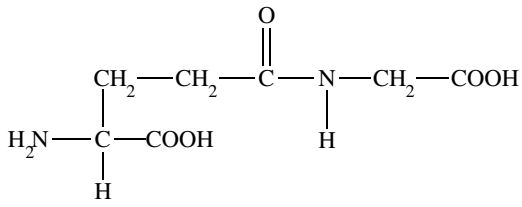


8 Glycine and leucine each have one amino group and one carboxylic acid group in their structures so can form the dipeptides shown below.



Glutamic acid has two carboxylic acid groups as well as its amino group. The amino group of glycine can react with either of the two carboxylic acid groups in glutamic acid so a third dipeptide is possible, as shown below.





10.3 Structures of proteins

1 9, peptide/amide, condensation polymerisation, alanine, lysine, glycine, valine, methionine

2 **a** α-helix

b α-helices result from hydrogen bonding in different regions of the amino acid sequence. In this case, the hydrogen bonds arise due to the attraction between the partial positive charge on the H of an –N–H bond in a peptide link with the partial negative charge on the O of a –C=O bond of a peptide link that is four amino acid units along the chain.

3

Bond type	Required components in R group	Amino acid examples
hydrogen bonds (can also have dipole–dipole interactions and dispersion forces but these are not dominant)	contains –O–H, –N–H and –C=O	serine, threonine, histidine
dipole–dipole interactions (can also have dispersion forces but these are not dominant)	any polar group such as those containing –S–H, –O–H or –N–H	cysteine, asparagine
ionic interactions	contains $-NH_3^+$ and another group that contains $-COO^-$	aspartic acid, glutamic acid, lysine, arginine
covalent cross-links	cysteine side groups react to form a disulfide bridge (–S–S–)	cysteine
dispersion forces	any non-polar group	alanine, leucine, phenylalanine

4 The sequence of amino acids gives proteins their unique shape. As protein shape is related to function, determining this sequence allows scientists to understand more about the role of specific proteins.

5 For the hydrogen bond interactions between the H of an –NH and O of –C=O to maximise, these groups need to be able to get close. Smaller R groups allow this close interaction.

6 α-helices result from the interaction between the hydrogen on the amino group and the oxygen of the carbonyl group of a peptide link specifically four amino acids along in the chain, causing a hydrogen bond to form. β-pleated sheets are also formed from hydrogen bonds between peptide links in regions where two or more parts of the polypeptide chain line up parallel to each other.

7 The polypeptides in globular proteins will include amino acids with polar side chains, including those capable of forming hydrogen bonds. When the polypeptide chains fold they do so in a way that places the polar side chains on the outside. These side chains can then form dipole–dipole or hydrogen bonds with water molecules, thus making the protein soluble in water.

8 Ionic attractions in proteins occur when the functional groups $-NH_2$ and –COOH become charged to form $-NH_3^+$ and $-COO^-$ within a specific pH range. Outside this range these functional groups lose their ionic charge and so the ionic bond will be broken.

10.4 Action of enzymes

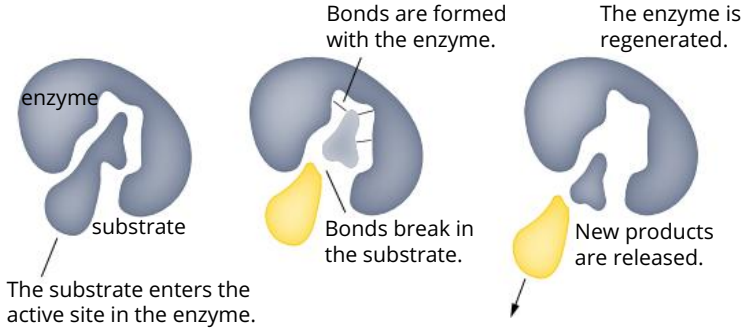
1 **a** both **b** enzymes **c** enzymes **d** both **e** both

2 the specific part of the enzyme molecule with which a reactant (substrate) can interact

3 **a** true **b** true **c** false **d** true **e** false

4 The shape of an enzyme is critical in determining its function, and as enzymes are proteins, their three-dimensional shape is affected by pH and temperature. A change in pH and/or temperature will disrupt the attractions in the protein (enzyme) that determine its tertiary shape.

5 **a**



b hydrogen bonds, ion–dipole interactions, dipole–dipole interactions, ionic interactions

6 The lock-and-key model implies a fixed shape, while the induced fit model better reflects the observed flexibility of the active site.

7 The enzyme activity is maximised at around 37–40°C because this is the temperature of the human body. The activity outside this temperature range diminishes. Outside the range 37–40°C the attractive forces that hold the enzyme in its three-dimensional shape are disrupted so it loses its shape and therefore its enzymatic activity.

8 Fumarate and maleate are geometrical isomers and have different three-dimensional shapes. The active sites of enzymes have a specific shape so only a substrate with the correct shape can bind to the active site. Maleate will not have the correct shape to bind to the active site of the fumarase enzyme and so will not react.

9 Four

10 In both models, the enzymes have an active site that binds with a substrate, and an enzyme is specific to one substrate or reaction type. In the lock-and-key model the active site has a fixed shape that does not change when it binds to the substrate. In contrast, in the induced fit model the active site is flexible, changing shape slightly to accommodate binding of the substrate. When the products leave the active site, the enzyme returns to its original shape.

11 Glycine is the smallest of the amino acids; the side chain is an H atom. With each third amino acid in the primary sequencing being glycine, the hydrogen bonds in the α-helices are shorter than when there is a larger side chain. The absence of large side chains also means the α-helices can be straight.

10.5 Fats and oils

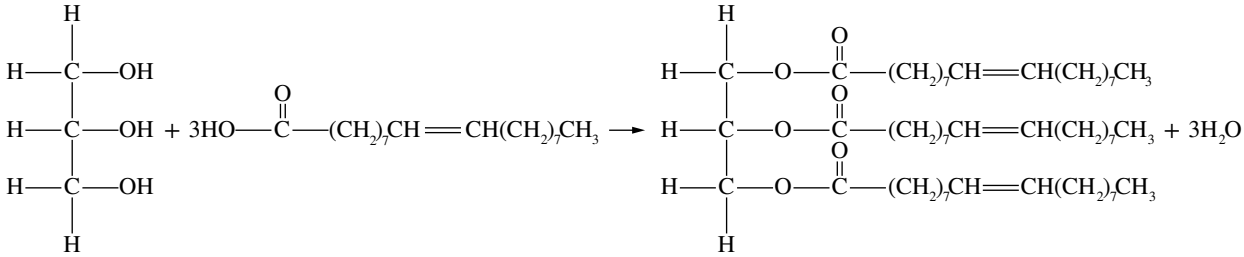
1 hydroxyl and carboxyl

2 saturated fatty acids—have hydrocarbon chains that contains only single carbon–carbon bonds; monounsaturated fatty acids—contain one carbon–carbon double bond in their hydrocarbon chain; polyunsaturated fatty acids—contain more than one carbon–carbon double bond in their hydrocarbon chain

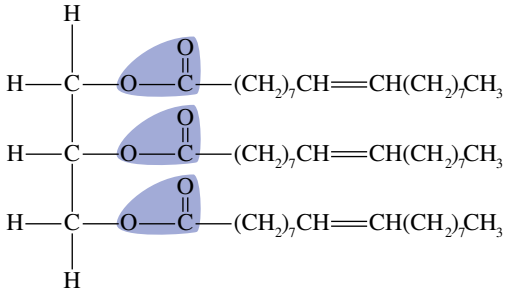
3 dispersion forces

4 because humans can only obtain it through the food we eat

5 **a**

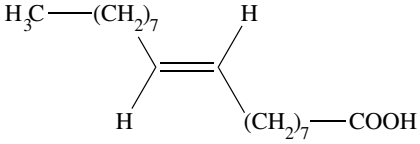


b

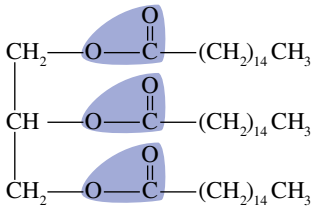


6 Saturation will allow the hydrocarbon chains in the fats to interact more closely by removing the 'kink' present when there is a double bond in the chain. This will increase the strength of the intermolecular forces between neighbouring chains and so increase the melting point of the substance.

7



8 **a**



b The fat is saturated because the alkyl groups in the molecules ($CH_3(CH_2)_{14}$) contain only single carbon–carbon bonds. Alkyl groups with the general formula C_nH_{2n+1} are saturated.

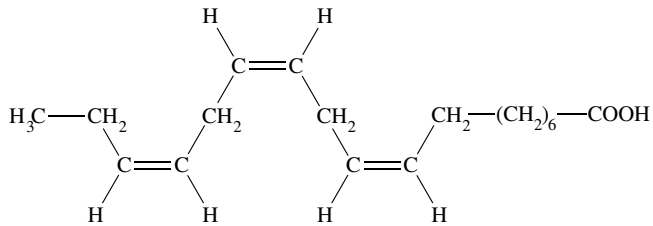
9 **a** saturated **b** monounsaturated **c** saturated
d polyunsaturated **e** polyunsaturated **f** saturated
g saturated
h monounsaturated

10 E < F < C < D < B < A
A and B are both saturated fatty acids so their hydrocarbon chains have only C–C single bonds, while C, D, E and F are unsaturated fatty acids so their hydrocarbon chains include one or more C=C double bonds. The hydrocarbon chains in A and B can interact more closely than the hydrocarbon chains in C, D, E and F, so A and B have stronger dispersion forces and, in turn, higher melting points. A has a higher melting point than B because it has a hydrocarbon chain of 20 carbon atoms compared to the 12 in B. C and D each have one C=C double bond, while F has three and E has four C=C double bonds. As a result, C and D will not have as many bends in their hydrocarbon chains, which allows their chains to interact more closely. This gives them higher melting points than E and F. C has a lower melting point than D because it has 16 carbon atoms in its chain compared to the 20 in D's chain. The four C=C double bonds in E make its chain more bent than F with its three C=C double bonds and so E's chains are less able to interact and has the lower melting point.

11 Omega-3 fatty acids are polyunsaturated fats so have relatively low melting points and will remain liquid at the cold ocean temperatures in which fish live. Saturated fats would solidify in the fish's body.

12 Margarine contains a higher proportion of unsaturated fats, while butter mainly contains saturated fats. Unsaturated fats contain C=C double bonds that can react with oxygen in the air, while the saturated fats contain only C–C single bonds that react very slowly with oxygen. It is the products from the reaction with oxygen that make the margarine rancid.

13 Two of the three double bonds are drawn as *trans* double bonds but all three should be *cis* double bonds.



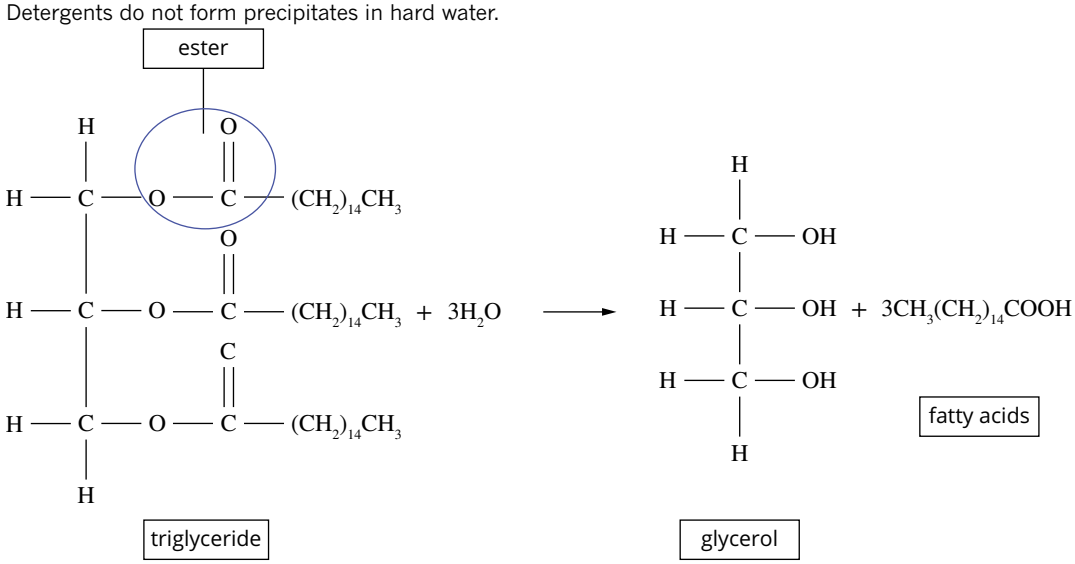
10.6 Soaps

1 triglyceride, base hydrolysis, salt, fatty acid, glycerol

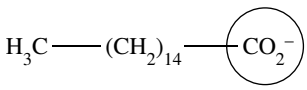
2 B, C, A

3 Detergents do not form precipitates in hard water.

4



5



6 Hard water contains Ca^{2+} and/or Mg^{2+} ions. When a soap ion is placed in hard water a precipitation reaction occurs with the Ca^{2+} and/or Mg^{2+} to produce a scum.

7 Oil dispersants will have a structure similar to soaps and detergents—a non-polar hydrocarbon chain and a charged end. The non-polar portion of the dispersant will dissolve in the oil and the charged end will dissolve in water. Droplets will form with the non-polar portion of the dispersant dissolved in oil surrounding the droplet and the charged end oriented towards the water.

8 Three soap molecules are formed: $CH_3(CH_2)_7CHCH(CH_2)7COO^-Na^+$, $CH_3(CH_2)_4CHCHCH_2CHCH(CH_2)_7COO^-Na^+$ and $CH_3(CH_2)_{14}COO^-Na^+$.

9 Both types of hydrolysis break the ester linkage of the triglyceride between the C–O bond, and both include glycerol as a product. Both reactions can be described as the reverse of a condensation reaction between a fatty acid and glycerol. Triglyceride hydrolysis in the body is catalysed by an enzyme (called a lipase enzyme), while saponification is not catalysed (although the hydroxide ion speeds the hydrolysis as it is consumed in the reaction). Saponification produces the sodium (or potassium) salt of a fatty acid while lipase-catalysed hydrolysis produces a fatty acid.

10 The hydroxide is consumed in the reaction; catalysts speed a reaction without being consumed.

11

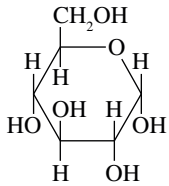
Feature of soap	Feature of detergent	Feature of both
• forms a scum in hard water • produced from renewable resources	• does not form a scum in hard water • produced from petroleum	• contains a hydrocarbon chain • forms micelles • is a surfactant • contains a charged end • contains a metal ion

10.7 Carbohydrates

1 C, D, E and F

2 **a** cellulose **b** glycogen **c** starch **d** lactose

3 The glucose molecule has five polar OH groups that form hydrogen bonds with water. As a result, glucose is highly soluble in water.



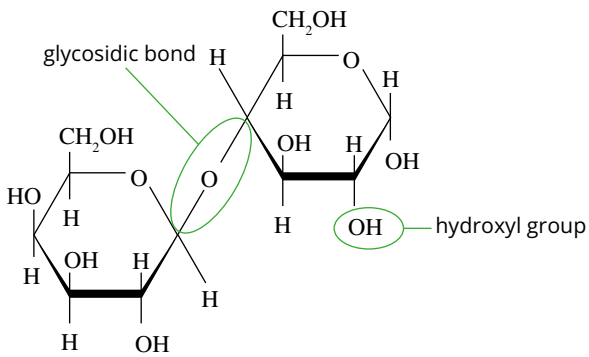
glucose

4 **a** Glucose is a monosaccharide. Maltose is made up of two monosaccharide molecules bonded together. Starch is a polymer of monosaccharide molecules.

b condensation **c** hydroxyl

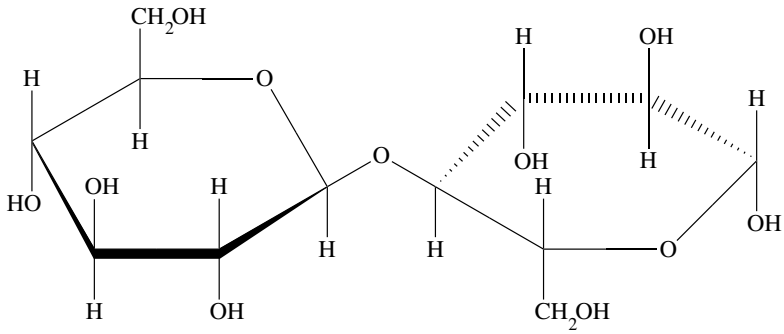
5 **a** A hydrolysis reaction is one in which water is a reactant.

b



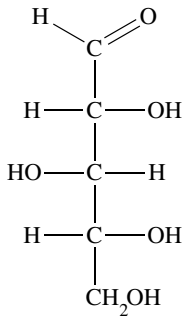
6 The orientation of the hydroxyl group on the first carbon in α-glucose points 'downwards' and in β-glucose it points 'upwards'.

7



8 **a** $C_5H_{10}O_5$

b



Chapter 11 Analysis of organic compounds

11.1 Chromatography

TY 11.1.1 R_f (fructose) = 0.60. The lolly contains fructose.

TY 11.1.2 3.0 μg mL^{-1}

1 The component at the top has a greater rate of adsorption and desorption than components at the bottom.

2 $R_f = \frac{\text{distance the component travels from the origin}}{\text{distance the solvent front travels form the origin}}$

3 **a** solvent, paper **b** solvent, layer of fine powder onto plate
c water/ethanol, alumina/silica

4 An HPLC instrument does not directly produce measurements of concentration. R_t indicates the identity of components in a mixture. A calibration curve can then be used to determine the concentration of the component.

5 **a** retention time **b** retention time **c** area under the peak

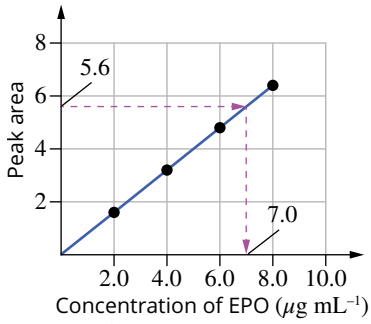
6 **a** A, B, C, D **b** D, C, A, B

7 Both identify the components of a mixture, whereas the thin-layer chromatography is more sensitive and is capable of greater resolution. A wider range of solvents can be used in thin-layer chromatography for further analysis.

8 serine, threonine, valine

9 **a** **i** two **ii** purple
iii A and B
b R_f (orange spot) = 0.28, R_f (green spot) = 0.83

10 **a**



b 7.0 μg mL^{-1}

11 **a** A: 0.60
B: 0.48
C: 0.38
D: 0.20
E: 0.10
b A: leucine and/or isoleucine
B: phenylalanine
C: proline and/or valine and/or tyrosine
D: threonine and/or hydroxyproline and/or serine and/or glycine
E: lysine and/or isoleucine
c A: leucine and/or isoleucine
B: phenylalanine
C: proline
D: serine
E: arginine
d In the second run the two solvents could not clarify the identity of A but did help identify C, D and E. A two-way chromatogram produces better separation of components of complex mixtures, permitting easier isolation and identification.

12 **a** stationary phase = powdered alumina; mobile phase = water or ethanol
b 7.5 cm
c The R_f values would not change. The movement of the component and solvent front both increase by the same proportion so there is no change in the R_f.
d taurine and glycine

13 **a** Obtain chromatograms of the athlete's blood sample and standard solutions of testosterone. Use R_t values to identify the testosterone peak on the chromatogram of blood. Measure the testosterone peak areas. Construct a calibration curve and mark the blood testosterone peak area on it. Determine testosterone concentration in the blood sample.
b 48.0 ng L^{-1}

14 2.7%

11.2 Electrophoresis

TY 11.2.1 George

1 **a** a technique used to sort protein fragments according to size
b It is useful in separating and estimating the size of proteins.

2 substances that have the ability to act as either an acid or base

3 A protein ladder is a set of protein standards, protein molecules of known size or charge. It is used for comparison and to estimate the size of protein fragments in samples being tested.

4 Charge must be removed as a factor. SDS is put in the gel buffer and in the sample buffer to give the proteins an overall negative charge. SDS also gives proteins identical charge to mass ratios, thus removing charge as a factor in migration.

5 **a** number 1 is the longest protein fragment in the protein standard; number 2 is the shortest protein fragment in the protein standard
b E2 **c** towards the positive electrode
d **i** six **ii** two **iii** two
e sample A fragments are 500 kDa and 400 kDa; sample B fragments are 400 kDa and 200 kDa

6 **a** all samples
b Sample C will inhibit coagulation more than sample A or B, as it contains two proteins that inhibit coagulation, whereas the other samples only contain one protein. Thus, sample C will be more venomous.
7 **a** Gamma globulin is the smallest protein fragment because it travelled the furthest down the gel.
b albumin, alpha-1, alpha-2, beta and gamma
c albumin
d Alpha-2 blue band will have a more intense colour as the concentration will increase. The gamma globulin band colour will be less intense as concentration decreases.

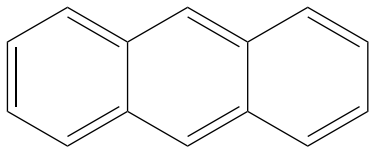
11.3 Mass spectrometry

TY 11.3.1 C_4H_{10}, butane

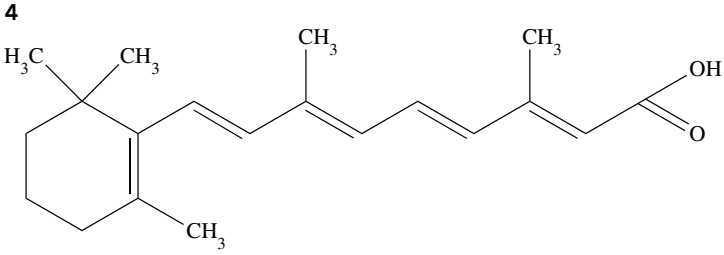
1 **a** a whole molecule with an overall positive or negative charge
b the highest intensity peak in a mass spectrum
c the mass of an ion relative to the charge of the ion which determines the deflection in the mass spectrometer
2 the compound contains isotopes
3 $C_2H_4{}^{79}Br_2{}^+$, $C_2H_4{}^{79}Br^{81}Br^+$, $C_2H_4{}^{81}Br_2{}^+$
4 **a** A molecule composed entirely of carbon, in the form of a hollow sphere or tube. Each carbon is bonded to three other carbon atoms.
b The two main peaks are C_{60} and C_{70} buckyballs (spherical fullerenes).
c The smaller peaks represent other fullerenes (allotropes) of carbon.
5 **a** $114\,g\,mol^{-1}$ **b** 43 **c** $C_6H_{13}{}^+$ **d** octane, C_8H_{18}
6 **a** C_3H_7Br
b the molecular ion containing Br, which might be due to the presence of ^{79}Br and ^{81}Br isotopes
c The two isotopes of bromine, ^{79}Br and ^{81}Br, are found in almost equal abundances so the peaks are almost equivalent in height.
d $CH_3CH_2CH_2{}^+$
7 **a** ethanamide **b** butanone
8 **a** 42 **b** $42\,g\,mol^{-1}$ **c** C_3H_6, propene

11.4 X-ray crystallography

TY 11.4.1



1 Single molecules are too small to be used and crystals contain a three-dimensional periodic array of molecules. This amplifies and simplifies the diffraction image.
2 X-rays have a shorter wavelength. The wavelength is close to the same length as the distance between atoms in molecules.
3 X-rays interact with electrons in the molecules. The diffraction image contains information about where the electrons are in the structure. Electron density describes how many electrons are at a given atomic position.
4



5 grow perfect crystals → diffraction pattern → electron density map → identification of organic structure
6 X-ray crystallography can be used in stereochemistry to reveal the relative position of atoms in space, bond length and distance between atoms.

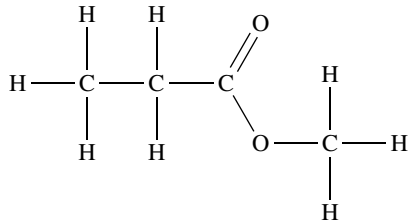
11.5 Infrared spectroscopy

TY 11.5.1 carbonyl group and C–H groups

1 **a** O–H at 3200–3600 cm^{-1} and C–O at 1050–1410 cm^{-1}
b N–H at 3300–3500 cm^{-1} and C=O at 1700–1750 cm^{-1}
c N–H at 3300–3500 cm^{-1}
d O–H at 2500–300 cm^{-1}, C=O at 1700–1750 cm^{-1} and C–O at 1050–1410 cm^{-1}
e C=O at 1700–1750 cm^{-1} and C–O at 1050–14100 cm^{-1}
f C=O at 1700–1750 cm^{-1}
2 Absorption bands are the inverted peaks in an infrared spectrum that represent the frequencies of infrared radiation absorbed by specific bonds. The fingerprint region is the part of the infrared (IR) spectrum below 1400 cm^{-1} that is unique to a particular molecule.
3 All alcohols and acids contain an O–H corresponding to a peak at 3000 cm^{-1}, which is absent from the other molecules.
4 The absorption bands from C–O and C–C bonds are located in the fingerprint region below 1400 cm^{-1}. Many molecules contain these bonds in various functional groups, and so they give few clues to the structure of a compound. The exact wavenumber of C–O and C–C absorption bands are highly specific to an individual molecule and can be used to compare the molecule to a reference standard for positive identification.
5 The spectrum shows absorption bands corresponding to the presence of N–H amine group, C=O carbonyl group, C=C and C–H groups.
6 **a** The IR spectrum is analysing the sample for ethanoic acid. Ethanoic acid will have O–H (2500–3000 cm^{-1}) and C=O (1700–1750 cm^{-1}) functional groups as well as bands due to C–O (1050–1410 cm^{-1}), C–H (2720–3100 cm^{-1}), masked by O–H and C–C (750–1100 cm^{-1}) bonds.
b Yes. The IR spectrum shows absorption bands for C=O at approximately 1700 cm^{-1} and a broad band for O–H at about 3000 cm^{-1}. The police will be able to find the concentration of the sample by comparison with a standard calibration curve of known concentration.
7 sample A is propanoic acid, sample B is propanone
8 ethanol

11.6 Spectral analysis of organic compounds

TY 11.6.1 methyl propanoate



1 infrared spectroscopy
2 More information is available to work out the structures. The components in a sample can be separated and the structure of each component can be determined.
3 Strong absorption around 1750 cm^{-1} is consistent with the presence of C=O. A strong peak at 3000 cm^{-1} corresponds to the absorption of a –CH bond (it cannot be due to an OH of a carboxylic acid because the formula only contains one oxygen). It must be a ketone; the structural formula is butan-2-one.
4 propanoic acid

Chapter 12 Chemical synthesis

12.1 Reaction pathways

1 a synthetic route where chemists start planning how to make the target molecule by working backwards to simpler, commercially available molecules
2 **a** The overall yield of a product is important when considering the economic and environmental implications of the reaction. Since reactions are very rarely 100% efficient, typically the greater the number of steps involved in the synthetic pathway the lower the overall yield.

b The efficacy of the chemical is related to how much of the chemical is present in the final product. Furthermore, an impurity may have a harmful effect, as was the case with thalidomide where the wrong enantiomer caused horrific birth defects.

c The yield of an equilibrium reaction is related to the position of the equilibrium. To increase the yield of a reaction the conditions should be analysed to shift the equilibrium as far towards the product side of the reaction, taking into account the rate of the reaction and cost of the industrial equipment required.

3 **a** $CH_3CH_2CH_2NH_2 \Rightarrow CH_3CH_2CH_2Cl \Rightarrow CH_3CHCH_2$

b $CH_3CH_2CH_2NH_2 \Rightarrow CH_3CH_2CN \Rightarrow CH_3CH_2Cl \Rightarrow CH_3CH_3$

4 pathway b

12.2 Modifying chemical properties

1 a biologically inactive derivative of a compound that is metabolised through chemical reactions or enzymes into the active form of the drug

2 The structure might be altered to reduce the unwanted side effects, improve how the compound is absorbed either once it has entered the blood or to improve its solubility, or improve its mode of action.

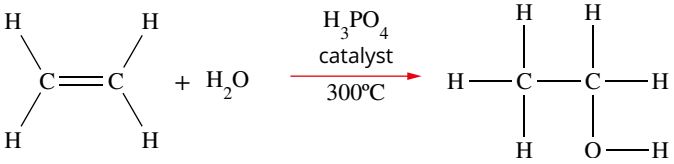
3 Water is a polar molecule that is strongly attracted to other water molecules. These intermolecular forces act inwards at the water surface pulling the molecules inwards and creating a surface tension. Detergents have a hydrophilic head and hydrophobic tail. At the surface, the hydrophobic tails are pushed between the water molecules reducing the intermolecular forces at the surface and therefore reducing the surface tension.

4 The active form of the drug is salicylic acid. Aspirin is the ester of the acid, where the –COOH group has been converted to a –COOR. In the body the ester is hydrolysed in acidic conditions in the stomach back to the –COOH group.

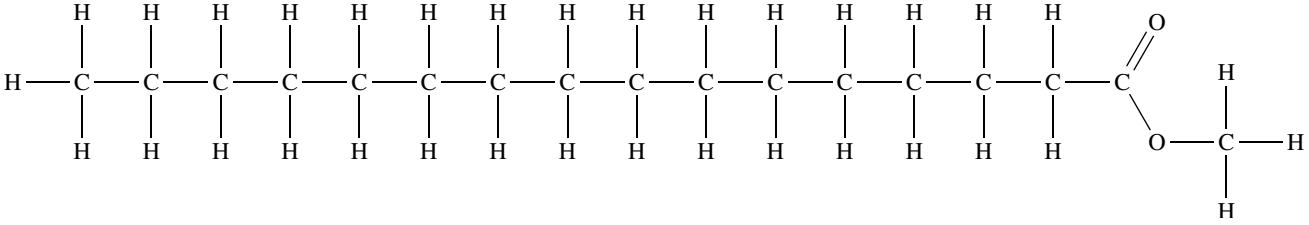
5 Structure b is more soluble due to the phosphate ion group that has replaced the OH group.

12.3 Synthesis of fuels

1 Industrially, ethanol is produced by the acid-catalysed reaction of steam with ethene.



2



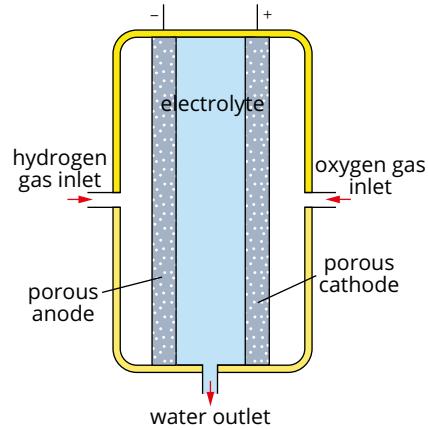
3 Biodiesel is manufactured from plants and other renewable crops, whereas petrodiesel is derived from crude oil. As long as the crops can be grown there is a continual supply of biodiesel. Also, depending on the crop from which the biodiesel is produced, there may be fewer pollutants.

4 In the laboratory, ethanol can be synthesised by either a base-catalysed substitution reaction involving a halothane or the acid-catalysed addition of water to ethene. The base-catalysed substitution competes with an alternative elimination pathway that forms ethene. This is controlled by the temperature of the reaction. In the industrial-scale process the substitution reaction is not viable as it would result in a mixture of products and so reduce the overall yield of the reaction and increase the number of products formed.

12.4 Fuel cells

1 a type of galvanic cell that generates electricity from redox reactions quietly and efficiently, and with almost no pollution; they do not run down or need recharging

2



3 **a** anode (oxidation): $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$
cathode (reduction): $O_2(g) + 4H^+(g) + 4e^- \rightarrow 2H_2O(l)$

b anode (oxidation): $H_2(g) + 2OH^- \rightarrow 2H_2O(l) + 2e^-$
cathode (reduction): $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

4 The overall equation for the reaction under either acidic or alkaline conditions is the same:
$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

5 **a** arrow A **b** O_2

c $4Al(s) + 3O_2(g) + 6H_2O(l) \rightarrow 4Al^{3+}(aq) + 12OH^-(aq)$

d A porous electrode will allow a large surface area for this reaction and thereby maximise the rate of reaction and hence the current/power output of the cell.

e cathode reaction: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ $E° = +0.40\,V$

anode reactions: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E° = -0.76\,V$

$Ag(s) \rightarrow Ag^+(aq) + e^-$ $E° = +0.80\,V$

Since $E°(Zn^{2+}/Zn) < E°(O_2, H_2O/OH^-)$ a spontaneous cell reaction will occur.

Since $E°(Ag^+/Ag) > E°(O_2, H_2O/OH^-)$ a spontaneous cell reaction will not occur.

f smaller, since $E°(Zn^{2+}/Zn) > E°(Al^{3+}/Al)$

$E°(O_2, H_2O/OH^-) - E°(Zn^{2+}/Zn) = (+0.40) - (0.76) = 1.16\,V$

$E°(O2, H_2O/OH^-) - E°(Al^{3+}/Al) = (+0.40) - (1.71) = 2.10\,V$

g With an acidic electrolyte:

cathode reaction: $O_2(g) + 4H^+(aq) - 4e^- \rightarrow 2H_2O(l)$ $E° = +1.23\,V$

anode reactions: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E° = -0.76\,V$

$Ag(s) \rightarrow Ag^+(aq) + e^-$ $E° = +0.80\,V$

Since $E°(Zn^{2+}/Zn) < E°(O_2, H^+/H_2O)$ a spontaneous cell reaction will occur.

Since $E°(Ag^+/Ag) < E°(O_2, H^+/H_2O)$ a spontaneous cell reaction will occur.

12.5 Industrial chemistry

1 if an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of the change

2 Step 1—the production of sulfur dioxide: $S(s) + O_2(g) \rightarrow SO_2(g)$

Step 2—a reversible reaction that converts the sulfur dioxide into sulfur trioxide: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -196\,kJ\,mol^{-1}$

Step 3—the conversion of the sulfur trioxide into concentrated sulfuric acid: $SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$

$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(aq)$

3 As there is a total of four gaseous molecules on the left-hand (reactant) side of the equilibrium, but only two gaseous molecules on the right-hand (product) side, increasing the pressure will cause a shift to the right and increase the amount of ammonia present at equilibrium.

Because the forward reaction in the Haber process is exothermic, decreasing the temperature will shift the equilibrium in the direction of the exothermic forward reaction; thereby increasing the equilibrium yield of ammonia.

4 A catalyst increases the rate of the forward and reverse reactions by the same amount and so increases the rate at which the equilibrium is established but does not shift the position of the equilibrium.

5 The reaction is exothermic.

6 **a** **i** increase **ii** increase

b In practice, satisfactorily high equilibrium yields of sulfur trioxide can be obtained without needing to use high pressures, which would involve more expensive equipment.

c The purpose of recycling the gases from the absorption tower is to increase the yield of sulfur trioxide and to minimise emissions of sulfur oxides, which act as pollutants.

d The rate of reaction and the magnitude of K_c.

7 **a** not at equilibrium; system will shift to the left

b not at equilibrium; system will shift to the right

8 As the reaction is an exothermic process, the gases are cooled before being pumped back into the reaction system to maximise equilibrium yield. Pumping hot gases into the reaction mixture would cause the temperature to rise and favour the back reaction, reducing the yield of ammonia.

9 Temperatures higher than 200°C are required to obtain an acceptably fast rate of reaction.

12.6 Use of enzymes in industry

1 a molecule that speeds up the rate of a reaction by providing an alternative pathway with a lower activation energy

2 transesterification

3 no soap formation, being able to esterify both fatty acids and the triglycerides in a single step, the production of a higher quality glycerol, the ability to transesterify triglycerides of different quality, lower energy consumption

4 Changes to pH or temperature can disrupt the intermolecular forces that create the α-helix and β-pleated sheet folding as well as the tertiary structure within an enzyme. Extremely high or low pH values generally cause complete loss of activity for most enzymes.

5 Because they are capable of catalysing the transesterification of fats to produce biodiesel at lower temperatures the energy cost of the production is reduced.

6 The fermentation of glucose to ethanol by yeast can occur with or without oxygen. However, once the ethanol is produced, the primary alcohol could be oxidised in the presence of oxygen to ethanoic acid.

7 Enzymes share similar features to inorganic catalysts in that they work by providing an alternative reaction pathway that has a lower activation energy. Unlike inorganic catalysts, enzymes are often specific for a particular reaction and operate within very narrow conditions.

In general, enzymatic catalysis has a number of benefits over traditional chemical catalysis because enzymes:

- have a high catalytic power
- work under mild conditions of temperature, pH and pressure
- display high specificity for the substrate can perform well in organic solvents.

12.7 Yield and the chemical industry

TY 12.7.1 55.8% **TY 12.7.2** 43.2%

1 percentage yield $= \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$

2 The theoretical yield is the maximum amount of the product that can be formed based on the stoichiometric mole ratios of the limiting reagent. The actual yield is the amount of the product actually produced. The actual yield cannot be greater than the theoretical yield.

3 **a** 31.5% **b** 6.3%

4 247 g

5 82.5%

12.8 Green chemistry

TY 12.8.1 55.2%

1 **a** The use of renewable raw materials means that the process is sustainable as the raw materials can be replaced.

b Since most chemical reactions produce some unwanted by-products, it is better if these substances have little or no toxicity to either humans or the environment.

2 a measure of how many of the atoms in the reactants end up in the desired product; if the atom economy of a reaction is high, then there are few, if any, waste products

3 Green chemistry aims to increase the atom economy of chemical processes by providing a set of principles that aim to produce chemicals that are less hazardous to human health and the environment, reduce our dependency upon non-renewable resources and produce less waste material.

4 Since catalysts are not used up in a reaction they only need to be used in small quantities. This means that less reactants need to be used. In addition, the use of catalysts means that the reaction can proceed at the same rate at a lower temperature than if the catalyst was not used. This increases the energy efficiency of the reaction since energy does not have to be used to heat the reaction vessel.

5 b is the greener pathway

6 2.61 kg

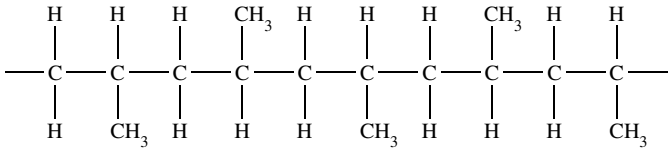
Chapter 13 Macromolecules: polymers, proteins and carbohydrates

13.1 Types of polymers

1 process by which polymers are made from many smaller molecules called monomers

2 –[O – $(CH_2)_2$ – OCO – (C_6H_4) – CO] –

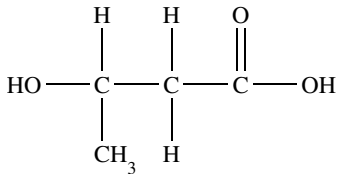
3



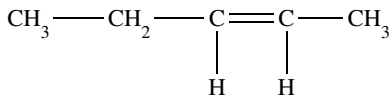
4 Monomers that form addition polymers must contain a double bond, whereas condensation polymers come from monomers containing functional groups that can join together by means of a condensation reaction.

5 HO – $(CH_2)_n$ – OH and HO_2C $(CH_2)_m$ – CO_2H
or
HO – $(CH_2)_n$ – CO_2H

6 **a**



b



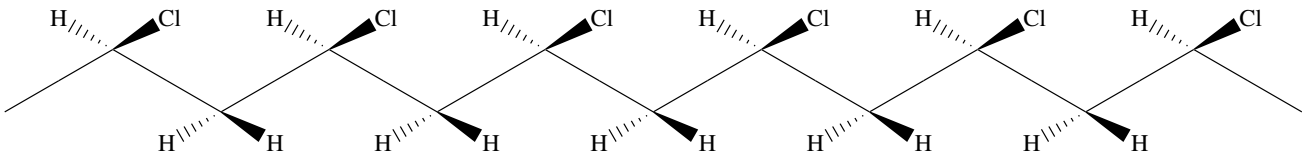
7 **a** Does not contain any functional groups so is an addition polymer. Therefore, the monomer needs to contain a double bond:
$CH_2 = CH_2$

b Contains two functional groups, amine and carbonyl groups, and is therefore formed by a condensation reaction between the two ends of the molecule. A possible monomer is:
$HO_2C – CH(CH_3)NH_2$

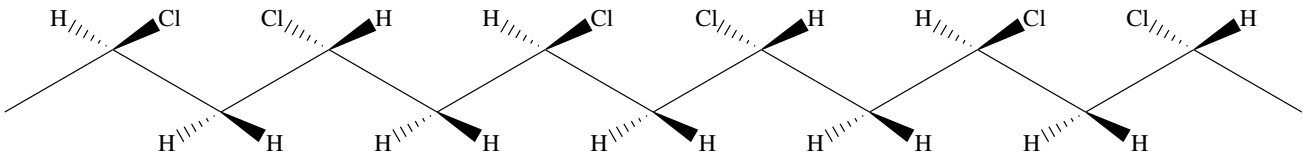
c Contains two different functional groups, amine and carbonyl groups, that are joined by an amide linkage and is therefore formed by a condensation reaction. The monomer could be the whole of the bracket; however, the two monomers could be:
$H_2N(CH_2)_6NH_2$ and $HO_2C(CH_2)_4CO_2H$

8 The terms apply to polyvinyl chloride, as shown.

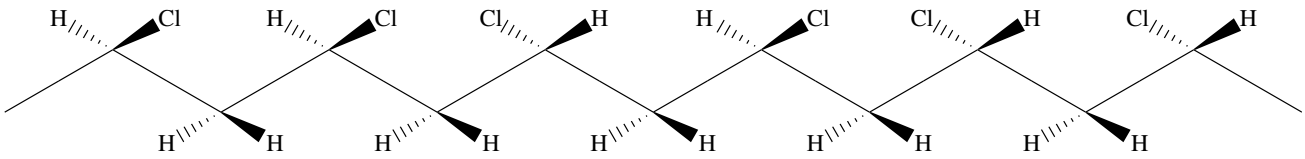
isotactic PVC



syndiotactic PVC



atactic PVC

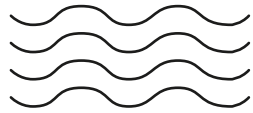


13.2 Properties of polymers

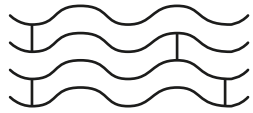
1 polymers with special cross-links that allow them to stretch

2 polymer that is made from more than one monomer

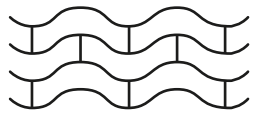
3 **a** **i**



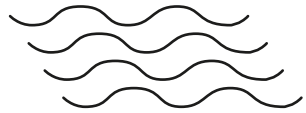
ii



iii

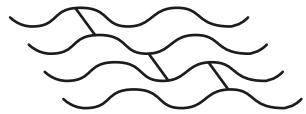


b **i**



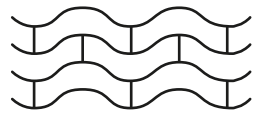
polymer easily stretched

ii



some stretching but polymer tends to return to its original shape

iii



no stretching possible

4 The covers of electrical cables must be flexible, non-conducting, strong, have high melting points and low flammability. Since PVC has no free charged particles it is non-conducting. The chlorine atom is more electronegative than the carbon atom it is bonded to and so PVC contains a dipole resulting in strong intermolecular forces between neighbouring PVC chains. This increases the strength of the PVC polymers and raises its melting point. PVC contains strong bonds that do not burn easily and it produces chemicals that extinguish flames when burned. PVC is plasticised to make it flexible.

5 A polymer is thermoplastic if it will soften when heated, allowing it to be reshaped. A thermoplastic polymer can be recycled by moulding it into a new shape. Thermoplastic materials have no strong bonds between polymer chains. They char on heating.

6 **a** the polymer used in saucepan handles

b Saucepan handles are much harder and more resistant to the effect of heat than elastic bands. The polymer on the outside of the golf ball is also very hard, but, unlike the polymer in saucepan handles, is quite elastic.

7 The relative molecular mass would have increased. The melting point of the polymer would have increased. The overall strength of interchain forces would have increased. The electrical conductivity of the polymer would have remained the same.

Chapter 14 Molecular manufacturing

14.1 Designer chemicals

1 **a** top-down **b** bottom-up **c** bottom-up **d** bottom-up

2 a situation where the forced physical proximity of two chemical species promotes a reaction between the two molecules

3 The shape of the molecule determines it reactivity. Its binding site(s) will allow certain reactions to proceed via the orientation effect.

4 Researchers can synthesise DNA strands of a predetermined sequence. This means that the folding and shape of the molecule can be predicted. Nucleotide sequences will bind to the complementary sequence and so associations will form and can be modified (e.g. DNA walking). DNA is compatible with the human body and can therefore be used as nanorobots.

5 Hydrogen bonding is an electrostatic attraction between a hydrogen atom on one area of a molecule, and a fluorine, oxygen or nitrogen atom on another area or molecule. It is not as strong as a covalent bond and can be broken. By adding heat energy, the structures will have greater kinetic energy (vibrate more) and the hydrogen bond will break when this energy is great enough.

6 Peptides are made in nature by a ribosome (the machine), which is a large protein complex. The ribosome binds to mRNA and tRNA (with amino acid attached). Ribosomes demonstrate the orientation effect because when they align two amino acids, peptide bonds are promoted. At least three amino acids are combined to form a peptide using a synthetic small molecule machine called a rotaxane. A macrocycle (ring molecule) moves down a central strand of amino acids, 'picking up' and bonding to each one in turn. This process forms a small peptide. Rotaxanes demonstrate the orientation effect because the starter amino acids attached to the macrocycle are closely aligned with the amino acids of the central strand of the rotaxane and peptide bonds are promoted.

Fully worked solutions to the Module review questions and Try yourself activities are available on Reader+ eBook. Your teacher has a set of fully worked solutions for all questions in the student book.

Glossary

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A

absolute uncertainty The uncertainty of a measurement due to the smallest available increment on an instrument.

absorbance The proportion of incident electromagnetic radiation absorbed by a sample.

absorbed A substance that has been incorporated into the interior of another substance or object, as in the absorption of water into a sponge.

absorption band The inverted peaks in an infrared spectrum that represent the frequencies of infrared radiation absorbed by specific bonds.

accumulator A secondary, or rechargeable, electrochemical cell.

accuracy The condition or quality of being true, correct or exact; freedom from error or defect; precision or exactness; correctness; in science, the extent to which a measurement result represents the quantity it purports to measure; an accurate measurement result includes an estimate of the true value and an estimate of the uncertainty.

accurate Precise and exact; to the point; consistent with or exactly conforming to a truth, standard, rule, model, convention or known facts; free from error or defect; meticulous; correct in all details.

acid A substance capable of donating a hydrogen ion (proton).

acid–base reaction A reaction in which one substance, an acid, donates a hydrogen ion (a proton) to another substance, a base.

acidic proton A proton bonded to an electronegative element (oxygen, nitrogen and fluorine) that is donated to a base during an acid–base reaction.

acidic solution An aqueous solution in which the concentration of hydronium ions (H_3O^+) is greater than the concentration of hydroxide ions (OH^-). At 25°C, pH < 7.

acidification To make or become acid; convert into an acid.

acidity The concentration of H_3O^+ ions in an aqueous solution. Acidity is measured using the pH scale.

acidity constant See *dissociation constant*.

activation energy The minimum energy required by reactants for a reaction to occur; symbol E_a. This energy is needed to break the bonds between atoms in the reactants to allow products to form.

active site The specific site of the enzyme that binds the substrate and where catalysis occurs.

actual yield The amount of the product actually produced in the reaction. Also referred to as simply 'yield'.

addition polymer A polymer that is formed by an addition reaction, where many monomers bond together by rearrangement of C=C double bonds without the loss of any atom or molecule. An addition polymer is made from unsaturated monomers.

addition polymerisation The process of forming a polymer by an addition reaction, where many monomers bond together by rearrangement of C=C double bonds without the loss of any atom or molecule. An addition polymer is made from unsaturated monomers.

addition reaction A reaction in which a molecule bonds to an unsaturated hydrocarbon, forming a single carbon–carbon bond. In this process two reactant molecules become one.

adsorption The attraction and binding of molecules or particles of one substance to the surface of another.

agarose A substance that is made up of agar and is used in gels for electrophoresis.

α-helix One type of secondary structure found in proteins. It has a spiral shape and is maintained by hydrogen bonding between amino acid units in the chain.

alcohol An organic molecule containing the hydroxyl (–OH) functional group.

alcohols A homologous series of hydrocarbon derivatives that contains the hydroxyl (–OH) functional group.

aldehyde An organic molecule containing a carbonyl (C=O) group on a terminal carbon atom, forming a –CHO functional group.

aldehydes A homologous series of hydrocarbon derivatives which contain the carbonyl functional group bonded to a hydrogen on one end of the molecule. Aldehydes can be recognised by the presence of a –CHO group at one end of a compound's condensed structural formula.

aldose A monosaccharide that includes an aldehyde functional group in its open chain form.

aliquot A volume of liquid measured by a pipette.

alkaline (solution) An aqueous solution in which the concentration of hydronium ions (H_3O^+) is less than the concentration of hydroxide ions (OH^-). At 25°C, pH > 7.

alkaline cell A commercial electrochemical cell with an alkaline electrolyte that is a moist paste rather than a solution.

alkanes A homologous series of hydrocarbons that contain only single covalent bonds. Alkanes are saturated hydrocarbons and have the general formula C_nH_{2n+2}.

alkenes A homologous series of hydrocarbons that contain one or more carbon–carbon double bonds. Alkenes are unsaturated hydrocarbons and have the general formula C_nH_{2n}.

alkyl group A group obtained by removing a hydrogen atom from an alkane, with a general formula C_nH_{2n+1}; for example, methyl ($–CH_3$). Alkyl groups make up branches in organic compounds.

alkyl side chain A side chain that has one less hydrogen atom than the corresponding alkane of the same name.

alkynes A homologous series of hydrocarbons that contain one or more carbon–carbon triple bonds. Alkynes are unsaturated hydrocarbons and have the general formula C_nH_{2n-2}.

alloy A substance formed when other materials (e.g. carbon, other metals) are mixed with a metal.

amide functional group A functional group found in the homologous series of amides. It consists of an amino group attached to a carbonyl group, $–CONH_2$.

amides A homologous series of hydrocarbon derivatives that contain the amide (–CONH–) functional group.

amines A homologous series of hydrocarbon derivatives that contains the amino ($–NH_2–$) functional group.

amino acid The monomer molecule used to make proteins.

2-amino acid An organic molecule that has an amino group, a carboxyl group, an H atom and an R group covalently bonded to the second carbon atom in the molecule's carbon chain. The R group consists of different sets of atoms.

amino functional group A functional group found in the homologous series of amines. It consists of a nitrogen atom covalently bonded to two hydrogen atoms, $–NH_2$.

amorphous region A region in a polymer in which molecules are tangled in a random arrangement.

amphiprotic The ability to act as an acid (proton donor) and also as a base (proton acceptor).

amphoteric A substance that is able to react as an acid or as a base.

amylopectin A form of starch that has occasional cross-links between glucose chains.

amylose A linear form of starch.

anode An electrode at which an oxidation reaction occurs.

anomalies Deviation from what is expected or considered to be normal or standard.

atactic Random orientation of side groups along a polymer chain.

atom economy A measure of how many of the atoms in the reactants end up in the desired product of a reaction. If the atom economy of a reaction is high, then there are few waste products.

average titre The average of concordant titres.

B

balanced chemical equation A chemical equation in which the number of atoms for each element on the reactant side of the equation is equal to the number of atoms for each element on the product side.

bar graph A graph in which categorical data is represented by horizontal bars. Each bar represents one category of independent variable (such as a range of values, or a particular type of thing), and the length of the bar represents the value of the dependent value for that range or thing.

base A substance capable of accepting a hydrogen ion (proton).

base hydrolysis The reaction with water in alkaline conditions is known as base hydrolysis and when it is applied specifically to esters it is called saponification.

base peak The highest intensity peak in a mass spectrum. It is assigned an intensity of 100%.

basic solution An aqueous solution in which $[H_3O^+] < [OH^-]$. For a basic solution at 25°C, pH > 7.

battery A combination of cells connected in series.

benzene A cyclic hydrocarbon with a formula of C_6H_6. A benzene molecule contains a six-carbon ring with delocalised electrons. The carbon–carbon bonds are intermediate between single and double bonds.

bias An inclination or prejudice towards something.

bile A greenish-brown alkaline fluid that aids digestion. It is secreted by the liver and stored in the gall bladder.

binding site The site where a molecule or atom binds to another molecule. A binding site can have a particular shape and/or charged areas to accommodate a substrate.

bioavailability The proportion of a drug that is available to have an active effect as a result of entering the circulation.

biocatalyst The term for a biologically produced industrial catalyst. It includes, but is not limited to, enzymes.

biodegradable Capable of being decomposed by the action of living organisms, such as bacteria and fungi.

biodegradation The breakdown of a substance by the action of living organisms, such as bacteria and fungi.

biodiesel A fuel derived from vegetable oils and fats with similar combustion properties to regular petroleum diesel fuel.

boiling point Temperature at which the vapour pressure of the liquid equals the pressure surrounding the liquid and the liquid changes into a vapour.

bond energy A measure of bond strength—the amount of energy required to break the covalent bond.

bond strength The amount of energy required to break the covalent bond.

bottom-up approach A type of processing where a structure or molecule is built by combining atoms or smaller structures.

β-pleated sheet One of the two types of secondary structure found in proteins. It consists of polypeptide strands bonded laterally. The parallel groups of a polypeptide chain are twisted back on themselves, forming a pleated sheet. It is maintained by hydrogen bonding.

Brønsted–Lowry model A theory introduced by Danish chemist Johannes Nicolaus Brønsted and English chemist Thomas Martin Lowry stating that any compound that can transfer a proton to any other compound is an acid, and the compound that accepts the proton is a base.

buffer A solution that resists changes in pH when an acid or base is added to it.

burette A graduated glass tube with a tap at one end that delivers known volumes of liquid.

by-products Incidental or secondary products made in a synthetic reaction in addition to the principal product.

C

calibration curve A plot of data involving two variables that is used to determine values for one of the variables. In spectroscopy and chromatography, it is a plot of absorbance versus concentration to determine the concentration of a solution. The curve is constructed by measuring the absorbance of a set of standard solutions.

carbohydrates Natuarlly occurring condensation polymers containing carbon, hydrogen and oxygen, which have the general formula $C_x(H_2O)_y$.

carbon nanotubes Nanoscale hollow carbon tubes with walls formed from graphene.

carbonyl functional group A functional group found in aldehydes, ketones, carboxylic acids and esters. It consists of a carbon atom doubly bonded to an oxygen atom, –CO–.

carboxyl functional group A functional group found in carboxylic acids. It consists of a hydroxyl group attached to the carbon of a carbonyl group, –COOH.

carboxylic acids A homologous series of hydrocarbon derivatives that contain the carboxyl functional group (–COOH).

cargo-sorting The process where DNA robots move across control DNA strands on a solid surface and first bind, then release, other molecules (cargoes).

catalyst A substance that increases the rate of a reaction but is not consumed in the reaction. The catalyst provides an alternative reaction pathway with a lower activation energy.

cathode An electrode at which a reduction reaction occurs.

cathodic protection Use of a low-voltage power supply to ensure that a reduction reaction occurs at a metal surface to prevent corrosion.

cellulose A carbohydrate that is a polymer of β-glucose and is the main component of the cell walls of plants.

chain isomers Isomers that are formed as a consequence of the branching that is possible in carbon chains.

chemical (HAZCHEM) code A system of codes and images that provide warning of hazardous substances and indicate the required emergency responses in the event of leaks, spills or fire.

chemical energy The sum of the chemical potential energy and kinetic energy in a substance. Chemical energy is stored in the bonds between atoms and molecules. The energy results from things such as attractions between electrons and protons in atoms, repulsions between nuclei, repulsions between electrons, movement of electrons, and vibrations and rotations around bonds.

chemical vapour deposition The production of carbon nanotubes by vaporising a hydrocarbon sample in the presence of a metal catalyst.

chiral carbon An asymmetric carbon atom that is attached to four different types of atoms or groups of atoms.

chromatogram The output of a chromatography procedure. In TLC and paper chromatography, it is the pattern of bands or spots formed on a plate or on paper. In high-performance liquid chromatography (HPLC), it is the graph produced.

chromatography A technique for separating the components of a mixture. The components are carried by a mobile phase (gas or liquid) over the adsorbent surface of a stationary phase, which can be solid or liquid.

***cis* arrangement** An arrangement of the alkyl groups at the double bond of most unsaturated fats, which produces a bend or 'kink' in the hydrocarbon chain.

***cis*-isomer** An isomer in which the groups attached to the carbon atoms of a double bond are on the same side of the double bond.

***cis-trans* isomers** See *geometric isomers*.

climate change A change in climate patterns, in particular changes apparent from the mid to late 20th century onwards, that can be largely attributed to increased levels of atmospheric carbon dioxide produced by the use of fossil fuels.

closed system System that only exchanges energy with its surroundings.

cloud point A measure of performance at low temperature. It refers to the temperature at which small crystals start to form.

coefficient of determination A calculated value that indicates the ability to predict the dependent variable value from the independent value.

collision theory A theoretical model that accounts for the rates of chemical reactions in terms of collisions between particles occurring during a chemical reaction.

column chromatography Chromatography technique where the solid stationary phase is packed into a glass column.

column graph A graph that shows the measured value (of value of central tendency) of the dependent variable by the height of the column.

combustion A rapid reaction with oxygen accompanied by the release of large amounts of energy.

complementary protein A combination of proteins that is able to provide the complete set of all the essential amino acids for the human diet.

complete combustion A combustion reaction that takes place with sufficient oxygen. The only carbon-containing product from complete combustion of hydrocarbons is carbon dioxide.

components The chemicals in a mixture. The components can be separated by chromatography.

concentrated solution A solution that has a relatively high ratio of solute to solvent.

concentration A measure of how much solute is dissolved in a specific volume of solution.

concentration fraction Ratio of the concentrations of the products of a reaction to the concentrations of the reactants. Each concentration is raised to the power of the stoichiometric coefficient in the chemical equation. The concentration fraction is also called the reaction quotient.

concordant titres A set of titres that vary within a narrow range, e.g. within 0.10 mL from smallest to largest titre.

condensation polymers A polymer formed by a condensation reaction, involving the elimination of a small molecule (often water) when monomers bond together. The monomers have functional groups at both ends of the molecule.

condensation reaction A reaction in which two molecules link together by eliminating a small molecule such as water.

condensed structural formula A formula used to indicate the connections in the structure of a compound without having to draw every bond.

conductive polymers Polymers that are able to conduct electricity.

confidence interval A calculated range in values that estimates where the true value is likely to be, according to a predetermined level of confidence.

conjugate acid The conjugate acid of a base contains one more hydrogen ion (proton) than the base, e.g. HCl is the conjugate acid of Cl^-.

conjugate acid–base pair An acid and its conjugate base. The conjugate base contains one less hydrogen ion (proton) than the acid.

conjugate base The conjugate base of an acid contains one less hydrogen ion (proton) than the acid, e.g. Cl^- is the conjugate base of HCl.

conjugate redox pair An oxidising agent (a reactant) and the reducing agent (a product) that are formed when the oxidising agent gains electrons. In this case, the oxidation number of the oxidising agent decreases, e.g. Cu_2^+/Cu. Alternatively, it may be a reducing agent (a reactant) and the oxidising agent (a product) that are formed when the reducing agent loses electrons. In this case, the oxidation number of the reducing agent increases.

contact process Industrial process to manufacture sulfuric acid from sulfur.

control group A selected test group that represents the experimental group, but is not exposed to any experimental treatment.

control strands DNA strands attached to a solid surface that a DNA robot or DNA walker will interact with and move across.

convergent synthesis A synthetic strategy by which a larger target is broken into smaller fragments. The smaller fragments are synthesised individually and then combined to make the final compound.

coomassie blue dye Dye commonly used to stain proteins in SDS-PAGE.

copolymer A polymer that is made from two or more monomers.

coral bleaching Caused by abnormally high sea surface temperatures as a result of climate change, corals expel the algae (zooxanthellae) living in their tissues, which causes the coral to turn completely white.

crown ethers Cyclic compounds consisting of a ring molecule and several ether groups.

crude oil A liquid found in Earth's crust that has been formed over millions of years by the effects of heat and pressure on dead animals, plants and microorganisms trapped beneath sediment.

crystalline region A region where polymer molecules line up parallel to each other and pack closely together.

crystal A crystalline solid of a substance.

C-terminal The end of a protein or polypeptide with a free carboxyl group (–COOH).

cyclic molecule A molecule in which the atoms are bonded to form a ring.

cycloalkane Regular alkane with a ring or loop.

cyclohexane A cyclic alkane consisting of six carbon atoms in a ring. It has the formula C_6H_{12}.

D

Dalton A unit of mass for expressing mass on an atomic or molecular scale (atomic mass). One Dalton is the mass of a hydrogen atom, 1.66×10^{-24} g.

data logger An electronic device that records data over time.

delocalised Not restricted to one area. See also *delocalised electrons*.

delocalised electrons Electrons that are not restricted to a single atom or covalent bond. The electrons can be shared between several atoms.

denature An irreversible change in the tertiary structure of a protein as a result, for example, or heating the protein above a critical temperature.

density A measure of the amount of mass per unit volume. It has the SI units of kg m^{-3}, but is commonly quoted in g cm^{-3}.

deoxyribonucleic acid (DNA) A self-replicating material that is present in nearly all living organisms as the main constituent of chromosomes. It is the carrier of genetic information.

dependent variable The variable that is measured or observed to determine the effect of changes in the independent variable.

derivative A compound that can be synthesised from a parent compound by replacement of one atom with another atom or group of atoms.

desorption The breaking of the bonds between a substance and the surface to which the substance is adsorbed.

diffraction A wave property of electromagnetic radiation that causes radiation waves to bend as it passes through a crystal.

diffraction pattern The closely spaced dark and light band pattern formed when radiation waves are diffracted by an opaque crystal.

dilution factor The ratio of the final volume to the aliquot volume.

dimers Molecules composed of two identical subunits that may be molecules in their own right, joined by strong intermolecular forces, such as hydrogen bonds.

dipeptide An organic molecule that has been produced by the condensation reaction between two amino acids.

dipolar ion A particle carrying both a positive and negative charge; for example, $+H_3NCH_2COO–$.

dipole A molecule that has two oppositely charged ends.

dipole–dipole intermolecular forces The attractive forces between polar molecules that result from the attraction between the positive and negative ends of the dipoles.

diprotic acid An acid that can donate two proton or hydrogen atoms per molecule to an aqueous solution.

direct corrosion Direct reaction with oxygen in the air to form a metal oxide, e.g. the reaction of magnesium with oxygen is written as $Mg(s) + O_2(g) \rightarrow 2MgO(s)$.

disaccharide A sugar formed when two monosaccharides are joined together by a glycosidic (or ether) bond, with the loss of a water molecule. Sucrose and lactose are common examples of disaccharides.

dispersion forces The intermolecular forces of attraction caused by temporary dipoles that are the result of random movement of the electrons surrounding the molecules.

displace The transfer of electrons from an element to a positive ion which results in the ion leaving the solution as an element, e.g. when zinc is placed in a solution of copper(II) ions the displacement reaction is $Cu_2^+(aq) + Zn(s) \rightarrow Zn_2^+(aq) + Cu(s)$.

dissociate Break up.

dissociation The separation of positive and negative ions as an ionic lattice melts or dissolves. The process is usually reversible.

dissociation constant Also known as an acid dissociation constant, K_a can be used to indicate the extent of dissociation of the acid or base (K_b) at a given temperature.

distillation The process of separating the components or substances from a liquid mixture by selective boiling and condensation.

disulfide bridge Also known as a disulfide bond (–S–S–). A covalently bonded set of two sulfur atoms (derived from the oxidation and joining of two nearby –SH groups in cysteine units) that can connect polypeptide chains together.

DNA origami A structure made of DNA strand(s) of predetermined sequence that folds to a particular shape when complementary sequences align and form hydrogen bonds.

DNA probe A short single-stranded DNA molecule designed to hybridise to a larger molecule of interest.

DNA walker A DNA molecule able to move across a surface by successive annealing to DNA control strands in the solid phase.

dry corrosion See *direct corrosion*.

dynamic equilibrium A point in a chemical reaction when the rate of the forward reaction is equal to the rate of the reverse reaction.

E

ecosystem A system formed by organisms interacting with one another and their physical environment.

electrochemical cell A device that converts chemical energy into electrical energy, or vice versa.

electrochemical series A list of half-equations, written as reduction reactions, arranged in order so that the strongest oxidising agents are on the top left side of the list.

electrode A solid conductor in a half-cell at which oxidation or reduction reactions occur.

electrolysis A process that produces a non-spontaneous redox reaction by the passage of electrical energy from a power supply through a conducting liquid.

electrolyte A chemical substance that conducts electric current as a result of dissociation into positively and negatively charged ions, which migrate towards the negative and positive terminals of an electric circuit.

electrolytic cell A cell in which electrolysis can occur.

electromagnetic spectrum The range of electromagnetic radiation. It is often represented in order of wavelength, from low energy radio waves to high-energy gamma rays.

electromotive force The 'electrical pressure' between two points in a circuit, such as the electrodes of an electrochemical cell; a measure of the energy given to electrons in a circuit.

electron density The measure of the probability of an electron being present at a specific location in an electron cloud.

electron density map An interpretation of the diffraction pattern as a plot of electron density versus position in the crystal.

electronegative The tendency of an atom to attract electrons towards itself.

electronic configuration The arrangement of electrons around the nucleus of an atom.

electroplating The deposition of a layer of one metal on the surface of another material by electrical means. Electroplating can be used to prevent corrosion by coating a relatively reactive metal, such as iron, with a less reactive metal, such as chromium.

electrorefining Extraction of metals from their ores using electrolysis.

elimination reaction An addition reaction that has been reversed.

eluent The solvent that carries the components and passes through a chromatography column.

emissions The production and release of a substance, especially waste products, a gas or radiation.

emulsion A suspension of small droplets of one liquid in another.

emulsion enantiomers A pair of molecules that are mirror images of each other that cannot be superimposed. Enantiomers are optical isomers.

end point A point in a titration at which the indicator changes colour, usually marking the completion of the reaction.

endothermic A reaction that absorbs energy.

energy content The amount of energy per gram or per 100 g or per mole (if a nutrient is a pure substance) that a food can supply. Units can be kJ g^{-1}, kJ 100 g or kJ mol^{-1}.

energy density The energy released when 1 litre of fuel undergoes complete combustion.

energy profile diagram Diagram that illustrates the energy change during a chemical reaction.

enthalpy Heat content. The sum of the chemical potential and kinetic energies in a substance; symbol H.

enzyme A protein molecule that catalyses (speeds up) biochemical reactions.

enzyme activity The amount of substrate converted to products per unit time by an enzyme. It represents the ability of the enzyme molecules to catalyse the reaction.

enzyme-substrate complex The intermediate molecule that forms when a substrate molecule interacts with the active site of an enzyme, during the catalysis of a chemical reaction.

equilibrium When a chemical reaction reaches equilibrium, the quantities of reactants and products in the reaction remain unchanged. The rates of the forward and reverse reactions are balanced.

equilibrium constant The value of the reaction quotient when equilibrium is reached; symbol K_c.

equilibrium law The equilibrium constant for the chemical equation:
$aW + bX \rightleftharpoons cY + dZ$
is given by the expression:
$$K_c = \frac{[Y]^c[Z]^d}{[W]^a[X]^b}$$

equilibrium yield The amount of products present at equilibrium.

equivalence point The point in a titration at which the reactants have reacted in their correct mole ratios.

error A measure of the estimated difference between the observed or calculated value of a quantity and its true value.

error bar A line drawn through a point on a graph that is parallel to one of the axes and which represents the uncertainty or variability of the data at that point.

essential amino acid An amino acid that must be included in the diet as it cannot be synthesised in the human body.

ester A homologous series of hydrocarbon derivatives that contain the ester (–COO–) functional group.

ester functional group The functional group resulting from the reaction between an alcohol and a carboxylic acid. It consists of a carbonyl group bonded to an oxygen atom, bonded to another carbon atom, –COO–.

ester link The link that is the result of the reaction between a hydroxyl and a carboxyl functional group. It consists of a carbonyl group bonded to an oxygen atom bonded to another carbon atom (–COO–).

esterification reaction The reaction between an alcohol and a carboxylic acid that forms an ester.

ether bond The connection between two monosaccharide units. In carbohydrates, an ether bond is also known as a glycosidic bond.

exothermic A reaction that yields energy. ΔH is negative.

experimental group The selected test group (sample group) in which the independent variable is changed to elicit a change in the measured results.

extend In science, to extend an experiment is to modify the methodology to overcome limitations of the scope or applicability of the data.

extended structural formula A formula that shows the spatial location of atoms relative to one another in a molecule, as well as the number and location of covalent bonds. Extended structural formulas use lines to show all of the bonds in molecules.

extent of reaction The relative amounts of products compared with reactants. The extent of a reaction at equilibrium is indicated by the value of the equilibrium constant.

external circuit The section of an electrochemical cell in which electrons move. This section of the circuit will include the wires attached to the electrodes.

extrapolate Infer or estimate by extending or projecting known information; conjecture; infer from what is known; extend the application of something (e.g. a method or conclusion) to an unknown situation by assuming that existing trends will continue or similar methods will be applicable.

F

fatty acid A carboxylic acid that has a relatively long carbon chain.

fermentation The breakdown of sugar solutions, by the action of enzymes in yeasts, into ethanol and carbon dioxide. The chemical equation for the fermentation of glucose is:
$C_6H_{12}O_6\ (aq) \rightarrow 2CH_3CH_2OH\ (aq) + 2CO_2\ (g)$

fingerprint region The part of the infrared (IR) spectrum below 1400 cm^{-1} that is unique to a particular molecule.

fractional distillation The separation of the components in a mixture on the basis of their boiling temperatures.

fragmentation The breaking up of a molecular ion into a number of smaller parts in mass spectrometry.

fuel cell A type of electrochemical cell in which the reactants are supplied continuously, allowing continuous production of electrical energy.

fullerene A hollow sphere made of carbon atoms—usually composed of 60 atoms. Each one is covalently bonded to three other carbon atoms.

functional group An atom or group of atoms that gives a characteristic set of chemical properties to a molecule containing those atoms.

G

galvanic cell A type of electrochemical cell also known as a voltaic cell; a device that converts chemical energy into electrical energy.

galvanometer An instrument for detecting electric current.

gel electrophoresis A separation technique that is based on the mobility of ions in an electric field used to separate and analyse macromolecules and their fragments based on their size and charge.

geometric isomers Stereoisomers that can occur when there is restricted rotation somewhere in a molecule. Restricted rotation can occur about a carbon–carbon double bond.

glucose A monosaccharide that plants can form through the process of photosynthesis. Its molecular formula is $C_6H_{12}O_6$.

glycerol The IUPAC name for glycerol is propane-1,2,3-triol.

glycogen A branched polysaccharide that is a polymer of α-glucose. Glycogen is the main form of carbohydrate storage in animals and is found primarily in the liver and muscle tissue.

glycosidic bond The ether link (C–O–C) formed when monosaccharide units bond to each other. It is the result of the reaction between two hydroxyl groups on two monosaccharides. Glycosidic bonds are found in disaccharides, trisaccharides and polysaccharides.

graph A diagram showing the relationship between variable quantities, usually two variables.

graphene A two-dimensional carbon lattice in which each atom is bonded to three other atoms.

green chemistry Chemistry that aims to design products and processes that minimise the use and generation of hazardous substances and wastes. Principles of green chemistry include prevention of waste; atom economy; design of less toxic chemicals and synthesis methods; use of safer solvents and auxiliaries; design for energy efficiency; use of renewable feedstocks; reduction of unnecessary derivatives; use of catalytic reagents rather than stoichiometric reagents; design for degradation; design of in-process analysis for pollution prevention; and safer chemistry for accident prevention.

greenhouse gas Gas that contributes to the warming of Earth's atmosphere due to the absorption of infrared radiation. Carbon dioxide and methane are examples of greenhouse gases.

H

Haber process The main industrial process for the production of ammonia from nitrogen and hydrogen using an iron catalyst.

half-cell Half an electrochemical cell, which contains the oxidant and conjugate reductant. When two half-cells are combined, a galvanic cell is formed.

half-equation A balanced chemical equation that shows the loss or gain of electrons by a species during oxidation or reduction, e.g. the oxidation of magnesium is written as the half-equation $Mg(s) \rightarrow Mg_2^+(aq) + 2e^-$.

halo functional group A functional group that consists of a halogen atom bonded to the carbon chain. The halo functional groups are named fluoro-, chloro-, bromo- and iodo-.

haloalkane A molecule derived from an alkane that contains at least one halogen functional group.

halogen An element in group 17 of the periodic table.

hard water Water that requires a lot of soap to obtain a lather or froth.

heat of reaction The exchange of heat between a system and its surroundings during a chemical reaction under constant pressure; ΔH. Also known as enthalpy change.

heterogeneous reaction A reaction in which reactants and products are in different phases.

high density polyethene (HDPE) A form of the polymer polyethene that is formed from polymer chains with very few, short branches. This means the polymer chains are packed together closely, making the polymer dense. HDPE can have a percentage crystallinity as high as 95% and has excellent mechanical properties. HDPE is used to make pipes, buckets and food containers, such as milk bottles.

high-performance liquid chromatography (HPLC) A very sensitive technique used to separate the components in a mixture, to identify each component, and to measure the concentrations of the components. It uses a pump to pass a pressurised liquid solvent containing the sample mixture through a column filled with solid adsorbent material. Also known as high-pressure liquid chromatography.

homogeneous reaction A reaction in which all reactants and products are in the same phase.

homologous series A class of molecules in which each member differs by $-CH_2-$ from the previous member. Compounds from the same homologous series have a similar structure, a pattern to their physical properties, similar chemical properties and the same general formula.

host–guest system Complexes containing a smaller molecule or particle specifically bound to a site on a larger molecule.

hydrocarbon skeleton The hydrocarbon backbone that makes up most organic compounds.

hydrocarbons Organic compounds composed only of carbon and hydrogen.

hydrogen bonds Particularly strong dipole–dipole forces that only occur between highly polar molecules in which a hydrogen atom is covalently bonded to an oxygen, nitrogen or fluorine atom.

hydrogen ion The $H_3O^+(aq)$ ion.

hydrolysis A reaction that forms two smaller molecules by the breaking of a bond in a molecule, using water as a reactant.

hydronium ion See *hydrogen ion*.

hydrophilic A molecule or portion of a molecule that interacts favourably with water and other polar substances.

hydrophobic A molecule or portion of a molecule that repels or does not mix with water; usually non-polar.

hydrosphere The total amount of water on a planet; can be liquid, vapour or ice.

hydroxide ion The $OH^-(aq)$ ion.

hygroscopic The property of absorbing moisture from the air.

hypothesis In science, a tentative explanation for an observed phenomenon, expressed as a precise and unambiguous statement that can be supported or refuted by experiment.

I

immiscible Describes a liquid that will not mix with or dissolve in another liquid; for example, oil in water.

independent variable The variable during an experiment that is deliberately altered, or selected to be tested, that is assumed to cause a change in the dependent variable.

indicator A substance that is different colours in its acid and base forms.

indicator range The range of pH values over which an indicator changes colour.

inert A substance that is unreactive, such as a platinum or graphite electrode.

inert electrode An electrode that is not consumed in the reaction that occurs at the electrode. The electrode serves only as a conductor of electrons. Precious metals and carbon are typically used as inert electrodes.

infrared (IR) spectroscopy An analytical technique that uses the infrared part of the electromagnetic spectrum to investigate the vibrational energy of molecular bonds.

insoluble Incapable of being dissolved.

internal circuit The part of an electrochemical cell in which ions move, e.g. solutions and salt bridge.

intermolecular forces Electrostatic forces of attraction between molecules, including dipole–dipole forces, hydrogen bonds and dispersion forces.

International Union of Pure and Applied Chemists (IUPAC) The international organisation that is the authority on naming compounds and terminology. See also *IUPAC nomenclature*.

ionic product of water See *ionisation constant of water*.

ionisation The removal of one or more electrons from an atom/ion; the reaction of a molecular substance with a solvent to form ions in solution.

ionisation constant of water The equilibrium constant K_w, where $K_w = [H_3O^+][OH^-]$ at 25°C, $K_w = 1.00 \times 10^{-14}$

ionise The reaction of a molecular substance with a solvent to form ions in solution. When some polar molecules dissolve in water, they ionise to form a hydronium, e.g. $HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$.

ion–dipole bonding The bond between dissociated ions and polar water molecules when an ionic solid dissolves in water.

irreversible reaction A reaction in which significant reaction can occur in one direction only.

isomers Molecules that have the same molecular formula but a different arrangement of atoms.

isotactic All the side groups of an isotactic polymer molecule are oriented along the same side of the polymer chain.

isotope Each of two or more forms of the same element that contain equal numbers of protons but different numbers of neutrons in their nuclei.

IUPAC nomenclature A set of rules established by the International Union of Pure and Applied Chemistry used for naming organic molecules. It is usually systematic and gives the number of carbon atoms and the location and type of functional groups present.

K

ketones A homologous series of hydrocarbon derivatives that contain the carbonyl functional group (–C=O) within, but not at the end of, the carbon chain.

ketose A monosaccharide that includes a ketone functional group in its open chain form.

L

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

lead–acid battery A secondary cell or accumulator used to start most cars.

line graph A graph that displays continuous data using a line from one point of measurement to the next.

line of best fit A straight line drawn through the centre of data points plotted on a scatterplot.

lipids A class of organic compounds that includes fats, oils, waxes and steroids. They are insoluble in water but soluble in non-polar solvents.

literature review An evaluative report that critically analyses the current body of knowledge.

lithium–ion cell A galvanic cell that generates electricity from the oxidation of lithium embedded in the lattice structure of a graphite rod and the reduction of a metal oxide. The reduction product combines with the lithium ions.

low density polyethene (LDPE) A form of the polymer polyethene that has a high degree of short and long chain branching. This means the polymer chains do not pack together closely in the crystal structure. It has therefore weaker intermolecular forces resulting in a lower tensile strength and increased ductility.

M

main group metal A metal in groups 1–3, such as lithium, sodium, potassium, magnesium, calcium, barium and aluminium.

Markovnikov's rule States that, during the addition of H_x or H_2O to an asymmetrical alkene, hydrogen adds to the carbon atom of the double bond having the greater number of hydrogens attached.

mass spectrometer An instrument designed to measure the mass-to-charge ratio, m/z, of particles.

mass spectrometry An analytical technique that uses the mass-to-charge ratio (m/z) of atoms, molecules and fragments of molecules to identify substances.

mass spectrum A graph of data produced from a mass spectrometer that shows the abundance or relative intensity of each particle, and their mass-to-charge (m/z) ratios.

materials-based storage A general name given to methods of storing hydrogen that includes adsorption to the surface of materials such as metal hydrides, absorption into the lattice structure of some solid materials and reversible reactions with a range of different chemicals.

mean A calculated value that represents the centre of a set of numbers that have been averaged.

mechanical bond The association of two molecules by physically interlocking, also allowing a range of movement of each molecule.

median The value of the middle number of a set of numbers arranged from smallest to highest number.

melting point The temperature at which a substance is in equilibrium between states but changes state as the temperature increases.

metabolised When a substance is metabolised in the body it undergoes a chemical reaction to produce energy, or other substances the body uses.

metal catalyst Metal atoms that increase the rate of a reaction without being consumed. Common metal catalysts are iron, nickel and palladium.

metal displacement reaction A reaction in which a metal causes the ions of another metal in solution to gain electrons and so precipitate out as the solid metal. The metal to be displaced must be less reactive (higher on the electrochemical series) than the metal that is added, e.g. Zn metal will displace Cu from a solution of Cu_2^+ ions.

micelle Lipid molecules arranged in a spherical form in aqueous solutions.

miscible Describes a liquid that will mix with or dissolve in another liquid; e.g. ethanol in water.

mistake An avoidable error.

mobile phase In chromatography, the phase that moves over the stationary phase.

mode The value that occurs most often in a list of values.

modify Change the form or qualities of; make partial or minor changes to something.

molarity The amount of solute, in moles, dissolved in 1 litre of solution ($mol\,L^{-1}$).

molecular formula A formula that indicates the number and type of atoms of each element present in a molecule but does not indicate how the atoms are actually arranged.

molecular ion A whole molecule with an overall positive or negative charge.

molecular ion peak A peak in a mass spectrum that is by the presence of a whole molecule ion. The peak with the greatest m/z value is likely to be due to the molecular ion in most cases.

monomer A small molecule that can combine with other like molecules to form long chains called polymers.

monoprotic acid An acid molecule that generates only one hydronium ion when ionised in water.

monosaccharide The simplest unit of carbohydrates. Monosaccharides are the building blocks of more complex carbohydrates and have the formula $C_6H_{12}O_6$. Examples are glucose, fructose and galactose.

N

nanoparticle Very small particles composed of tens or hundreds of atoms and having dimensions measured in nanometres.

nanorobot The name given to molecules designed to automatically carry out mechanical tasks. Also known as nanomachine.

neutral solution A solution in which the concentration of H_3O^+ ions equals the concentration of OH^- ions; is neither acidic nor basic. At 25°C, a neutral solution has a pH of 7.

neutralisation reaction An acid reacts with a base in stoichiometric proportions to form a salt + water.

nickel–metal hydride cell A rechargeable cell that generates an electric current by the oxidation of nickel metal hydride and the reduction of NiOOH.

nitrile functional group A functional group that consists of a carbon atom triple bonded to a nitrogen atom.

nitriles A homologous series of hydrocarbon derivatives that contains the nitrile (also known as cyano–) functional group $-C{\equiv}N$.

nitrogenase Enzymes that are produced by certain bacteria, such as cyanobacteria (blue-green algae), responsible for the reduction of nitrogen (N_2) to ammonia (NH_3).

non-polar Bonds or molecules that do not have a dipole. They have an even distribution of electrons.

non-rechargeable cell A primary galvanic cell.

non-renewable (fuel) Energy resources that are being used at a faster rate than they can be replaced.

non-spontaneous reaction A reaction that would not normally occur without the application of electrical energy. The reverse of spontaneous reaction, which produces energy.

N-terminal The end of a protein or polypepide with a free amine group ($–NH_2$).

nucleotide A monomer comprising a nitrogen-containing base, a sugar and a phosphate group. The four nucleotides—thymine, adenine, guanine and cytosine—form the DNA polymer.

O

observation Witnessing an event or phenomenon.

ocean acidity The ongoing decrease in the pH of Earth's oceans, caused by the uptake of carbon dioxide (CO_2) from the atmosphere. Seawater is slightly basic (pH > 7) and ocean acidification involves a shift towards pH-neutral conditions rather than a transition to acidic conditions (pH < 7).

oleum Also known as fuming sulfuric acid. It is a solution of various compositions of sulfur trioxide in sulfuric acid.

omega-3 fatty acid Essential fatty acid that contains a carbon–carbon double bond on the third carbon from the end of the hydrocarbon chain.

omega-6 fatty acid Essential fatty acid that contains a carbon–carbon double bond on the sixth carbon from the end of the hydrocarbon chain.

omega carbon The carbon in the methyl group at the end of the hydrocarbon chain in an unsaturated fatty acid.

open system System that exchanges energy and matter with the surroundings.

optical isomer A type of stereoisomer.

ores Minerals or an aggregate of minerals that contains a valuable constituent, such as a metal, which is mined or extracted.

organic chemistry The study of carbon-based compounds.

orientation effect The situation where functional groups of molecules are aligned so that a particular association and/or chemical reaction is promoted.

origin In paper or thin-layer chromatography, the point at which a small spot of a mixture is placed so that it can be separated.

outlier A value that 'lies outside' (is much smaller or larger than) most of the other values in a set of data.

overall yield The percentage yield of a substance that is formed in a multistep synthetic pathway based on the 100% conversion of each of the individual reactions.

oxidant A reactant that causes another reactant to lose electrons during a redox reaction. This reactant is, itself, reduced and gains electrons, e.g. in the reaction between magnesium and oxygen, the oxygen is the oxidising agent, as it causes magnesium to lose electrons and form Mg_2^+: $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$.

oxidation The process by which a chemical species such as a metal atom or a non-metal ion loses electrons. An oxidation half-equation will show the electrons as products (on the right-hand side of the arrow).

oxidation number A number assigned to an atom in a compound or as the free element, which represents the charge that the atom would have if it was an ion. A series of oxidation number rules are used to determine the oxidation number of an element in a compound. Oxidation numbers are used to identify redox reactions.

oxidation–reduction reaction See *redox reaction*.

oxidation state See *oxidation number*.

oxidised The loss of electrons. When a substance is oxidised, the electrons are written on the right-hand side of the arrow.

oxidising agent See *oxidant*.

P

paper chromatography An analytical technique for separating and identifying mixtures that uses paper as the stationary phase.

parallax error The perceived shift in an object's position as it is viewed from different angles.

parent alkane The parent is the longest continuous carbon chain in the compound, and the base name of the compound is the alkane that corresponds to the parent chain.

parent molecule Usually refers to the parent alkane from which the name of the molecule is derived but can also refer to the parent alkene or parent alkyne.

partially dissociate Only some of the molecules are broken into ions.

peptide link The –CONH– functional group between amino acid units in a polypeptide chain. See also *amide link*.

percentage yield A measure of the quantity of a product obtained from a chemical process compared to the maximum amount possible if the reaction were complete, expressed as a percentage:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

personal protective equipment (PPE) The equipment specifically designed and used during activities to protect the user from hazards.

petrodiesel The most common form of diesel fuel. It is produced from crude oil by fractional distillation. The composition of petrodiesel varies but is generally around 75% alkanes and 25% aromatic hydrocarbons. The alkanes range from $C_{10}H_{22}$ to $C_{15}H_{32}$.

petroleum Refined crude oil.

pH scale A measure of acidity and the concentration of hydronium ions, in solution. Acidic solutions have a pH value of less than 7 at 25°C, and bases have a pH value of greater than 7 at 25°C.

pH curve A graph that plots pH against volume of titrant.

photoconductive The increased electrical conductivity of a polymer when exposed to light.

photosynthesis The endothermic reaction occurring in green plants that produces simple sugars from carbon dioxide and water.

pie chart A spherical display of either qualitative or quantitative data showing the proportion of each data set (measurement, independent variable, observation) as a part of the whole.

pipette A calibrated glass tube used to transfer known volumes of liquid.

plagiarism Taking someone else's ideas or work and passing it off as your own.

plastic A property of a material that can be reshaped by application of heat and pressure. Polymers are often referred to as plastics.

polar Bonds or molecules that have a dipole. They have an uneven distribution of electrons.

polyacrylamide gels (PAGE) A polymer formed from acrylamide subunits used as gel in gel electrophoresis.

polyester A large molecule composed of many esters.

polymer A compound containing large numbers of repeating units of monomers.

polymerisation The process of synthesising a polymer.

polypeptide An organic polymer molecule made from a condensation reaction between amino acids.

polyprotic acid An acid molecule that generates more than one hydronium ion when ionised in water.

polysaccharide A long-chain carbohydrate made up of smaller carbohydrates called monosaccharides. Each monosaccharide is connected by glycosidic bonds. Starch, glycogen and cellulose are polysaccharides.

position of equilibrium The relative amounts of reactants and products at equilibrium.

positional isomers Constitutional isomers that have the same carbon skeleton and the same functional groups but differ from each other in the location of the functional groups on or in the carbon chain.

potential difference The electromotive force between two points in a circuit, such as the electrodes of an electrochemical cell.

precise Definite or exact; definitely or strictly stated, defined or fixed; characterised by definite or exact expression or execution.

precision Accuracy; exactness; exact observance of forms in conduct or actions. In science, exactness; how close two or more measurements of the same object or phenomena are to each other.

prefix A symbol written at the front of a unit to indicate that the measurement is a power of 10 higher or lower than the unit itself.

primary alcohol An alcohol in which the carbon that is bonded to the –OH group is only attached to one alkyl group.

primary amides A homologous series of hydrocarbon derivatives that contain a carbonyl functional group attached to an amino functional group, ($–CONH_2$).

primary amines An amine in which the amino functional group consists of one nitrogen atom covalently bonded to two hydrogen atoms.

primary cell A galvanic cell that is non-rechargeable because the products of the reaction migrate away from the electrodes.

primary haloalkane A haloalkane in which the carbon atom bonded to the halogen functional group is only bonded to one alkyl group.

primary source Information created by the person or persons directly involved in a study, investigation or experiment or observing an event.

primary standard A substance of known high purity which may be dissolved in a known volume of solvent.

primary structure The sequence (number, order and type) of amino acids in a polypeptide chain.

processed data Manipulated data to produce meaningful information; a set of displayed data in an appropriate form such as tables or graphs; required information that has been extracted from a set.

prodrug A compound that is metabolised into a pharmacologically active drug within the body.

promoters Molecules that increase the activity of a reaction and also affect the temperature of a reaction.

protecting group A molecule or functional group that is attached to a specific area of a molecular machine to block the reactivity of that area.

Protein Data Bank (PDB) A crystallographic database for the three-dimensional structural data of large biological molecules, such as proteins and nucleic acids.

protein sequencing A technique used to determine the amino acid sequence of a polypeptide.

protein Organic polymer molecules made from amino acids by condensation polymerisation. Approximately 50 or more amino acids form a protein.

proteomes The complete set of proteins expressed by a cell, tissue or organism.

Q

qualitative analysis An analysis based on apparent, non-measurable qualities that may be subjective. In chromatography, this type of analysis is used to determine the identity of the chemical(s) present in a substance.

qualitative data Information that is not numerical in nature.

quantitative analysis An analysis to determine the concentration of the chemicals present in a mixture.

quantitative data Numerical information.

quaternary structure The highest level of organisation in protein structure. Proteins have a quaternary structure if they are composed of two or more polypeptide chains.

R

R group The side group in an amino acid molecule or amino acid unit in a polypeptide chain. It can be composed of different sets of atoms. The amino acids used to make the proteins in the human body have 20 different R groups.

random error Uncontrollable effects of the measurement equipment, procedure and environment on a measurement result; the magnitude of random error for a measurement result can be estimated by finding the spread of values around the average of independent, repeated measurements of the quantity.

range The variation in values between upper and lower limits on a particular scale or the largest and smallest measurements.

rate of reaction Measure of the change in concentration of the reactants and products with time.

rationale A set of reasons, or logical basis for a course of action or decision.

raw data Unprocessed and/or unanalysed data; data that has been collected without any additional processing.

reaction pathway A series of chemical reactions that converts a starting material into a product, in a number of steps.

reaction quotient Ratio of the concentrations of the products of a reaction to the concentrations of the reactants. Each concentration is raised to the power of the stoichiometric coefficient in the chemical equation. The reaction quotient is also called the concentration fraction.

reaction table Method of setting out in tabular fashion calculations to determine equilibrium concentrations of reactants and products.

reactive electrode An electrode that is consumed in an electrochemical cell reaction.

reactivity series of metals A ranking of metals in order of their reactivity (ability to be oxidised), with the half-equations written as reduction equations of the corresponding ion. Least reactive metals are at the top and most reactive metals are at the bottom.

rechargeable cell A type of cell in which the chemical energy can be replenished repeatedly through application of electrical energy.

redirect In science, to redirect an experiment is to modify the methodology to gain further insight into the phenomena observed in the original experiment.

redox reaction A reaction in which electron transfer occurs from the reducing agent to the oxidising agent. In a redox reaction, the oxidation number of one element will increase (be oxidised) and the oxidation number of another element will decrease (be reduced).

reduced Has gained electrons. When a substance is reduced, the electrons are written on the left-hand side of the arrow (as reactants) in the half-equation.

reducing agent A reactant that causes another reactant to gain electrons during a redox reaction. This reactant is oxidised and loses electrons; e.g. in the reaction between magnesium and oxygen, the magnesium is the reducing agent as it causes oxygen to gain electrons and form $O_2–$ ions: $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$.

reductant A substance that causes another substance to be reduced; in the process the reductant is oxidised. A reductant is also called a reducing agent.

reduction The process by which a chemical species gains electrons. A reduction half-equation will show the electrons on the reactant side (left-hand side) of the equation. Generally, oxygen is removed or hydrogen is added to a species.

reference list A list of resources that is cited or in-text referenced in the document.

refine In science, to refine an experiment is to modify the methodology to obtain more accurate or precise data.

regioselective Any process that favours bond formation at a particular atom over other possible atoms.

regression The calculated estimate of the strength of a relationship between variables.

relative intensity Intensity of peak relative to the base peak which has an intensity of 100.

relative uncertainty The measured uncertainty displayed as a percentage of the measurement.

renewable (fuel) Energy resources that can be replaced at the same rate as they are used.

repeat trial Repeatedly conducting a process, activity or trial in an attempt to replicate the results.

replication Repeatedly conducting or choosing a process, activity or sample attempting to replicate the results, event or set-up.

restriction enzyme A type of enzyme, also called an endonuclease, that occurs naturally in bacteria and can cut DNA at a particular site (a recognition site). Restriction enzymes are widely used in DNA analysis, genetic testing and genetic engineering.

retardation factor (R_f) In paper and thin-layer chromatography, the ratio of the distance a component has moved from the origin to the distance the solvent (mobile phase) has moved from the origin.

retention time (R_t) The time taken for a component to pass through a chromatography column.

retrosynthetic pathway The planned route from the product molecule into simpler precursor structures without assumptions regarding starting materials.

reversed-phase HPLC A form of HPLC that uses a non-polar stationary phase.

reversible reaction A reaction in which significant reaction can occur in both the forward and reverse directions.

risk assessment Evaluations performed to identify, assess and control hazards in a systematic way that is consistent, relevant and applicable to all school activities; requirements for risk assessments related to particular activities will be determined by jurisdictions, schools or teachers as appropriate.

rotaxane A molecule that has a circular structure (called a macrocycle) associated with a linear dumbbell-shaped molecule so that they can move relative to each other.

S

sacrificial anode A highly reactive metal used to prevent a less reactive material surface from corroding.

sacrificial protection Protecting a metal from corrosion by coating it with a more reactive metal that will be preferentially oxidised.

safety data sheet (SDS) A document that outlines specific details about items that are required to be considered when handling the item for experimentation.

salt A substance formed from a metal or ammonium cation and an anion. Salts are the products of reactions between acids and bases, metal oxides, carbonates and reactive metals.

salt bridge An electrical connection between the two half-cells in a galvanic cell; it is usually made from a material saturated in electrolyte solution.

sample size The number of individual measurements or observations undertaken for each tested variable.

saponification A process in which soap is produced by heating a fat or vegetable oil with an alkali.

saturated molecule A molecule that contains only single carbon–carbon bonds. Alkanes are saturated molecules.

saturated solution Solution that contains the maximum amount of solute dissolved in the solution at the given temperature.

scatterplot A graph that displays the measured values for two variables plotted along two axes.

scientific journal A book containing the entire collection of work related to an experiment or investigation.

scientific notation A measured value written as a mathematical expression, between 1 and 10, including decimals displaying all significant figures, multiplied by 10 raised to a specific power.

scientific report A document that follows the report genre, systemically organising the main information and findings of scientific research or work.

secondary alcohol An alcohol in which the carbon that is bonded to the –OH group is attached to two alkyl groups.

secondary cell A accumulator or rechargeable cell. Recharging can occur because the products formed in the cell during discharge remain in contact with the electrodes in a convertible form.

secondary haloalkane A haloalkane in which the carbon bonded to the halogen functional group is bonded to two alkyl groups.

secondary source A source of information or data that was not created or measured by its author, but rather cited from another.

secondary structure Initial level of spatial arrangement of a polypeptide chain. There are two forms of secondary structure–α-helics and β-pleated sheets.

self-ionisation An ionisation reaction of pure water in which water behaves as both an acid and a base.

side chain The R-group is an amino acid molecule; there are 20 different side chains on the 2-amino acids used to make human proteins.

side group A group of atoms attached to a backbone chain of a long molecule.

significant figures The use of place value to represent a measurement result accurately and precisely.

smelting The process where a metal ore is heated in order to separate the desirable components from the other parts of the ore.

sodium dodecyl sulfate An anionic surfactant used as a emulsifier.

solubility A measure of the amount of solute dissolved in a given amount of solvent at a given temperature.

solute A substance that dissolves in a solvent, e.g. sugar is the solute when it dissolves in water.

solution A homogeneous mixture of a solute dissolved in a solvent.

solvent The liquid in which a solute is dissolved to form a solution.

solvent front Describes the movement of the solvent during chromatography. It is visible as the wet moving edge of the solvent as it travels along the stationary phase.

spiking A procedure used to tentatively identify a component within a mixture by high-performance liquid chromatography. If a chemical is thought to be one of the components of a mixture, it can be added to the sample. If there are no extra peaks in the chromatogram, just a larger peak for one of the components, it is assumed that the added chemical is one of the components of the mixture.

spontaneous reaction A reaction that occurs naturally, either in electrochemical cells or when chemicals are mixed directly. The reaction does not need to be driven by an external source of energy.

spontaneous redox reaction A redox reaction that occurs naturally.

standard conditions Established reference conditions to compare testing of experimental activities. Conditions at which gas pressure is 1 bar (100 kPa), the concentrations of dissolved species are 1.0 mol L^{-1} and the temperature is 25°C (298 K).

standard deviation A calculated spread of data that estimates the quartile boundaries from the mean, assuming a normalised (bell) curve.

standard electrode potential The electromotive force that is measured when a half-cell, at standard conditions (gas pressures 1 bar, solution concentrations of 1.0 mol L^{-1} and temperature of 25°C) is connected to a standard hydrogen half-cell; symbol E°. Gives a numerical measure of the tendency of a half-cell reaction to occur as a reduction reaction.

standard hydrogen half-cell An $H^+(aq)/H_2(g)$ half-cell made from a platinum electrode placed in acid solution with hydrogen gas bubbled over it. The pressure of the gas is 1 bar, the H^+ concentration is 1.0 mol L^{-1} and the temperature is 25°C.

standard reduction potential A numerical measure of the tendency of a half-cell reaction to occur as a reduction reaction. It is measured by connecting a half-cell, at standard conditions (gas pressures 1 bar, solution concentrations of 1.0 mol L^{-1} and temperature of 25°C), to a standard hydrogen half-cell.

standard solution A solution that has an accurately known concentration.

starch A polysaccharide formed from the polymerisation of α-glucose molecules. Starch is an odourless and tasteless white substance that occurs widely in plant tissue. It is used by plants to store energy.

stationary phase A solid, or a viscous liquid that is coated into a solid, used in chromatography. The components of a mixture undergo adsorption to this phase as they are carried along by the mobile phase.

steam reforming A process that produces hydrogen, carbon monoxide or other useful products from hydrocarbon fuels such as natural gas.

stem name The first part of the name of a molecule derived from the number of carbon atoms in the longest continuous carbon chain.

stereoisomers Isomers in which the atoms in two molecules are connected in the same order, but have different arrangements in space.

stereospecificity Specificity, such as the specificity of a binding site for a molecule or atom of interest, which is based on shape.

stoichiometric The relative amounts of reactants and products in a chemical reaction. Chemical equations give the ratios of the amounts (moles) of the reactants and products.

strong acid An acid that readily donates a hydrogen ion (proton) to a base.

strong base A base that readily accepts a hydrogen ion (proton) from an acid.

structural formula A formula that indicates the arrangement of atoms in a molecule.

structural isomers Molecules that have the same molecular formula but a different order of attachment of atoms (a different structure).

substitution reaction A reaction that involves the replacement of an atom or group of atoms with another atom or group of atoms.

substrate A reactant in a reaction that is catalysed by an enzyme.

substrate molecule A molecule that is acted on or bound to a larger molecule.

superacid An acid that has an acidity greater than the acidity of 100% sulfuric acid.

surfactant A substance consisting of long molecules with one hydrophobic 'tail' and one hydrophilic 'head' that are able to form micelles and modify the surface properties of a liquid. The name is an abbreviation of 'surface-active agent'.

syndiotactic The side groups of the polymer molecule are oriented in regular alternating directions along the polymer chain.

synthetic pathway The route taken to prepare a specific product.

system A group of interacting objects, materials or processes that form an integrated whole; systems can be open or closed.

systematic error An error that is affected by the accuracy of a measurement process that causes readings to deviate from the accepted value by a consistent amount each time a measurement is made.

T

TD_{50} The amount of an ingested substance that kills 50% of the test sample (expressed in mg/kg, or milligrams of substance per kilogram of body weight).

temporary dipoles Temporary dipole moments occur in bonds where the probability of electrons being equally shared between two atoms is high, but bonds are just where electrons are most likely to be found.

teratogenic A compound that can disturb the development of the embryo or foetus during pregnancy, or produce a congenital malformation (a birth defect).

tertiary alcohol An alcohol in which the carbon that is bonded to the –OH group is attached to three alkyl groups.

tertiary haloalkane A haloalkane in which the carbon that is bonded to the halogen functional group is attached to three alkyl groups.

tertiary structure (enzyme) The overall three-dimensional shape of a polypeptide chain.

tetrahedral In the shape of a tetrahedron, where four points at equal distances are spread as far as possible in three dimensions.

theoretical yield The mass of product that would be formed if the limiting reagent reacted fully. The mass that is expected for a particular product in a chemical reaction, based on the mass of limiting reactant used.

thermochemical equation A chemical equation that includes the enthalpy change of the reaction, ΔH. For example:
$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$
$\Delta H = -572\,kJ\,mol^{-1}$

thermostability The quality of a substance to resist irreversible change in its chemical or physical structure, often by resisting decomposition or polymerisation, at a high relative temperature.

thin-layer chromatography (TLC) A chromatography technique that uses a thin layer of fine powder spread on a glass or plastic plate as the stationary phase.

titration The process used to determine the concentration of a reactant where one solution is added from a burette to a known volume of another solution.

titration curve See *pH curve*.

titre The volume of liquid, measured by a burette, used in a titration.

top-down approach A type of processing where a larger mass of bulk substance is changed to produce a product.

***trans*-isomer** An isomer in which the groups attached to the carbon atoms of a double bond are on opposite sides of the double bond.

transesterification A process in which triglyceride reacts with an alcohol to form esters.

transition element An element, such as iron, copper, nickel or chromium, that is found in the middle block of the periodic table, in groups 3–12.

transition point The midpoint of an indicator colour change.

transmittance The ratio of light that passes through a sample compared to the light given off by the source.

trend line A line drawn onto a graph to accurately display a relationship between the variables.

triglyceride An ester derived from a glycerol molecule and three fatty acids.

tripeptide An organic molecule made from three amino acid units linked by peptide bonds.

triprotic acid An acid molecule that generates three hydronium ions when ionised in water.

true value An ideal measurement of a phenomenon without error.

U

uncertainty 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; indicators of uncertainty may include percentage and/or absolute measurement uncertainty, confidence intervals, inferential statistics, statistical measures of spread, e.g. range and standard deviation.

universal indicator A mixture of dyes that changes colour gradually over a range of pH, used to test for acids and alkalis.

unsaturated molecule A molecule that contains one or more double or triple carbon–carbon bonds. Alkenes and alkynes are unsaturated molecules.

US EPA United States Environmental Protection Agency.

V

valence electron The electrons in the outermost shell of an atom.

valence number The number of electrons in the outermost shell of an atom.

validity In science, the extent to which tests measure what was intended; the extent to which data, inferences and actions produced from tests and other processes are accurate.

vapour Describes a gaseous species that is normally a liquid at room temperature and pressure.

vapour pressure The pressure exerted by a vapour in equilibrium with its liquid in a closed container.

variable *adjective*
apt or liable to vary or change; changeable; inconsistent; (readily) susceptible or capable of variation; fluctuating, uncertain;
noun
in science, a factor that can be changed, kept the same or measured in an investigation, e.g. time, distance, light, temperature.

vibrational energy levels Different fixed energies that molecules can have as a result of the bending and stretching of bonds.

viscosity A measure of a liquid's resistance to flow. Honey has a high viscosity and petrol has a low viscosity.

volatility Describes the ease with which a liquid can evaporate. Liquids that are highly volatile have weak intermolecular forces holding their molecules together.

volt The unit of potential difference.

voltaic cell A type of electrochemical cell that is also known as a galvanic cell; a device that converts chemical energy into electrical energy.

voltmeter An instrument for measuring the electrical potential difference between two points in a circuit.

volumetric analysis Quantitative analysis using measurement of solution volumes, usually involving titration.

volumetric flask A laboratory flask calibrated to contain a precise volume.

W

wavenumber A unit of frequency used in infrared spectroscopy. It is equal to the inverse of the wavelength of the radiation and is measured in cm^{-1}.

weak acid An acid that dissociates incompletely, releasing only some of its hydrogen atoms into the solution.

weak base A base that accepts hydrogen ions (protons) from acids, to a limited extent.

wet corrosion The corrosion of iron in the presence of oxygen and water. It takes place in stages; the final product is hydrated iron(III) oxide ($Fe_2O_3 \cdot H_2O$), known as rust.

X

x-ray crystallography A technique used for determining the atomic and molecular structure of a crystal.

Y

yield The amount of product resulting from a chemical reaction.

Z

Ziegler–Natta catalyst A catalyst for addition polymerisation developed by Karl Ziegler and Giulio Natta. The catalyst contains a mixture of titanium chloride ($TiCl_3$) and triethylaluminium ($Al(CH_2CH_5)_3$).

zwitterion A dipolar ion formed when the amino and carboxyl groups in an amino acid or polypeptide are both charged.

zymase An enzyme complex that catalyses the fermentation of sugar into ethanol and carbon dioxide.

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The following abbreviations are used in this list: t = top, b = bottom, l = left, r = right, c = centre.

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	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** hydrogen 1.01					Atomic number **Symbol** Name Relative atomic mass												2 **He** helium 4.00
2	3 **Li** lithium 6.94	4 **Be** beryllium 9.01											5 **B** boron 10.81	6 **C** carbon 12.01	7 **N** nitrogen 14.01	8 **O** oxygen 16.00	9 **F** fluorine 19.00	10 **Ne** neon 20.18
3	11 **Na** sodium 22.99	12 **Mg** magnesium 24.31											13 **Al** aluminium 26.98	14 **Si** silicon 28.09	15 **P** phosphorous 30.97	16 **S** sulfur 32.06	17 **Cl** chlorine 35.45	18 **Ar** argon 39.95
4	19 **K** potassium 39.10	20 **Ca** calcium 40.08	21 **Sc** scandium 44.96	22 **Ti** titanium 47.87	23 **V** vanadium 50.94	24 **Cr** chromium 52.00	25 **Mn** manganese 54.94	26 **Fe** iron 55.85	27 **Co** cobalt 58.93	28 **Ni** nickel 58.69	29 **Cu** copper 63.55	30 **Zn** zinc 65.38	31 **Ga** gallium 69.72	32 **Ge** germanium 72.63	33 **As** arsenic 74.92	34 **Se** selenium 78.97	35 **Br** bromine 79.90	36 **Kr** krypton 83.80
5	37 **Rb** rubidium 85.47	38 **Sr** strontium 87.62	39 **Y** yttrium 88.91	40 **Zr** zirconium 91.22	41 **Nb** niobium 92.91	42 **Mo** molybdenum 95.95	43 **Tc** technetium (98.91)	44 **Ru** ruthenium 101.07	45 **Rh** rhodium 102.91	46 **Pd** palladium 106.42	47 **Ag** silver 107.87	48 **Cd** cadmium 112.41	49 **In** indium 114.82	50 **Sn** tin 118.71	51 **Sb** antimony 121.76	52 **Te** tellurium 127.60	53 **I** iodine 126.90	54 **Xe** xenon 131.29
6	55 **Cs** caesium 132.91	56 **Ba** barium 137.33	71–57 lanthanoids	72 **Hf** hafnium 178.49	73 **Ta** tantalum 180.95	74 **W** tungsten 183.84	75 **Re** rhenium 186.21	76 **Os** osmium 190.23	77 **Ir** iridium 192.22	78 **Pt** platinum 195.08	79 **Au** gold 196.97	80 **Hg** mercury 200.59	81 **Tl** thallium 204.38	82 **Pb** lead 207.2	83 **Bi** bismuth 208.98	84 **Po** polonium (210.0)	85 **At** astatine (210.0)	86 **Rn** radon (222.0)
7	87 **Fr** francium (223.0)	88 **Ra** radium (226.1)	103–89 actinoids	104 **Rf** rutherfordium (261.1)	105 **Db** dubnium (262.1)	106 **Sg** seaborgium (263.1)	107 **Bh** bohrium (264.1)	108 **Hs** hassium (265.1)	109 **Mt** meitnerium (268)	110 **Ds** darmstadtium (281)	111 **Rg** roentgenium (272)	112 **Cn** copernicium (285)	113 **Nh** nihonium (284)	114 **Fl** flerovium (289)	115 **Mc** moscovium (288)	116 **Lv** livermorium (293)	117 **Ts** tennessine (294)	118 **Og** oganesson (294)

57 **La** lanthanum 138.91	58 **Ce** cerium 140.12	59 **Pr** praseodymium 140.91	60 **Nd** neodymium 144.24	61 **Pm** promethium (146.9)	62 **Sm** samarium 150.36	63 **Eu** europium 151.96	64 **Gd** gadolinium 157.25	65 **Tb** terbium 158.93	66 **Dy** dysprosium 162.50	67 **Ho** holmium 164.93	68 **Er** erbium 167.26	69 **Tm** thulium 168.93	70 **Yb** ytterbium 173.05	71 **Lu** lutetium 174.97
89 **Ac** actinium (227.0)	90 **Th** thorium 232.0	91 **Pa** protactinium 231.0	92 **U** uranium 238.0	93 **Np** neptunium (237.0)	94 **Pu** plutonium (239.1)	95 **Am** americium (241.1)	96 **Cm** curium (244.1)	97 **Bk** berkelium (249.1)	98 **Cf** californium (252.1)	99 **Es** einsteinium (252.1)	100 **Fm** fermium (252.1)	101 **Md** mendelevium (258.1)	102 **No** nobelium (259.1)	103 **Lr** lawrencium (262.1)

*Values in brackets are for the isotopes with the longest half-life.