PEARSON

CHEMISTRY

WESTERN AUSTRALIA

STUDENT BOOK

12

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This book is dedicated to Pat and Mike Quinton.

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CEA offers scholarship and bursaries to students and teachers to further their interest in chemistry. CEA supports STAV with sponsorship for the Chemistry, Science Drama Awards and The Science Talent Search.

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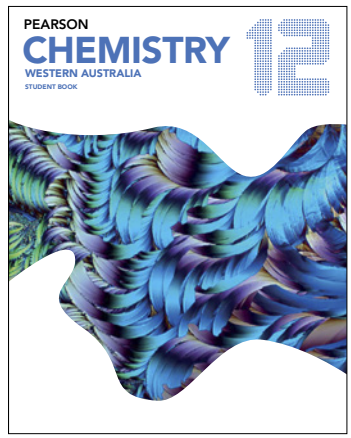
Writing and Development Team



Geoff Quinton
President of ASTA
Head of science
Coordinating author

Erin Bruns
Senior science teacher
Author

John Clarke
Chief Executive Officer STAWA
Author

Chris Commons
Chemistry lecturer
Author and reviewer

Penny Commons
Chemistry lecturer
Author

Lanna Derry
Teacher
Contributing author

Bob Hogendoorn
Senior consultant
Contributing author

Elissa Huddart
Teacher
Contributing author

Faye Jeffery
Teacher and lecturer
Author

Phil Jones
Educator
Author

Allan Knight
Science education consultant
Former WACE chemistry examiner
Author

Don Marshall
Head of chemistry
Author

Claire Molinari
Chemistry teacher
Author

Nicholas O'Brien
Chemistry teacher
Author

Bill Offer
Former head of science and science teacher
Reviewer

Pat O'Shea
Teacher
Contributing author

Maria Porter
Teacher
Contributing author

Bob Ross
Teacher
Contributing author

Patrick Sanders
Teacher
Contributing author

Robert Sanders
Teacher
Contributing author

Sophie Selby-Pham
Master of science
Answer checker

Lyndon Smith
Former member of the SCSA curriculum development team
Reviewer and answer checker

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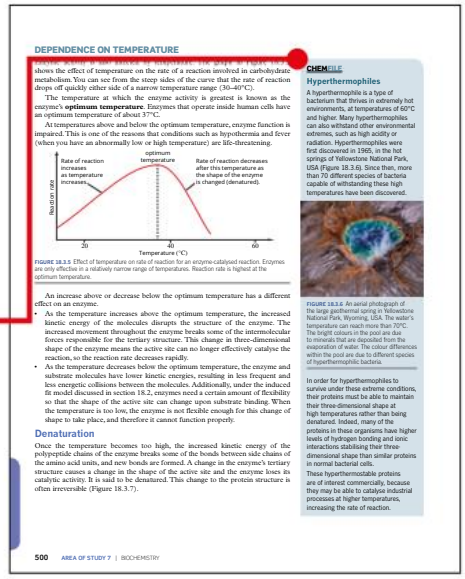
How to use this book

Pearson Chemistry 12 Western Australia

Pearson Chemistry 12 Western Australia has been written to the *WACE Chemistry ATAR Course, Year 12 Syllabus 2017*. Each chapter is clearly divided into manageable sections of work. Best practice literacy and instructional design are combined with high quality, relevant photos and illustrations. Explore how to use this book below.

Chapter opening page

The chapter opening page links the syllabus to the chapter content. Science Understanding and Science as a Human Endeavour addressed in the chapter is clearly listed.



CHEMFILE

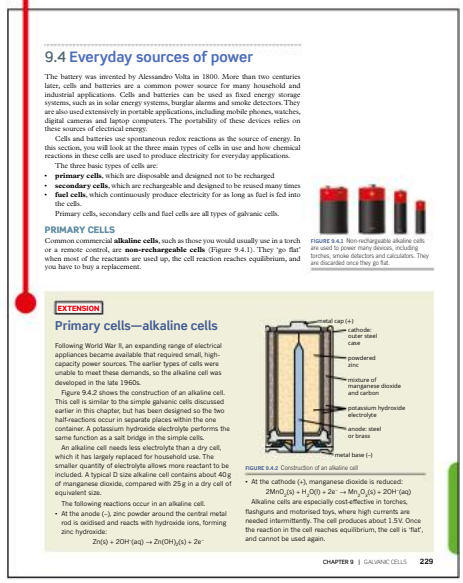
ChemFiles include a range of interesting information and real world examples.

CHEMISTRY IN ACTION

Chemistry in Action boxes place Chemistry in an applied situation or relevant context and encourages students to think about the development of chemistry and its use and the influence of chemistry in society.

EXTENSION

Extension boxes include material that goes beyond the core content of the syllabus. They are intended for students who wish to expand their depth of understanding in a particular area.



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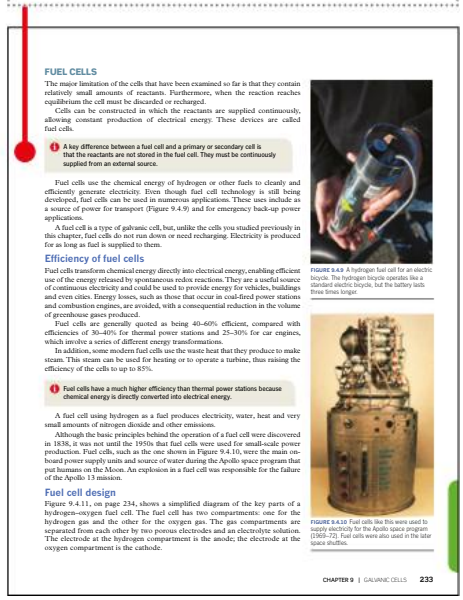
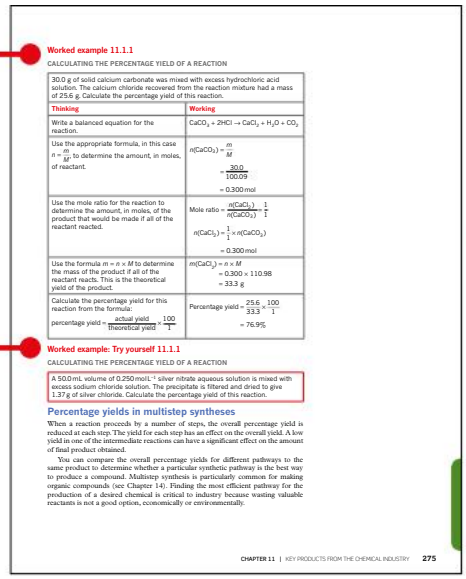
Focuses students' attention on important information, such as key definitions, formulae and summary points.



Worked example

Worked examples are set out in steps that show both thinking and working. This enhances student understanding by clearly linking underlying logic to the relevant calculations.

Each Worked example is followed by a Worked example: Try Yourself. This mirror problem allows students to immediately test their understanding.



Worked example 11.1.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

30.0 g of solid calcium carbonate was mixed with excess hydrochloric acid solution. The calcium chloride recovered from the reaction mixture had a mass of 25.6 g. Calculate the percentage yield of this reaction.

Thinking	Working
Write a balanced equation for the reaction.	$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$
Use the appropriate formula, in this case $n = \frac{m}{M}$ to determine the amount, in moles, of reactant.	$n(CaCO_3) = \frac{m}{M}$ $= \frac{30.0}{100.09}$ $= 0.300\ mol$
Use the mole ratio for the reaction to determine the amount, in moles, of the product that would be made if all of the reactant reacted.	Mole ratio $= \frac{n(CaCl_2)}{n(CaCO_3)} = \frac{1}{1}$ $n(CaCl_2) = \frac{1}{1} \times n(CaCO_3)$ $= 0.300\ mol$
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.	$m(CaCl_2) = n \times M$ $= 0.300 \times 110.98$ $= 33.3\ g$
Calculate the percentage yield for this reaction from the formula: percentage yield $= \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$	Percentage yield $= \frac{25.6}{33.3} \times \frac{100}{1}$ $= 76.9\%$

Worked example: Try yourself 11.1.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

A 50.0 mL volume of 0.250 mol·L^{-1} silver nitrate aqueous solution is mixed with excess sodium chloride solution. The precipitate is filtered and dried to give 1.37 g of silver chloride. Calculate the percentage yield of this reaction.

Percentage yields in multistep syntheses

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.

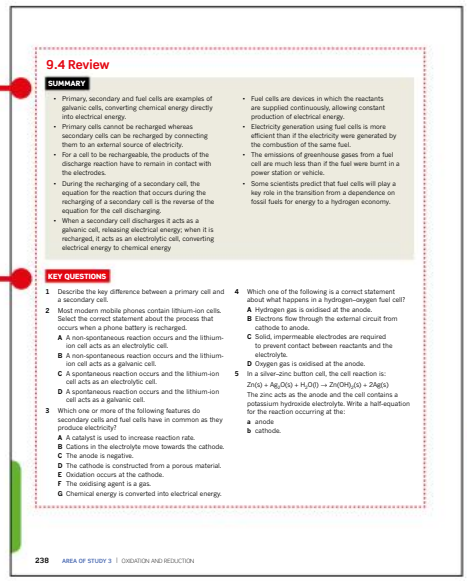
You can compare the overall percentage yields for different pathways to the same product to determine whether a particular synthetic pathway is the best way to produce a compound. Multistep synthesis is particularly common for making organic compounds (see Chapter 14). Finding the most efficient pathway for the production of a desired chemical is critical to industry because wasting valuable reactants is not a good option, economically or environmentally.

Section SUMMARY

Each section includes a summary to assist students consolidate key points and concepts.

Section review
Key questions

Each section finishes with questions to test students' understanding and ability to recall the key concepts of the section.



9.4 Review

SUMMARY

- Primary, secondary and fuel cells are examples of galvanic cells, converting chemical energy directly into electrical energy.
- Primary cells cannot be recharged whereas 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 equation for the reaction that occurs during the recharging of a secondary cell is the reverse of the equation for the cell discharging.
- When a secondary cell discharges it acts as a galvanic cell, releasing electrical energy; when it is recharged, it acts as an electrolytic cell, converting electrical energy to chemical energy
- Fuel cells are devices in which the reactants are supplied continuously, allowing constant production of electrical energy.
- Electricity generation using fuel cells is more efficient than if the electricity were generated by the combustion of the same fuel.
- The emissions of greenhouse gases from a fuel cell are much less than if the fuel were burnt in a power station or vehicle.
- Some scientists predict that fuel cells will play a key role in the transition from a dependence on fossil fuels for energy to a hydrogen economy.

KEY QUESTIONS

1 Describe the key difference between a primary cell and a secondary cell.

2 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 non-spontaneous reaction occurs and the lithium-ion cell acts as an electrolytic cell.
B A non-spontaneous reaction occurs and the lithium-ion cell acts as a galvanic cell.
C A spontaneous reaction occurs and the lithium-ion cell acts as an electrolytic cell.
D A spontaneous reaction occurs and the lithium-ion cell acts as a galvanic cell.

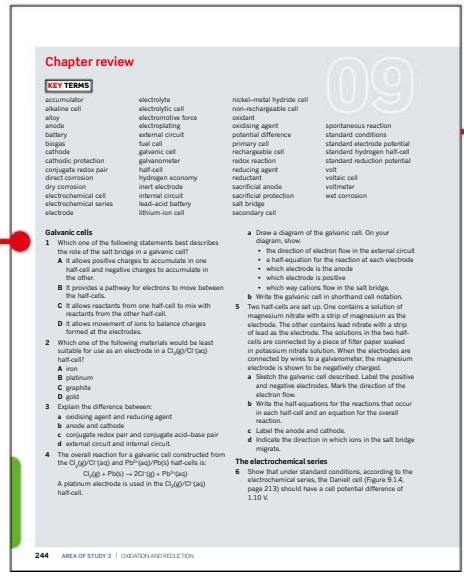
3 Which one or more of the following features do secondary cells and fuel cells have in common as they produce electricity?
A A catalyst is used to increase reaction rate.
B Cations in the electrolyte move towards the cathode.
C The anode is negative.
D The cathode is constructed from a porous material.
E Oxidation occurs at the cathode.
F The oxidising agent is a gas.
G Chemical energy is converted into electrical energy.

4 Which one of the following is a correct statement about what happens in a hydrogen–oxygen fuel cell?
A Hydrogen gas is oxidised at the anode.
B Electrons flow through the external circuit from cathode to anode.
C Solid, impermeable electrodes are required to prevent contact between reactants and the electrolyte.
D Oxygen gas is oxidised at the anode.

5 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. Write a half-equation for the reaction occurring at the:
a anode
b cathode.

Chapter review

Each chapter finishes with a set of higher order questions to test students' ability to apply the knowledge gained from the chapter.



Chapter review

09

KEY TERMS

accumulator, alkaline cell, alloy, anode, battery, biogas, cathode, cathodic protection, conjugate redox pair, direct corrosion, dry corrosion, electrochemical cell, electrochemical series, electrode, electrolyte, electrolytic cell, electromotive force, electroplating, external circuit, fuel cell, galvanic cell, galvanometer, half-cell, hydrogen economy, inert electrode, internal circuit, lead–acid battery, lithium-ion cell, nickel–metal hydride cell, non-rechargeable cell, oxidant, oxidising agent, potential difference, primary cell, rechargeable cell, redox reaction, reducing agent, reductant, sacrificial anode, sacrificial protection, salt bridge, secondary cell, spontaneous reaction, standard conditions, standard electrode potential, standard hydrogen half-cell, standard reduction potential, volt, voltaic cell, voltmeter, wet corrosion

Galvanic cells

1 Which one of the following statements best describes the role of the salt bridge in a galvanic cell?
A It allows positive charges to accumulate in one half-cell and negative charges to accumulate in the other.
B It provides a pathway for electrons to move between the half-cells.
C It allows reactants from one half-cell to mix with reactants from the other half-cell.
D It allows movement of ions to balance charges formed at the electrodes.

2 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 platinum
C graphite
D gold

3 Explain the difference between:
a oxidising agent and reducing agent
b anode and cathode
c conjugate redox pair and conjugate acid–base pair
d external circuit and internal circuit.

4 The overall reaction for a galvanic cell constructed from the $Cl_2(g)/Cl^-(aq)$ and $Pb^{2+}(aq)/Pb(s)$ half-cells is:
$Cl_2(g) + Pb(s) \rightarrow 2Cl^-(g) + Pb^{2+}(aq)$
A platinum electrode is used in the $Cl_2(g)/Cl^-(aq)$ half-cell.
a Draw a diagram of the galvanic cell. On your diagram, show:
- the direction of electron flow in the external circuit
- a half-equation for the reaction at each electrode
- which electrode is the anode
- which electrode is positive
- which way cations flow in the salt bridge.

b Write the galvanic cell in shorthand cell notation.

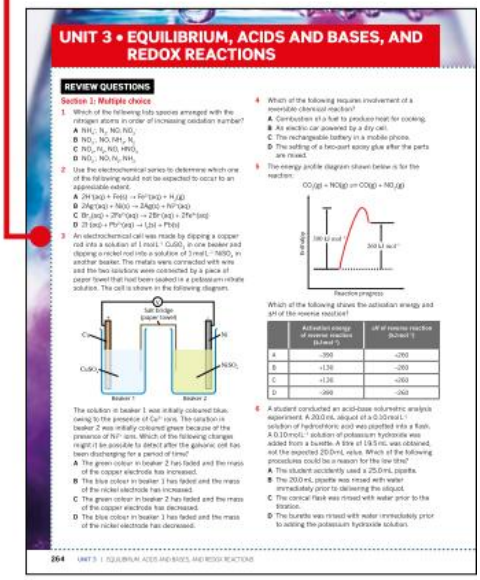
5 Two half-cells are set up. One contains a solution of magnesium nitrate with a strip of magnesium as the electrode. The other contains lead nitrate with a strip of lead as the electrode. The solutions in the two half-cells are connected by a piece of filter paper soaked in potassium nitrate solution. 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 Write 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.

The electrochemical series

6 Show that under standard conditions, according to the electrochemical series, the Daniell cell (Figure 9.1.4, page 213) should have a cell potential difference of 1.10 V.

Unit review

Each unit finishes with a comprehensive set of exam-style questions that assist students to draw together their knowledge and understanding and apply it to this style of questions.



UNIT 3 • EQUILIBRIUM, ACIDS AND BASES, AND REDOX REACTIONS

REVIEW QUESTIONS

Section 1: Multiple choice

1 Which of the following lists species arranged with the nitrogen atoms in order of increasing oxidation number?
A NH_3, N_2, NO, NO_2
B NO_2, NO, NH_3, N_2
C NO_2, N_2, NO, HNO_3
D NO_2, NO, N_2, NH_3

2 Use the electrochemical series to determine which one of the following would not be expected to occur to an appreciable extent.
A $2H^+(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + H_2(g)$
B $2Ag(aq) + Ni(s) \rightarrow 2Ag(s) + Ni^{2+}(aq)$
C $Br_2(aq) + 2Fe^{2+}(aq) \rightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$
D $I_2(aq) + Pb^{2+}(aq) \rightarrow I_2(s) + Pb(s)$

3 An electrochemical cell was made by dipping a copper rod into a solution of 1 mol·L^{-1} $CuSO_4$ in one beaker and dipping a nickel rod into a solution of 1 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. Which of the following changes might it be possible to detect after the galvanic cell has been discharging for a period of time?
A The green colour in beaker 2 has faded and the mass of the copper electrode has increased.
B The blue colour in beaker 1 has faded and the mass of the nickel electrode has increased.
C The green colour in beaker 2 has faded and the mass of the copper electrode has decreased.
D The blue colour in beaker 1 has faded and the mass of the nickel electrode has decreased.

4 Which of the following requires involvement of a reversible chemical reaction?
A Combustion of a fuel to produce heat for cooking.
B An electric car powered by a dry cell.
C The rechargeable battery in a mobile phone.
D The setting of a two-part epoxy glue after the parts are mixed.

5 The energy profile diagram shown below is for the reaction:
$CO_2(g) + NO(g) \rightleftharpoons CO(g) + NO_2(g)$

Which of the following shows the activation energy and ΔH of the reverse reaction?

	Activation energy of reverse reaction (kJ·mol^{-1})	ΔH of reverse reaction (kJ·mol^{-1})
A	−350	+210
B	+130	−210
C	+130	+350
D	+350	−130

6 A student conducted an acid–base volumetric analysis experiment. A 20.0 mL aliquot of a 0.10 mol·L^{-1} solution of hydrochloric acid was pipetted into a flask. A 0.10 mol·L^{-1} solution of potassium hydroxide was added from a burette. A titre of 19.5 mL was obtained, not the expected 20.0 mL value. Which of the following procedures could be a reason for the low titre?
A The student accidentally used a 25.0 mL pipette.
B The 250 mL pipette was rinsed with water immediately prior to delivering the aliquot.
C The conical flask was rinsed with water prior to the titration.
D The burette was rinsed with water immediately prior to adding the potassium hydroxide solution.

Key terms and glossary

Key terms are shown in bold and listed at the end of each chapter. A comprehensive glossary at the end of the book includes and defines all the key terms.

Answers

Numerical answers and key short response answers are included at the back of the book. Comprehensive answers and fully worked solutions for all section review questions, Worked example: Try yourself, Chapter review questions and Unit review questions are provided via *Pearson Chemistry 12 Western Australia Teacher Reader+*

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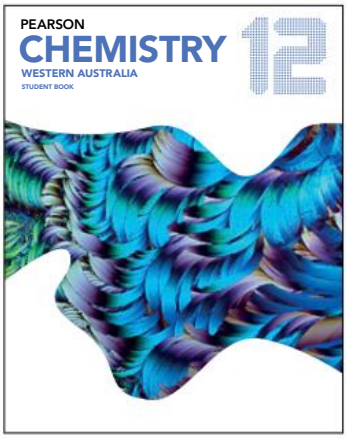

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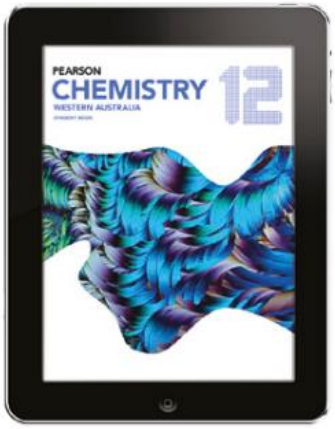

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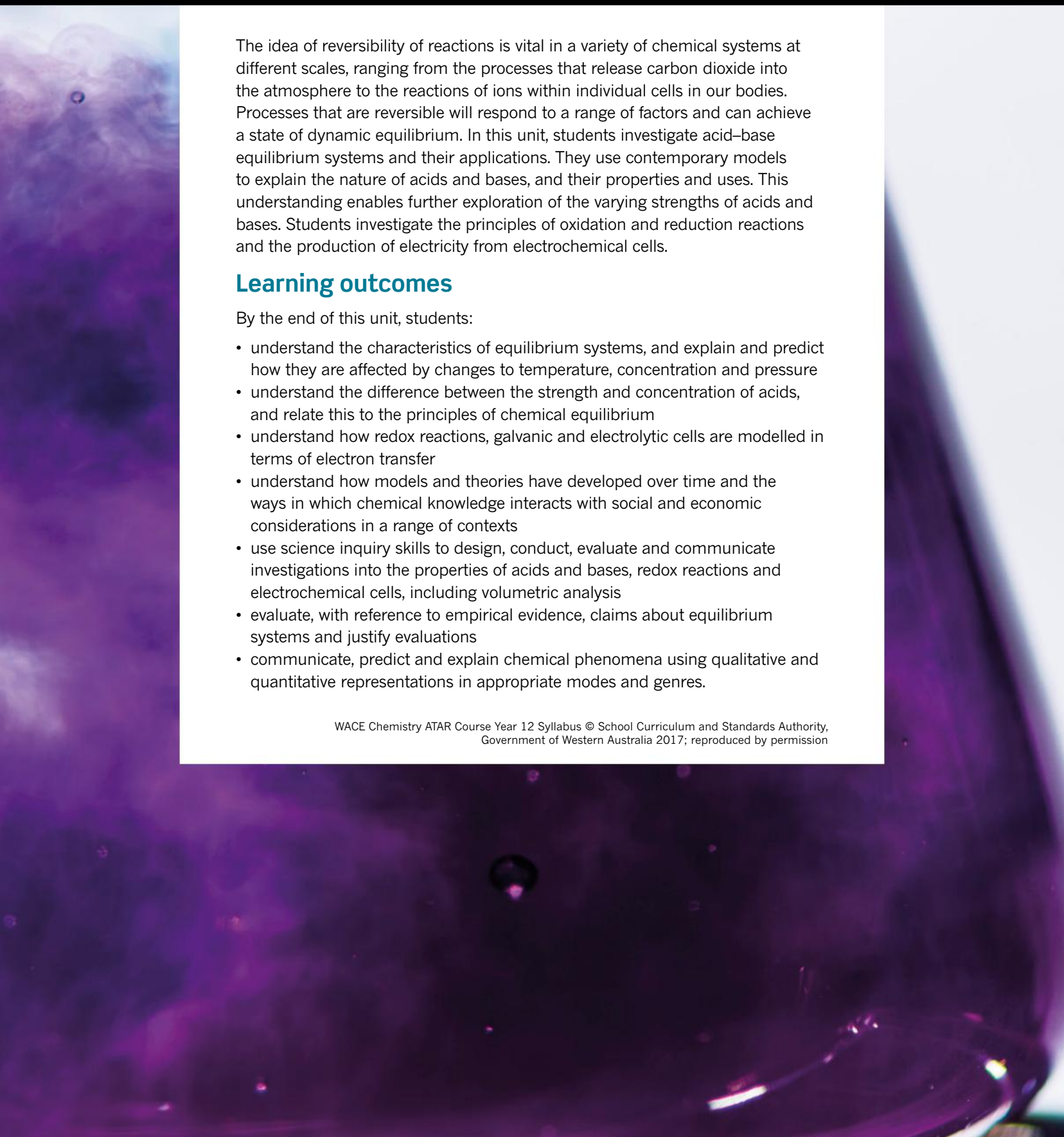
UNIT 3

Equilibrium, acids and bases, and redox reactions



The idea of reversibility of reactions is vital in a variety of chemical systems at different scales, ranging from the processes that release carbon dioxide into the atmosphere to the reactions of ions within individual cells in our bodies. Processes that are reversible will respond to a range of factors and can achieve a state of dynamic equilibrium. In this unit, students investigate acid–base equilibrium systems and their applications. They use contemporary models to explain the nature of acids and bases, and their properties and uses. This understanding enables further exploration of the varying strengths of acids and bases. Students investigate the principles of oxidation and reduction reactions and the production of electricity from electrochemical cells.

Learning outcomes

By the end of this unit, students:

- understand the characteristics of equilibrium systems, and explain and predict how they are affected by changes to temperature, concentration and pressure
- understand the difference between the strength and concentration of acids, and relate this to the principles of chemical equilibrium
- understand how redox reactions, galvanic and electrolytic cells are modelled in terms of electron transfer
- understand how models and theories have developed over time and the ways in which chemical knowledge interacts with social and economic considerations in a range of contexts
- use science inquiry skills to design, conduct, evaluate and communicate investigations into the properties of acids and bases, redox reactions and electrochemical cells, including volumetric analysis
- evaluate, with reference to empirical evidence, claims about equilibrium systems and justify evaluations
- communicate, predict and explain chemical phenomena using qualitative and quantitative representations in appropriate modes and genres.

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CHAPTER

01 Rate of chemical reactions

A premise of kinetic theory is that all particles are in a constant state of motion. A result of this constant chaotic movement is that the particles that make up a substance can, and often do, collide with each other. Usually, these collisions result in no change to the particles, but under the right conditions the force of the collision can cause chemical bonds to break, which allows for the formation of new chemical bonds.

As you saw in Year 11, how rapidly this breaking and formation of chemical bonds takes place is influenced by a range of experimental factors and can be explained through the application of collision theory.

Science understanding

- collision theory can be used to explain and predict the effects of concentration, temperature, pressure, the presence of catalysts and surface area of reactants on the rates of chemical reactions
- observable changes in chemical reactions and physical changes can be described and explained at an atomic and molecular level
- the reversibility of chemical reactions can be explained in terms of the activation energies of the forward and reverse reactions

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1.1 Rate of chemical reactions

Some chemical reactions occur very rapidly, while others can take an extended period of time. Acid–base reactions and reactions involving ions in solution, such as precipitation, tend to occur rapidly, whereas reactions involving the breaking and formation of covalent bonds, particularly in large molecules, tend to be slower. The nature of the reactants, including the type and strength of bonds involved, can greatly influence the rate of conversion of reactants into products.

Experimentally, the **rate of a reaction** can be determined by measuring, either directly or indirectly, the formation of products or the depletion of reactants over time. Factors that can be measured to determine the rate of a reaction include:

- mass lost by reagent
- mass gained by product
- volume of gas
- pressure of gas
- colour intensity
- solution concentration
- pH.

Different reactions may lend themselves to specific experimental methods of determining the reaction rate. For a reaction that generates a gaseous product, it may be convenient to capture the gas and measure its pressure or volume. For a redox reaction involving coloured compounds, a spectrophotometer could be used to measure the intensity of colour as a function of ion concentration.

In a chemical reaction, reagents are normally mixed together in some way and the particles that make up the substances—atoms, molecules or ions—collide with each other. The number of collisions that takes place is astonishingly large. However, the vast majority of these collisions are not successful and do not result in the formation of products. For a collision to be successful, two criteria must be met. Our understanding of these criteria and their impact on the rate of reaction is explained by **collision theory**.

COLLISION THEORY

A chemical reaction is the result of a successful collision between reactant particles. In order for a collision to be successful, the reactant particles must collide with:

- correct orientation
- sufficient energy.

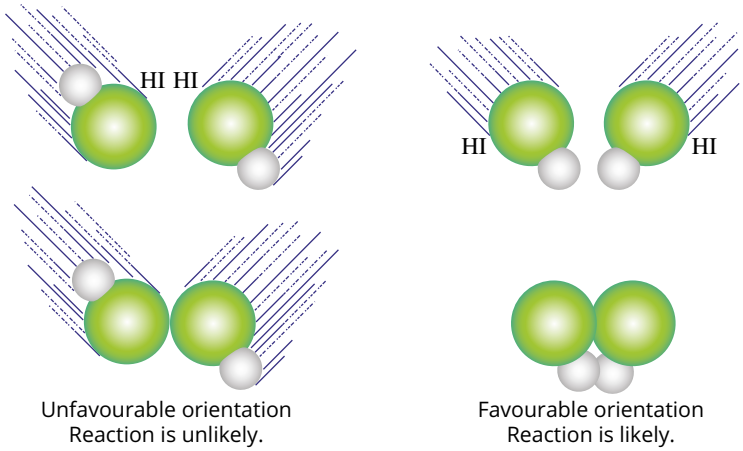
If either of these criteria is not met, the collision will not be successful and no chemical change will occur.

Correct orientation

Molecules that collide with sufficient energy only do so successfully if they collide with an orientation that allows for the breaking of existing chemical bonds and formation of new chemical bonds.

Figure 1.1.1 shows the importance of collision orientation. In the decomposition of hydrogen iodide gas into hydrogen gas and iodine gas, two hydrogen iodide molecules must collide with hydrogen and iodine atoms orientated towards each other, for a reaction to possibly occur. If the collision orientation is incorrect, the particles simply bounce off each other, and no reaction occurs.

The orientation of colliding particles is the result of their random motion and it is not something that can be easily modified to increase the rate of reaction. Large or complex molecules where the reactive sites represent only a small part of the whole molecule only have a very small number of collisions with the appropriate orientation; this tends to result in a slow reaction rate. Similarly, molecules with extensive structures where the reactive sites are obscured from colliding with other reactant particles don't always react to any appreciable extent.



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

FIGURE 1.1.1 A reaction between colliding molecules is more likely to occur if the orientation of the collision is favourable.

However, the energy required for the particles to collide successfully is more easily modified.

Sufficient energy

When two reactant particles collide, even if they are in the correct orientation, they still need to have a certain amount of **kinetic energy** for the collision to be successful and generate products. This energy is a requirement of the bond breaking (and formation) process. However, at any given temperature, the energies possessed by the particles are not all the same. The particles have a range of kinetic energies as a result of the particles moving at different velocities. This range of kinetic energies can be illustrated by a probability distribution known as a **Maxwell–Boltzmann distribution curve**, or a **kinetic energy distribution diagram**.

Distribution curves such as the Maxwell–Boltzmann distribution are different from most other graphs that you use in Chemistry. Maxwell–Boltzmann distribution curves do not show the relationship between two simple variables. They represent how a specific variable (in this case, kinetic energy) is distributed among the population of particles.

Kinetic energy is the energy that a particle or body has due to its motion ($KE = \frac{1}{2}mv^2$)

Maxwell–Boltzmann distribution

A Maxwell–Boltzmann distribution curve (Figure 1.1.2) is a probability distribution function that shows the range of kinetic energies possessed by the particles in a substance at a specific temperature.

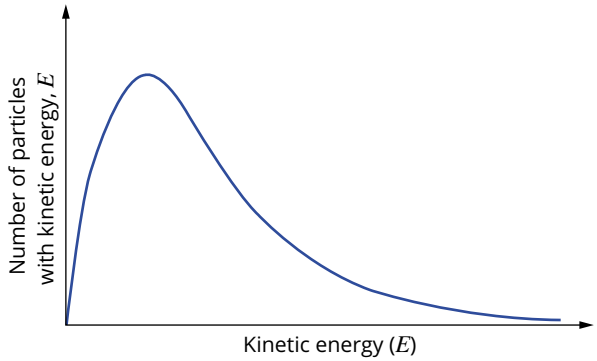


FIGURE 1.1.2 This Maxwell–Boltzmann curve shows the distribution of energies of particles in a sample at a particular temperature.

There are a number of important details you can observe from the kinetic energy distribution. There are zero particles with zero kinetic energy, a large number of particles with a moderate amount of kinetic energy, and fewer and fewer particles with higher levels of kinetic energy. Note that the curve approaches, but never touches, the *x*-axis, which shows that although the probability is very small, there will always be the chance of some particles possessing extremely high kinetic energies.

The maximum of this graph does not show the maximum energy, it represents the energy possessed by the greatest number of particles in the substance. The average kinetic energy of the particles (which represents the temperature of the substance) occurs slightly to the right of this maximum. The area beneath the curve represents the total number of particles in the sample.

Only the particles that have kinetic energy greater than a certain value will (assuming correct orientation) successfully collide to generate products. This minimum amount of energy required to break the existing chemical bonds, allowing the collisions to be successful, is known as the **activation energy**, E_a.

Activation energy

When the energy of a collision is equal to, or greater than, the activation energy, there is potential for a reaction to occur. If this activation energy is included on a Maxwell–Boltzmann distribution curve (Figure 1.1.3), it is easy to see how only a small fraction of the total particles in a substance actually has sufficient energy to collide successfully. Of this small fraction, even fewer will collide with the correct orientation.

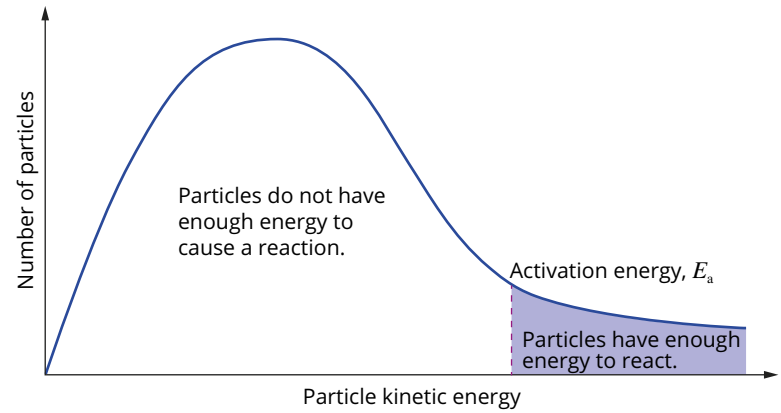


FIGURE 1.1.3 Only a small number of higher energy particles (represented by the shaded area) have sufficient energy to overcome the activation energy barrier.

The activation energy of a reaction can also be illustrated by an **energy profile diagram**. In Figure 1.1.4, the activation energy is represented by the difference in energy from the reactants to the transition state. The **transition state** is the highly energised and highly unstable arrangement of reactant particles where the bond breaking and formation takes place.

An exothermic reaction releases energy to the surroundings; ΔH is negative.

While we are accustomed to reactions converting reactants into products, some reactions exist in a constant state of flux. This means that at the same time as some reactant particles are converted into products, some of the product particles revert to the original reactant particles. Note that in the energy profile diagram Figure 1.1.4, the activation energy for the **reverse reaction** (products → reactants) is the sum of the activation energy and the change of enthalpy for the forward reaction. These reversible chemical systems and the state they establish, known as equilibrium, are covered in Chapter 2.

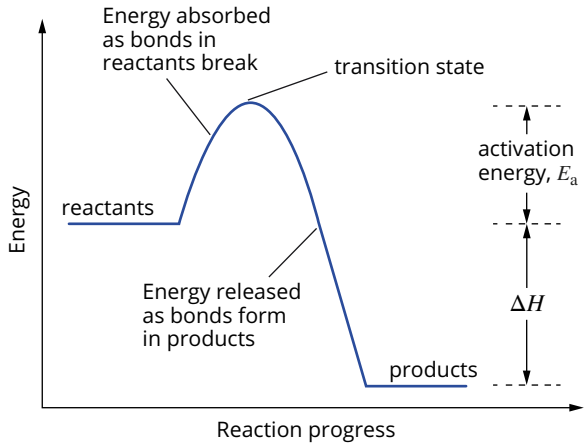


FIGURE 1.1.4 The energy profile diagram for an exothermic reaction such as the combustion of natural gas

It is important to note that although the energy profile diagram and the kinetic energy distribution diagram both include the activation energy, the two diagrams show the same event from very different perspectives. The energy profile diagram shows the reaction 'journey' of individual atoms, ions or molecules, whereas the kinetic energy distribution diagram shows the overall picture of all particles potentially involved in a reaction.

Activation energy and reaction rate

The magnitude of a reaction's activation energy determines the ease with which a given reaction occurs. A reaction that has been determined to be viable may not happen because of its high activation energy. For such reactions, the activation energy is usually supplied from a spark or flame (Figure 1.1.5).

FIGURE 1.1.5 The reagents required for the combustion of the candle wax are present and their particles are colliding, but not with sufficient energy. The activation energy to start the reaction is provided by the flame.

CHEMFILE

A little too reactive!

In 1846, the Italian chemist Ascanio Sobrero reacted glycerol with a mixture of sulfuric and nitric acids to make the explosive liquid nitroglycerin. Nitroglycerin is so unstable that even a small bump can cause it to explode. It decomposes according to the equation:

$$4C_3H_5N_3O_9(l) \rightarrow 12CO_2(g) + 10H_2O(g) + 6N_2(g) + O_2(g)$$

Despite being many times more powerful than conventional gunpowder, nitroglycerin was far too dangerous to be practical. Some years later, the Swedish scientist Alfred Nobel learnt how to manage nitroglycerin more safely through his invention of dynamite.

The reason for nitroglycerin's instability is the very small activation energy for its decomposition reaction (Figure 1.1.6).

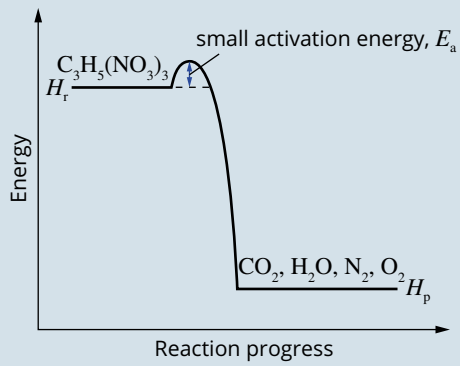


FIGURE 1.1.6 Nitroglycerin has a very low activation energy, making its rate of reaction very large.

1.1 Review

SUMMARY

- The rate of a reaction is the formation of products or the depletion of reactants over time.
- A range of experimental quantities can be used to calculate the rate of a reaction; they include:
  - mass lost by reagent
  - mass gained by product
  - volume of gas
  - pressure of gas
  - colour intensity
  - solution concentration
  - pH.
- The activation energy of a reaction is the minimum amount of energy required to break reactant bonds to allow a reaction to proceed. It is the minimum amount of energy that a collision between reactant particles must possess for a reaction to occur.
- Collision theory is a theoretical model that accounts for the rates of chemical reactions in terms of collisions between particles during a chemical reaction.
- According to collision theory, for a reaction to occur, the reactant particles must:
  - collide with sufficient energy to break the bonds within the reactants
  - collide with the correct orientation to break the bonds within the reactants and so allow the formation of new products.
- The range of kinetic energies possessed by particles in a substance at a given temperature is shown by a Maxwell–Boltzmann distribution curve.

KEY QUESTIONS

1 Which one of the following would not be a suitable method to measure the rate of the reaction between zinc metal and hydrochloric acid?

A loss of mass from the reaction vessel
B mass of hydrogen gas produced
C the concentration of zinc metal remaining
D the volume of hydrogen gas produced

2 What are the two criteria required for a collision to be successful?

3 **a** Draw a fully labelled Maxwell–Boltzmann distribution curve to represent the range of kinetic energies possessed by the particles in a substance at a certain temperature.

b On the same diagram, in a different colour, draw the distribution that would exist at a higher temperature.

4 What is activation energy?

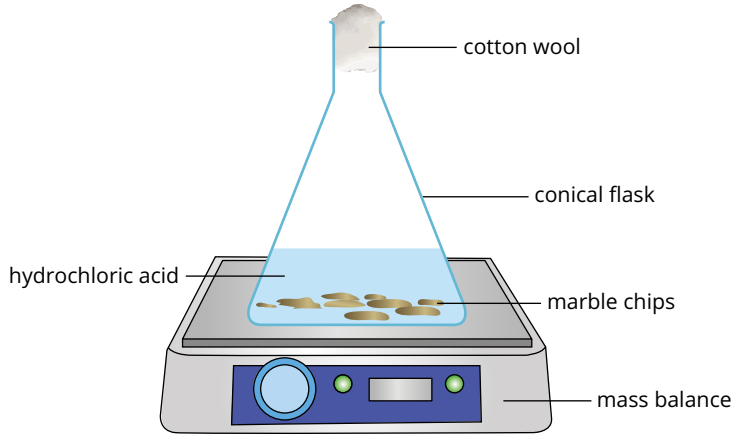
5 Draw a fully labelled energy profile diagram for an endothermic reaction.

6 The diagram below shows the apparatus used to measure the rate of reaction between marble chips and hydrochloric acid.

a Write a fully balanced chemical equation for this experiment.

b Once the reaction has finished, describe how you can determine which reagent is completely used up (the limiting reagent).

c A student stated that the data obtained from this experiment violated the law of conservation of mass because the mass of the chemicals in the flask reduced during the reaction. Explain why this statement is incorrect.



1.2 Factors that influence reaction rate

The rate of a reaction depends on the number of successful collisions between reactant particles per unit of time. Successful collisions require both the correct orientation and sufficient energy to meet or exceed the activation energy of the reaction.

Experimental investigations have shown that five main factors can change the rate of a chemical reaction:

- surface area of solid reactants
- concentration of reactants in a solution
- gas pressure
- temperature
- the presence of a catalyst.

The effect on the reaction rate demonstrated by these factors can be attributed to either: (i) generating a greater number of collisions (both successful and unsuccessful) per unit time or (ii) increasing the probability that any given collision will be successful.

INCREASING COLLISION FREQUENCY

In any given reaction mixture, only a certain percentage of the collisions that occur are successful. If you can increase the overall frequency of collisions, because a certain percentage of these collisions will be successful, then you can increase the total number of successful collisions per unit of time, and hence increase the reaction rate.

The experimental factors that rely on an increased frequency of collisions to achieve a higher reaction rate include:

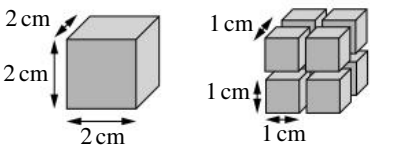
- surface area
- concentration
- gas pressure.

Surface area

When a solid is involved in a reaction, only the particles at the surface of the solid are available to collide with other reactant particles. The number of particles at the surface depends on the surface area of the substance.

The **surface area** is a consequence of the particle size. As can be seen in Figure 1.2.1, when the size of the particles of a substance is reduced, the total surface area of the substance increases.

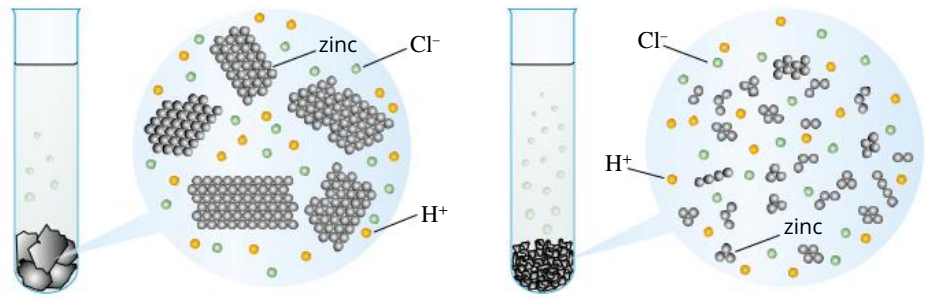
Grinding or breaking a solid into smaller pieces provides a greater total surface area, allowing more reactant particles to collide (Figure 1.2.2). This increased frequency of collisions results in a higher number of successful collisions per unit of time and hence an increased reaction rate.



surface area = $6 \times (2 \times 2)\ cm^2 = 24\ cm^2$

surface area = $8 \times (6 \times (1 \times 1))\ cm^2 = 48\ cm^2$

FIGURE 1.2.1 Given two samples of equal volume of a solid, it is clear that the sample with the smaller particle size has a greater total surface area.



granules of Zn

Granules of zinc metal react slowly with HCl.

powdered Zn

Zinc powder with large surface area reacts rapidly with HCl.

FIGURE 1.2.2 The reaction of hydrochloric acid and zinc. As the surface area of zinc increases, the rate of reaction with hydrochloric acid increases.

CHEMFILE

Oil fires and water don't mix

At some stage, many cooks will encounter a fat, oil or grease fire in the kitchen. In the first moment of panic, some people would think to throw water on the fire, but that action can lead to disastrous and possibly fatal results (Figure 1.2.3).

Water is denser and has a lower boiling point than the fat or oil fuelling a grease fire. When water is added to a pan with burning oil, the water sinks beneath the oil and instantly boils. The expansion of the water vapour ejects the oil from the pan as a fine spray of droplets. This fine spray of droplets collectively has a much larger surface area than the oil in the pan. This causes the combustion reaction to accelerate with explosive results.The safest way to extinguish an oil fire is to eliminate one of the reactants of the combustion reaction: oxygen. Covering the pan or spreading a large amount of baking soda or salt over it will prevent additional oxygen molecules from colliding with the oil, stopping the combustion.

FIGURE 1.2.3 Using water on a fat, an oil or a grease fire can accelerate the rate of a combustion reaction with life-threatening results.

Concentration

The **concentration** of a substance is the number of particles per unit of volume; for example, the number of moles of a substance per litre of a solution. A high concentration of solutes dissolved in a solution increases the frequency of collisions.

In Figure 1.2.4, you can see that the concentration of one of the reactants has been increased ten-fold while the volume remains constant. This more concentrated solution will experience a greater total number of collisions between reactant particles. A certain percentage of collisions will be successful, resulting in a greater number of successful collisions per unit of time and hence, a faster reaction rate.

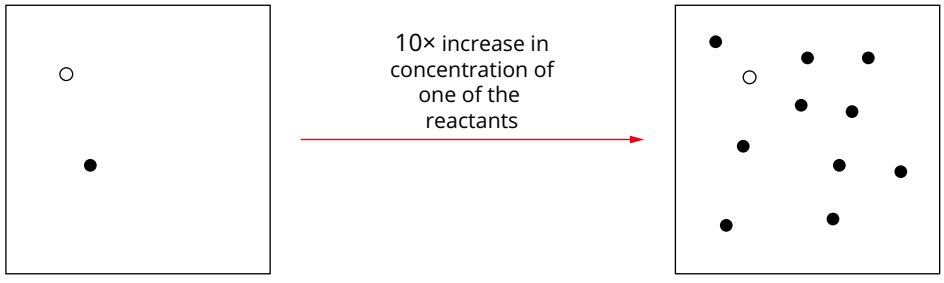


FIGURE 1.2.4 A greater number of reactant particles in the same volume will result in a greater number of collisions.

CHEMISTRY IN ACTION

Acid rain

Stone statues in locations prone to **acid rain** deteriorate relatively rapidly. This deterioration provides an example of the effect of concentration on the rate of a chemical reaction.

Most rainwater is slightly acidic as a result of the presence of carbonic acid, formed by carbon dioxide gas dissolved in the water. Oxides of nitrogen and sulfur released by cars and industry also dissolve in water, further raising the concentration of acids in rainwater. As a result, the rates of the reactions that disfigure stone statues (Figure 1.2.5) are also increased.

FIGURE 1.2.5 A reaction between acid rain and the limestone used to make this statue of a stone lion has caused the statue to deteriorate significantly.

Pressure

Pressure is the force per unit area that gas particles exert when they collide with the walls of their container. A high gas pressure is the consequence of having an increased number of gas particles in a given volume, at constant temperature.

When more gas particles are introduced into a given volume, raising the pressure, the frequency of collisions per unit time increases. Of this greater total number of collisions, a certain percentage will be successful, resulting in a greater number of successful collisions per unit of time and hence, a faster reaction rate.

Partial pressures

For a mixture of gases, such as air, the total pressure exerted by the mixture is the sum of the individual pressures of the composite gases. These individual gas pressures, when considered as part of a mixture, are known as **partial pressures**. The partial pressure of a gas in a mixture of gases can be considered as the equivalent of the concentration of a solute in a solution.

For example, air is generally considered to be composed of 78% nitrogen (N_2), 21% oxygen (O_2) and about 1% argon (Ar) and other gases. Atmospheric pressure at sea level is 101.3 kPa. So 78% of this value can be attributed to the partial pressure of nitrogen, 21% to the partial pressure of oxygen and the remaining 1% to the partial pressure of argon and other gases.

In this course, you will not need to undertake calculations involving partial pressures. However, if required, the partial pressure of nitrogen in air could be calculated according to the equation:

$$\text{partial pressure } (N_2) = \frac{78}{100} \times 101.3 = 79.0\,\text{kPa}$$

This also means that if two reacting gases are in a vessel of fixed volume, and the total pressure is increased by adding an inert gas such as helium, although the total pressure of the system increases, the partial pressure of the two reacting gases does not change, and hence the reaction rate remains unchanged.

INCREASING COLLISION PROBABILITY

Most collisions between reactant particles are unsuccessful. Even if particles have the correct orientation, the particles may not have the required activation energy. If you can increase the probability of a given collision being successful, you can increase the total number of successful collisions per unit of time and hence increase the reaction rate.

Experimental conditions that can affect the probability of a successful collision, and so produce a higher reaction rate, include:

- temperature
- the presence of catalysts.

Temperature

An increase in the **temperature** of a substance corresponds with an increase in the average kinetic energy of the particles that make up the substance. This is illustrated in Figure 1.2.6 in which the range of kinetic energies for a gas at three different temperatures is shown. As the temperature increases, the increasing average kinetic energy of the particles can be seen by the movement to the right of the peak in the Maxwell–Boltzmann curve.

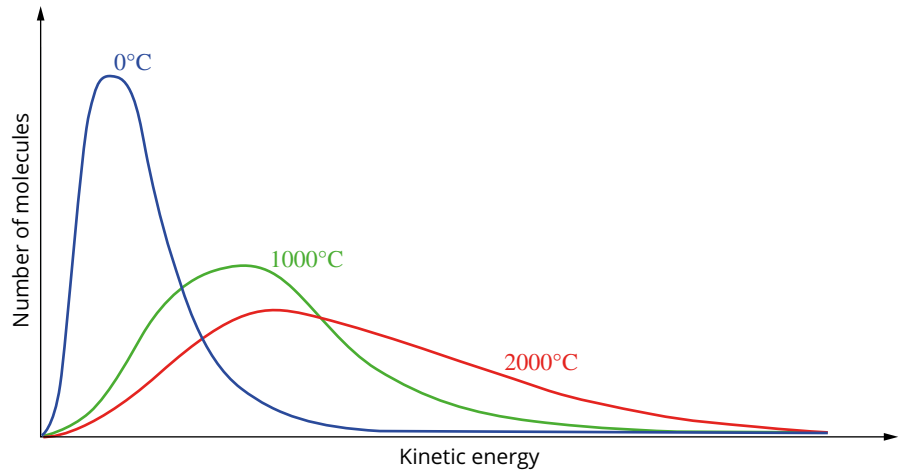


FIGURE 1.2.6 The Maxwell–Boltzmann distribution for a sample of gas at a range of temperatures. Note the reducing height of the maximum of each curve in the graph. This is to maintain the same area under the curve (which is equal to the total number of particles in the sample) as heating the gas does not generate additional particles.

This increase in average kinetic energy causes the particles to move, on average, with an increased speed, causing a greater frequency of collisions, both successful and unsuccessful. An increase in the temperature of the substance will also result in a greater percentage of these collisions satisfying the activation energy requirement for the reaction (Figure 1.2.7). This will cause a higher percentage of the existing collisions to be successful per unit of time and hence, a faster reaction rate.

So, a higher temperature increases the overall number of collisions and increases the proportion of successful collisions.

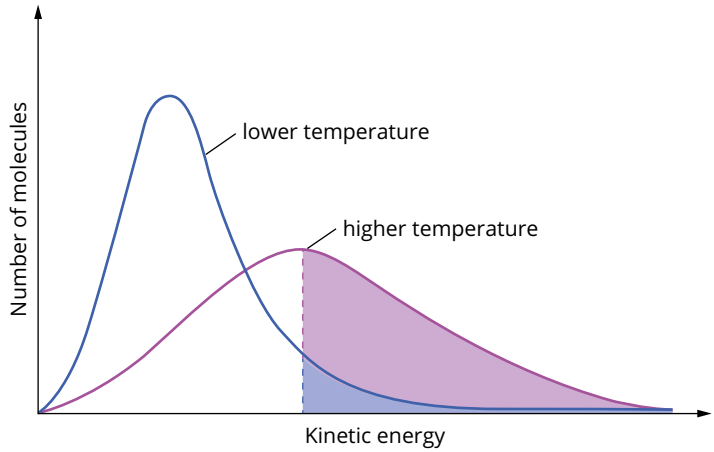


FIGURE 1.2.7 The proportion of particles that exceed the activation energy, E_a, is much greater for the sample at the higher temperature than the lower temperature.

A temperature increase of just 10°C doubles the rate of many reactions, but it can be shown that this is not due to the increased frequency of collisions. The frequency of collisions only increases by about 3% when the temperature increases by 10°C. The main reason the reaction rate increases is that a greater proportion of the particles have sufficient energy to overcome the activation energy barrier of the reaction.

The presence of catalysts

Most collisions are unsuccessful, even when they have correct orientation, because the particles don't have enough energy to overcome the activation energy. A **catalyst** works by providing an alternative **reaction pathway** with lower activation energy. In this way, a greater proportion of the reactant particles will have enough energy to overcome the, now reduced, activation energy (Figure 1.2.8). This increased probability of a successful collision results in a greater number of successful collisions per unit time and hence a faster reaction rate.

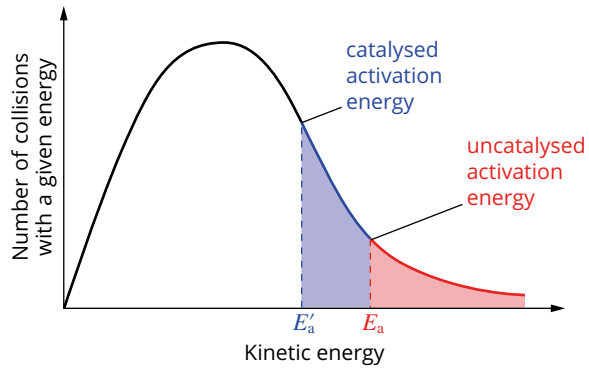


FIGURE 1.2.8 A catalyst provides an alternative reaction pathway with a low activation energy, increasing the proportion of collisions that exceed the activation energy and lead to a reaction.

Catalysts are specific to certain reactions; what catalyses one reaction may not catalyse another. Catalysts are not consumed in the reactions they catalyse and can be recovered and reused. However, they can be deactivated or poisoned, at which point they cease to increase the reaction rate. The alternative reaction pathway with a lower activation energy can be illustrated on a reaction energy profile (Figure 1.2.9).

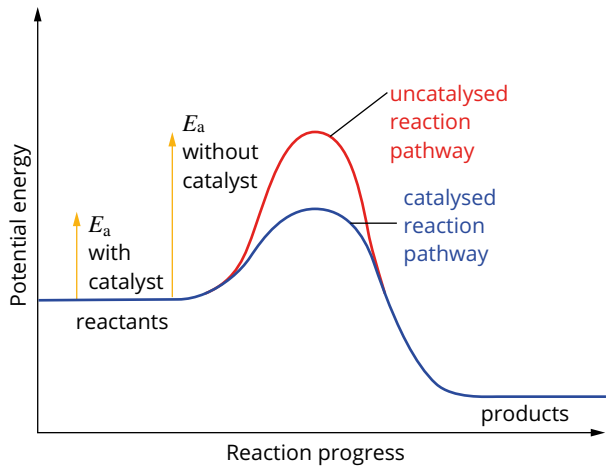


FIGURE 1.2.9 Energy profile diagrams with a catalysed and uncatalysed reaction. Note that the presence of a catalyst also reduces the activation energy for the reverse (products → reactants) reaction.

1.2 Review

SUMMARY

- The rate of a reaction can be increased by:
  - increasing the surface area of solid reactants
  - increasing the concentration of a reactant in solution
  - increasing the pressure of a gaseous reactant
  - increasing the temperature of the reaction system
  - adding a suitable catalyst.
- Increasing the surface area of solid reactants:
  - exposes a greater number of reactant particles to collisions
  - increases the frequency of collisions between reactants
  - increases the number of successful collisions in a given time.
- Increasing the concentration of a reactant in solution increases the:
  - number of solute particles per unit of volume
  - frequency of collisions between reactant particles
  - number of successful collisions in a given time.
- Increasing the pressure of a gaseous reactant increases the:
  - number of gas particles per unit of volume (assuming constant temperature)
  - frequency of collisions between reactant particles
  - number of successful collisions in a given time.
- Increasing the temperature of the reaction system increases the:
  - frequency of collisions between reactant particles
  - proportion of collisions that are successful
  - and therefore number of successful collisions in a given time.
- Adding a suitable catalyst:
  - provides an alternative reaction pathway with a lower activation energy
  - increases the proportion of successful collisions
  - increases the number of successful collisions in a given time.
- A Maxwell–Boltzmann distribution curve may be used to represent the range of kinetic energies possessed by particles in a substance at a given temperature.
- Energy profile diagrams, which can include catalysed and uncatalysed pathways, may be used to represent the enthalpy changes and activation energy associated with a chemical reaction.

KEY QUESTIONS

1 According to the collision theory, which one of the following is *not* essential for a reaction to occur?

A Molecules must collide to react.
B The reactant particles should collide with the correct orientation.
C The reactant particles should collide with enough energy to overcome the activation energy barrier.
D The reactant particles should collide with double the energy of the activation energy.

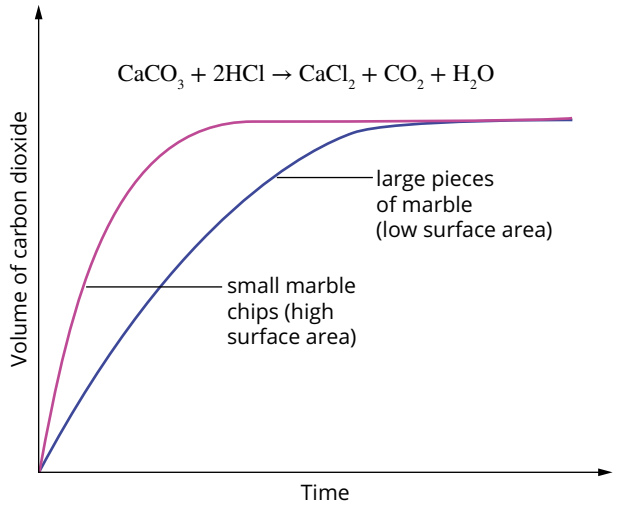
2 Which one of the following is the energy required to produce the transition state in a reaction?

A activation energy
B difference in energy between the products and reactants
C difference in energy between the products and the activation energy
D transition state energy

3 Which one of the following correctly explains why a sample of magnesium reacts more rapidly with 1 mol L^{-1} HCl than with 0.1 mol L^{-1} HCl?

A The energy of collisions between reactant particles is greater for the reaction containing 1 mol L^{-1} HCl.
B The rate of collisions between reactant particles is greater for the reaction containing 0.1 mol L^{-1} HCl.
C There are more collisions between the magnesium and 1 mol L^{-1} HCl.
D The frequency of collisions between reactant particles is greater for the reaction containing 1 mol L^{-1} HCl.

4 The effect of particle size on the reaction rate between marble chips and hydrochloric acid was examined. Carbon dioxide gas was collected by the downward displacement of water and its volume measured at regular intervals until the reaction had stopped. The results are given in the following graph.



a What does the steeper gradient of the small marble chips signify?

b What does the region of zero gradient on the curve represent?

c Why do both curves plateau at the same point?

5 When 1.00 mol of methane gas burns completely in oxygen, the process of bond breaking uses 3380 kJ of energy and 4270 kJ of energy is released as new bonds form.

a Write a balanced chemical equation for the reaction.

b Calculate the value of the heat of reaction, ΔH, for the reaction.

c Draw and label a diagram to show the changes in energy during the course of the reaction.

6 The formation of hydrogen iodide from its elements is represented by the equation:

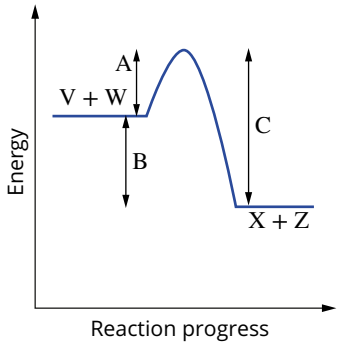
$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

This reaction has an activation energy of 167 kJ mol^{-1} and the heat of reaction, ΔH, is +28.0 kJ mol^{-1}. What is the activation energy for the reverse reaction, the decomposition of 2.00 mol of hydrogen iodide?

7 Consider the reaction between solutions V and W that produces X and Z according to the equation:

$$V(aq) + W(aq) \rightarrow X(aq) + Z(aq)$$

The energy profile diagram for this process is shown below.



a Is the reaction endothermic or exothermic?

b What does the value marked A represent for the forward reaction?

c What does the value marked B represent for the forward reaction?

d What does the value marked B represent for the reverse of this reaction?

e What does the value marked C represent for the reverse of this reaction?

8 Draw the Maxwell–Boltzmann distribution curve for an uncatalysed and catalysed reaction on the same set of axes. In what way do they differ?

Chapter review

01

KEY TERMS

acid rain
activation energy
catalyst
collision theory
concentration
energy profile diagram
kinetic energy
kinetic energy distribution diagram
Maxwell–Boltzmann distribution curve
partial pressure
pressure
rate of reaction
reaction pathway
reverse reaction
surface area
temperature
transition state

Rate of chemical reactions

1 According to collision theory, what must happen for a reaction to occur?

2 Which of the following combinations of reactants will produce the greatest initial reaction rate?
$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$
A $CaCO_3$ chips and 1.0 mol L^{-1} HCl
B $CaCO_3$ chips and 2.0 mol L^{-1} HCl
C $CaCO_3$ powder and 2.0 mol L^{-1} HCl
D $CaCO_3$ powder and 1.0 mol L^{-1} HCl

3 Which one of the following alternatives correctly explains why the rate of reaction between 1.0 mol L^{-1} $CuSO_4$ and powdered zinc is greater than with an equal amount of large zinc pieces?
A The energy of collisions between the $Cu^{2+}(aq)$ ions and powdered zinc is greater than with the large zinc pieces.
B The frequency of collisions between the $Cu^{2+}(aq)$ ions and powdered zinc is greater than with the large zinc pieces.
C The energy of collisions between the $Cu^{2+}(aq)$ ions and large zinc pieces is greater than with the powdered zinc.
D The frequency of collisions between the $Cu^{2+}(aq)$ ions and large zinc pieces is greater than with the powdered zinc.

4 Which one of the following statements correctly describes what must occur when reactant particles collide and react?
A Colliding particles must have an equal amount of kinetic energy.
B Colliding particles must have different amounts of kinetic energy.
C Colliding particles must have kinetic energy equal to or greater than the average kinetic energy.
D Colliding particles must have kinetic energy equal to or greater than the activation energy of the reaction.

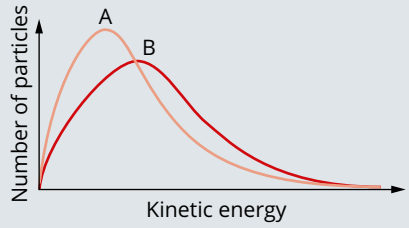
5 Explain why time on its own is not a useful quantity to measure the rate of a reaction.

6 In situations where the reaction mixture is heterogeneous, stirring can increase reaction rate. Explain this using collision theory.

7 A characteristic of all materials is their auto ignition temperature. This is the lowest temperature at which a substance will spontaneously ignite under normal atmospheric conditions without an external ignition source such as a spark or flame. Explain, using collision theory, what is occurring to a substance at its auto ignition temperature.

8 Evaluate the statement 'Put food in the freezer so it doesn't go off', using your knowledge of collision theory and reaction rates.

9 **a** The following graph shows the distribution of energies of particles in a substance at two different temperatures, 40°C and 60°C. Indicate the temperatures represented by graphs A and B.



b Copy this diagram for temperature B and use the diagram to show the effect of a catalyst on a reaction.

c Use the diagram you have drawn in part **b** to explain in terms of collision theory how a catalyst increases the rate of a reaction.

Factors that influence reaction rate

10 **a** List the five factors that influence the rate of a reaction.

b Classify the five factors from part **a** according to whether they increase the proportion of successful collisions by increasing:

i collision frequency.

ii the proportion of collisions that have energy equal to or greater than the activation energy.

11 Which one of the following factors would *not* increase the rate of decomposition of hydrogen peroxide?

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

A increasing the pressure of oxygen gas

B increasing the concentration of hydrogen peroxide

C increasing the temperature of hydrogen peroxide

D adding a potassium iodide catalyst

12 A student is attempting to use an excess of 1.0 mol L^{-1} hydrochloric acid to dissolve an iron nail. If the student doubles the initial starting volume of acid, using collision theory, predict and explain how this would change the time taken to completely dissolve the nail.

13 The first step in most toffee recipes is to dissolve about three cups of sugar in one cup of water. Although sugar is quite soluble in water, this step could be time-consuming. Use your knowledge of reaction rates to suggest at least three things you could do to increase the rate of dissolution without ruining the toffee.

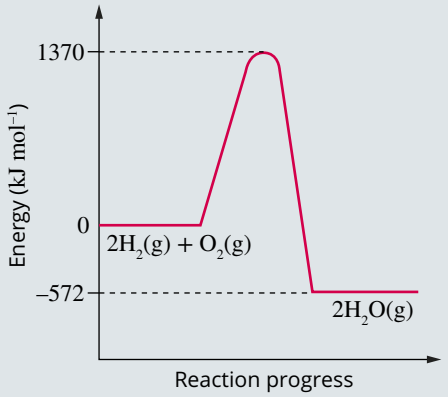
14 Which statement is correct for the effects of catalyst and concentration on the rate of reaction?

	Adding a catalyst	Increasing the concentration
A	Collision frequency increases	Collision frequency increases
B	Activation energy decreases	Activation energy decreases
C	Activation energy decreases	Collision frequency increases
D	Collision frequency increases	Activation energy decreases

15 Many major car-makers have plans for hydrogen-powered cars. In the fuel cells of these cars, hydrogen reacts with oxygen from the air to produce water:

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

Energy changes for the reaction are shown in the following graph.



a What is the magnitude of the activation energy of this reaction?

b What is ΔH for this reaction?

c Several groups of scientists have claimed to have split water into hydrogen and oxygen using a molybdenum catalyst:

$$2H_2O(g) \xrightarrow{Mo} 2H_2(g) + O_2(g)$$

Sketch energy change graphs for this reaction with and without the presence of a catalyst.

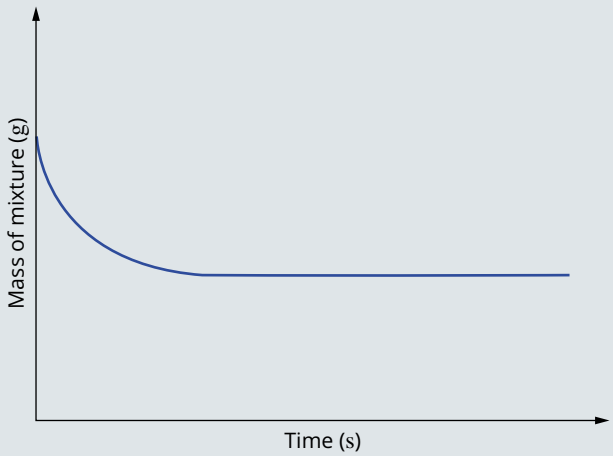
d What is the value of ΔH for this water-splitting equation?

Connecting the main ideas

16 A 5.00 g piece of copper was dissolved in a beaker containing an excess of 2.00 mol L^{-1} nitric acid. The equation for the reaction that occurred is:

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

The changing mass of the mixture was observed for a period of time, and the following graph was obtained.

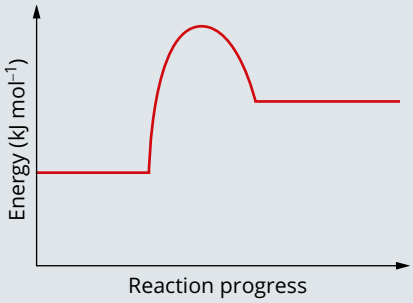


a Describe the rate of the reaction over the duration of the experiment and explain it using collision theory.
b Explain why the graph levels out.
c Redraw the graph in Figure 1.3.3, then sketch in the expected curve if an excess of 1.00 mol L^{-1} nitric acid had been used instead. Label your new graph line. Explain the difference in shape.
d Redraw the graph, then sketch in the expected curve if 5.00 g of powdered copper was used instead. Label this new graph line. Explain the difference in shape.

17 Lumps of limestone, calcium carbonate, react readily with dilute hydrochloric acid. Four large lumps of limestone, mass 10.0 g, were reacted with 100 mL 0.100 mol L^{-1} acid.
a Write a balanced equation to describe the reaction.
b Use a calculation to prove that calcium carbonate is in excess.
c Describe a technique that you could use in a school laboratory to measure the rate of the reaction.
d 10.0 g of small lumps of limestone will react at a different rate from four large lumps. Will the reaction with the smaller lumps be faster or slower? Explain your answer in terms of collision theory.
e List two other ways in which the rate of this reaction can be altered. Explain your answer in terms of collision theory.

18 The following graph shows the energy profile diagram for the reaction of hydrogen and iodine to form hydrogen iodide:

$$H_2(g) + I_2(s) \rightarrow 2HI(g)$$



a Copy the diagram and label the following: $H_2(g)$ and $I_2(s)$; HI(g); ΔH; activation energy.
b Is the reaction endothermic or exothermic?
c On the diagram draw the energy profile that would result if a catalyst was used in the reaction.

19 Read the article and answer the questions that follow.

Exploding iron

In 1996, while the Turkish ship MV *B. Onal* was riding at anchor in Delaware Bay, near Philadelphia in the USA, a 2-tonne hatch cover suddenly blew off. As the ship was carrying a cargo of iron, the surprised crew asked themselves, 'Can iron explode?'

As you may be aware, traditionally iron oxide (Fe_2O_3) is reduced to molten iron in a blast furnace.

A new process that uses less energy has been developed. Iron oxide is converted directly to solid iron without having to heat the reactants to the melting point of iron. Iron oxide is heated to 550°C in the presence of carbon monoxide and hydrogen gas. The iron oxide is reduced to iron by both gases with the formation of carbon dioxide or water.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \quad (1)$$

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g) \quad (2)$$

The pellets of pure iron that are formed are extremely porous and full of many tiny holes, in contrast to the solid formed when the molten iron from a blast furnace cools. Under the right conditions the iron pellets can be oxidised back to iron oxide.

In most cases, iron is oxidised slowly by oxygen back to iron oxide and the resulting heat can readily escape. If the pellets are more than 1 metre deep, as in the hold of a ship, the heat cannot escape quickly enough and the temperature rises. This speeds up the reaction rate. If the temperature increases sufficiently and water is present, another reaction occurs and the oxidation rate is speeded up 100-fold, with the release of more heat:

$$Fe(s) + H_2O(g) \rightarrow FeO(s) + H_2(g) \quad (3)$$

Any spark or fire will set off an explosion of hydrogen gas, and that is what happened on the MV *B. Onal*.

a What is the main reason the new reduction process uses less energy than the old process?
b Write equations showing the oxidation of iron by oxygen to form iron(II) oxide and iron(III) oxide.
c If water is present, the oxidation reaction speeds up 100-fold. Is water acting as a catalyst? Explain your answer.
d Is the reaction shown in equation 3 endothermic or exothermic?
e List the factors that increased the rate of reaction in equation 3.
f Firefighters were not able to use water to put out the fire in the cargo hold. Why not? Suggest how they could put out the fire.

CHAPTER

02 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 you 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 has serious consequences for the efficiency of chemical manufacturing industries. An understanding of the principles of equilibrium allows reaction conditions used for an industrial process to be adjusted to ensure optimum efficiency.

You will also learn how to write a mathematical relationship, known as an equilibrium law, for an equilibrium system. This law can be used to calculate the relative amounts of reactants and products present when a reaction is at equilibrium.

Science understanding

- chemical systems include physical changes and chemical reactions and may be open (which allow matter and energy to be exchanged with the surroundings) or closed (which allow energy, but not matter, to be exchanged with the surroundings)
- observable changes in chemical reactions and physical changes can be described and explained at an atomic and molecular level
- over time, in a closed system, reversible physical and chemical changes may reach a state of dynamic equilibrium, with the relative concentrations of products and reactants defining the position of equilibrium
- the characteristics of a system in dynamic equilibrium can be described and explained in terms of reaction rates and macroscopic properties
- the reversibility of chemical reactions can be explained in terms of the activation energies of the forward and reverse reactions
- the effect of changes of temperature on chemical systems initially at equilibrium can be predicted by considering the enthalpy changes for the forward and reverse reactions; this can be represented on energy profile diagrams and explained by the changes in the rates of the forward and reverse reactions
- the effects of changes in concentration of solutions and partial pressures of gases on chemical systems initially at equilibrium can be predicted and explained by applying collision theory to the forward and reverse reactions
- the effects of changes in temperature, concentration of species in solution, partial pressures of gases, total volume and the addition of a catalyst on equilibrium systems can be predicted using Le Châtelier's principle
- equilibrium law expressions can be written for homogeneous and heterogeneous systems; the equilibrium constant (K_c), at any given temperature, indicates the relationship between product and reactant concentrations at equilibrium
- the relative amounts of reactants and products (equilibrium position) can be predicted qualitatively using equilibrium constants (K_c)

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2.1 Chemical systems

In this section, 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 cells in your body and the reactions that carbon dioxide undergoes in the environment.

OPEN AND CLOSED SYSTEMS

In Year 11, 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 chemical system absorbs energy from the surroundings, whereas in an **exothermic** reaction, energy is released to the surroundings.

Figure 2.1.1 illustrates how you can distinguish between two different types of systems: open systems and closed systems.

The most common situation is an open system. In an **open system**, matter and energy can be exchanged with the surroundings. In contrast, a **closed system** can exchange energy but not matter with the surroundings.

Open systems exchange energy and matter with the surroundings.

Closed systems only exchange energy with the surroundings.

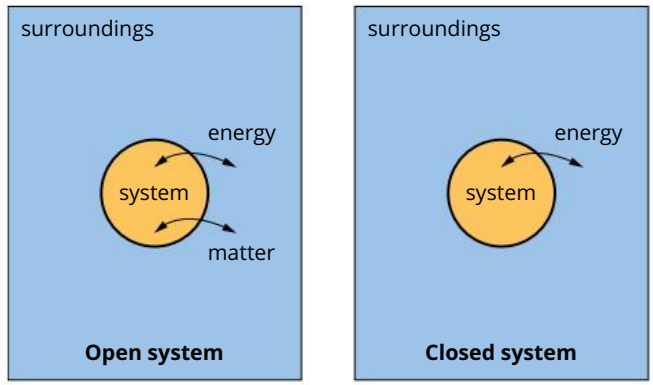


FIGURE 2.1.1 Open systems exchange energy and matter with the surroundings. Closed systems only exchange energy with the surroundings.

Some everyday examples of open and closed systems are illustrated in Figure 2.1.2.

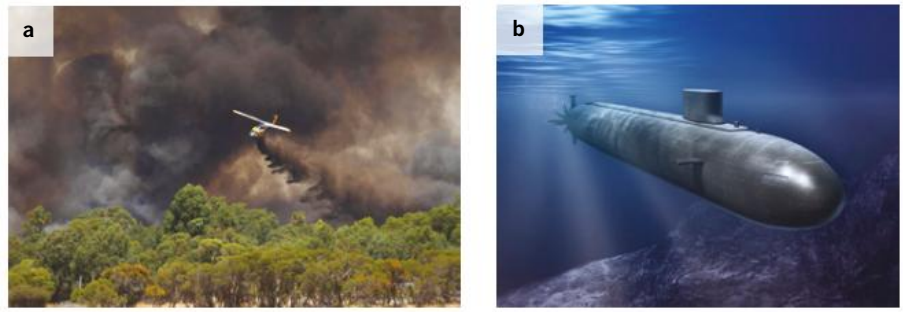


FIGURE 2.1.2 Examples of open and closed systems. (a) A bushfire burning through a forest on 3 February 2014 in Banjip, Western Australia. This is an example of an open system. Carbon dioxide and water vapour produced by the burning trees are released into the atmosphere. (b) A nuclear submarine in operation underwater. The carefully monitored environment of the submarine can be regarded as a closed system.

IRREVERSIBLE AND REVERSIBLE SYSTEMS

When some chemical reactions occur, the products cannot be converted back to the reactants. Such reactions, which occur in one direction, are called non-reversible or **irreversible reactions**.

Baking a cake (Figure 2.1.3) involves several irreversible 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.

However, other reactions are **reversible reactions**, where the products, once formed, can react again re-forming the reactants.

FIGURE 2.1.3 Baking a cake involves a series of irreversible chemical reactions.

REVERSIBILITY OF PHYSICAL AND CHEMICAL CHANGES

Three examples of systems that can be reversibile are:

- the evaporation and condensation of water
- a saturated sugar solution
- the reaction of haemoglobin and oxygen gas.

Evaporation and condensation of water

You are familiar with the idea that a physical change, such as a change of state, 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:

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

In chemistry, a double arrow ($\rightleftharpoons$) 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 2.1.4, 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.

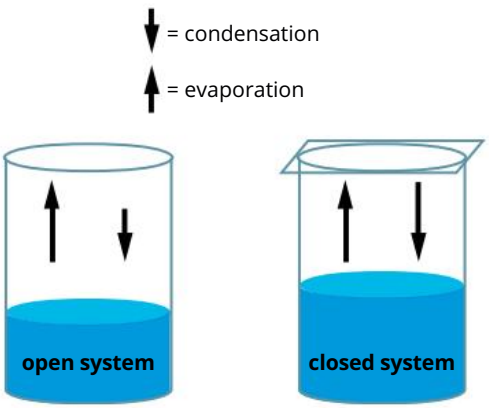


FIGURE 2.1.4 A physical change—the condensation and evaporation of water—in open and closed systems. In the open system, all the water eventually evaporates.

Saturated sugar solutions

Consider a **saturated solution** (a solution that contains the maximum possible concentration of a solute) of sugar in contact with undissolved sugar crystals at a constant temperature (Figure 2.1.5).

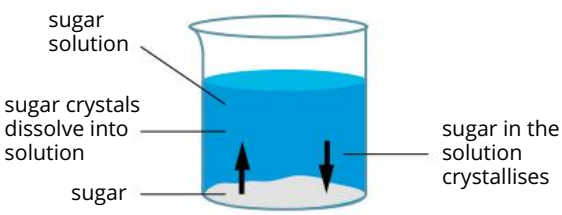


FIGURE 2.1.5 A representation of the reactions occurring in a saturated sugar solution

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:

$$C_{12}H_{22}O_{11}(s) \rightleftharpoons C_{12}H_{22}O_{11}(aq)$$

Even though there is no lid on the beaker, this system can 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

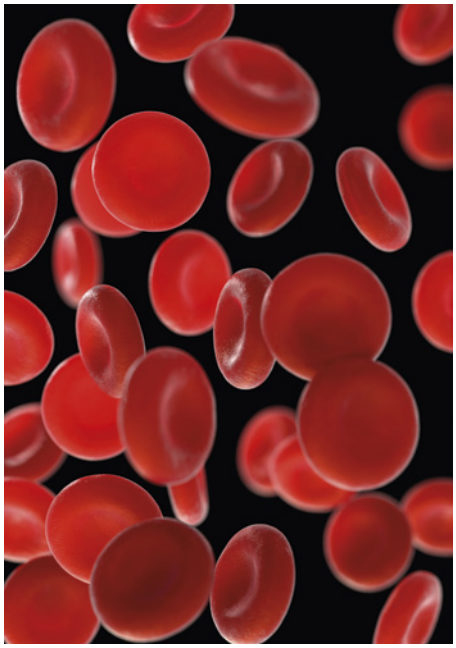


FIGURE 2.1.6 Blood cells contain a red pigment, haemoglobin, that transports oxygen from the lungs to other cells in the body.

Haemoglobin is a large protein molecule that is the pigment in red blood cells (Figure 2.1.6). It is responsible for the transport of oxygen from your lungs to the cells in your 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.

CHEMFILE

Soft drink and equilibrium

In a sealed bottle of soft drink, CO_2 gas is in equilibrium with dissolved CO_2 according to the equation:

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

The rate at which the gas dissolves in the solution is equal to the rate at which it leaves the solution to form a gas. To someone looking at the bottle, there appears to be nothing happening.

When the cap is removed from the bottle, the pressure is reduced and carbon dioxide escapes to the atmosphere. The system changes from a closed system to an open system and a net reverse reaction occurs as carbon dioxide comes out of solution. Bubbles of gas are observed when the bottle is opened.

This normally happens slowly, but when Mentos® mints are added to a bottle of soft drink, the drink erupts violently, as you can see in Figure 2.1.7. The high surface area of the mints provides many sites for bubbles to form, increasing the rate of the reaction, and quickly producing an eruption of soft drink from the bottle.

FIGURE 2.1.7 Erupting soft drink when mints have been added

CHEMISTRY IN ACTION

Limestone caves

An example of reversibility in nature is the formation of stalactites and stalagmites in limestone caves.

The main mineral in limestone is calcite ($CaCO_3$). Water saturated with carbon dioxide from the atmosphere drips through the roof of the cave, resulting in the following reaction:

$$CO_2(g) + H_2O(l) + CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$$

As the water seeps through the rocks, it becomes saturated with Ca^{2+} ions and HCO_3^- ions. The water then evaporates and the reverse reaction produces stalactites from the ceiling of the cave:

$$Ca^{2+}(aq) + 2HCO_3^-(aq) \rightleftharpoons CO_2(g) + H_2O(l) + CaCO_3(s)$$

Some of the solution drips onto the floor of the cave, where more deposits of $CaCO_3$ are produced, forming stalagmites. Stalactites and stalagmites grow in pairs and can produce the beautiful columns like the ones seen in the Ngligi cave system in Figure 2.1.8.

FIGURE 2.1.8 Stalactites in the Ngilgi Cave in Western Australia. They are made of the mineral calcite.

EXPLAINING REVERSIBILITY

The reason reversible reactions can occur can be understood by referring to an energy profile diagram like the ones you saw in Chapter 1.

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 the bonds of the reactants is known as the **activation energy** of the reaction.

You can see from the energy profile diagram in Figure 2.1.9 that once the products form it is possible for the reverse process to occur. If the newly formed 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.

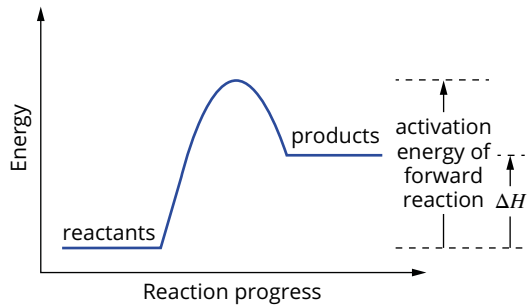


FIGURE 2.1.9 An energy profile diagram for an endothermic reaction showing the activation energy required for both the forward (formation of products) and reverse (re-formation of reactants) reactions.

Note that if the forward reaction is endothermic, the reverse reaction will be exothermic, and vice versa.

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 be converted back to the reactants.
- An irreversible reaction is a reaction in which the products cannot be converted back to the reactants.
- Reactions where the activation energy for the forward and reverse reactions are similar, are likely to be reversible.
- Reversible reactions can reach a point where the rates of the forward and reverse reactions are equal. At this point, equilibrium has been achieved.
- Equilibrium can be achieved in closed systems, but not in open systems.

KEY QUESTIONS

1 Which one of the following statements about a closed system is correct?

A A closed system must be completely sealed to stop reactants or products from escaping.

B In a closed system, the reactants and products cannot be exchanged with the surroundings.

C Energy cannot enter or leave a closed system.

D In a closed system, only products remain when the reaction is complete.

2 Indicate 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 which ionises: $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

d Burning toast

3 Select the correct answers from the list to complete the following paragraph about equilibrium. Some terms may be used more than once.

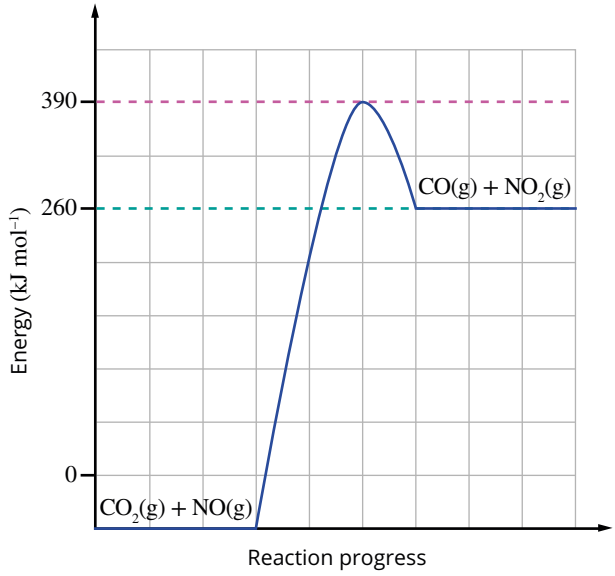
rates, processes, remains constant, increases, decreases, energy, matter, reversible, irreversible

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 _____.

4 The following graph shows the energy profile diagram for the reaction:

$$CO_2(g) + NO(g) \rightarrow CO(g) + NO_2(g)$$

What is the activation energy for the reverse reaction in kJ mol^{-1}?



2.2 Dynamic equilibrium

In the previous section, you learnt that reversible reactions can occur in both the forward and reverse directions.

Some reversible reactions can reach a point where they appear to stop. To someone observing an equilibrium system it would appear as if nothing is changing. 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 serious 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 of the reaction—the extent of conversion of reactants into products.

Although these reactions appear to stop, they actually continue to proceed. As reactants are forming products, the products are re-forming reactants at the same rate. This situation can be likened to the queue shown in Figure 2.2.1. 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.

FIGURE 2.2.1 A queue of constant length can be likened to a reaction that appears to have stopped, with people leaving the queue at one end at the same rate as others join it at the other end.

In this section, you will look more closely at how the particles in a chemical reaction behave as a reaction reaches an equilibrium.

EXPLAINING EQUILIBRIUM

As you have seen, in reversible reactions the formation of products as a result of collisions between reactant particles is not the end of the process. Once some products are formed, collisions between product particles can result in the reactants being re-formed.

Consider the production of ammonia from hydrogen gas and nitrogen gas, known as the Haber process.

The equation for the reaction can be written as:

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

Suppose you mix 1 mol of nitrogen gas and 3 mol of hydrogen gas in a sealed container. From the equation, you might expect that 2 mol of ammonia would eventually be formed. However, no matter how long you wait, the reaction seems to 'stop' when much less than 2 mol of ammonia is present, as shown in Figure 2.2.2.

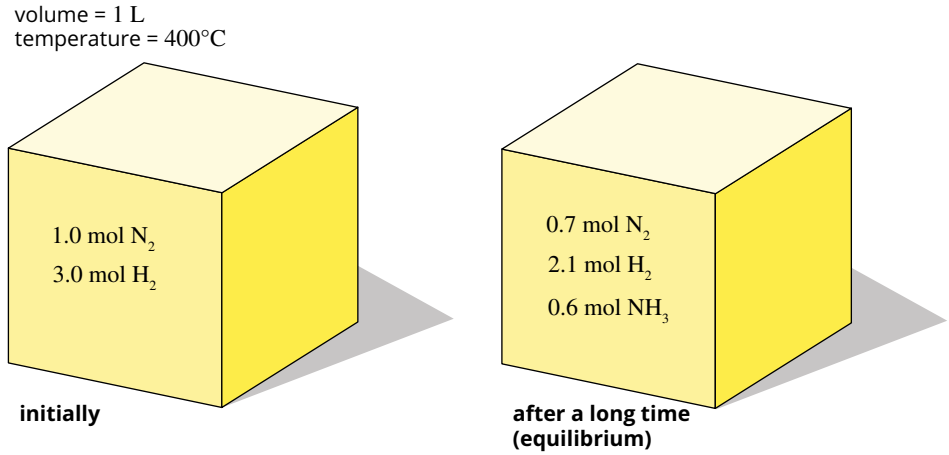


FIGURE 2.2.2 When 1 mol of nitrogen and 3 mol of hydrogen are mixed, the reaction to form ammonia appears to stop before all the reactants are consumed.

The reaction vessel this process occurs in can be thought of as a closed system from which the reactants and products cannot escape. Reversible reactions in a closed system eventually reach a situation where the rate of the forward reaction and the rate of the reverse reaction are equal.

At this point, there appears to be no further change to the observer. When the reaction appears to have 'stopped', the system is described as having reached equilibrium. At equilibrium, there still may be significant amounts of reactants in the system.

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 2.2.3.

If you consider the graph in Figure 2.2.3, 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.

Reversible reactions can reach a state of equilibrium where the overall concentrations of reactants and products do not change.

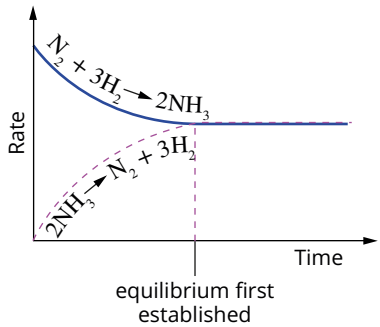


FIGURE 2.2.3 The variation of the rates of the forward and reverse reactions with time when nitrogen and hydrogen are mixed

The concentration versus time graph in Figure 2.2.4 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.

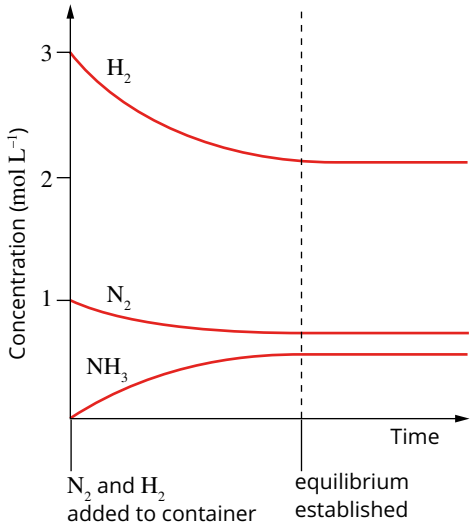


FIGURE 2.2.4 Changes in the concentrations of N_2, H_2 and NH_3 as a mixture of nitrogen and hydrogen gas reacts. As indicated by the coefficients of the equation for the reaction, for every mole of N_2 that reacts, three times as much H_2 reacts and twice as much NH_3 is produced.

When considering graphs involving equilibrium systems, always check if the data is presented as a plot of concentration versus time or reaction rate versus time.

Partial pressures

The pressure exerted by an individual gas in a container is known as its **partial pressure**. In a vessel containing the gaseous equilibrium:

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

the partial pressure of the nitrogen gas is the pressure that amount of nitrogen would exert if it were the only gas in the container. Similarly, the partial pressure of the hydrogen and the partial pressure of the ammonia are the pressures these gases would exert if they were the only gases in the container. The molecules of each gas move independently and collide with the walls of the container almost as though the other gases were not there.

The total pressure of a gas mixture is the sum of the effects of the collisions of all the individual gases. Therefore, the total pressure of the gaseous mixture of nitrogen, hydrogen and ammonia shown in Figure 2.2.5 is the sum of their partial pressures.

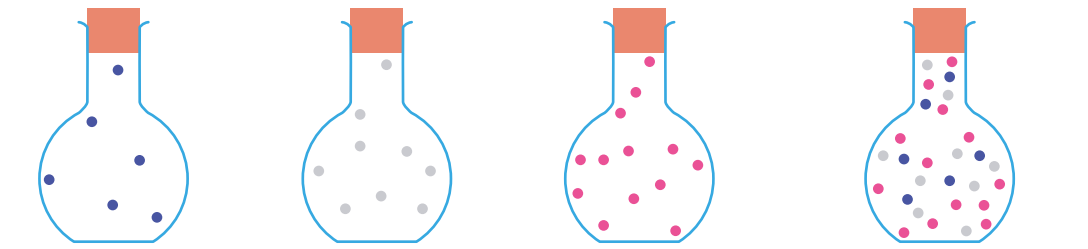


FIGURE 2.2.5 The total pressure of a mixture of gases is the sum of the partial pressures (individual pressures) of each of the gases in a mixture.

CHEMFILE

Fritz Haber

Fritz Haber (Figure 2.2.6) was a German chemist who invented the process for producing ammonia that now bears his name. The reaction produces ammonia from atmospheric nitrogen and hydrogen according to the equation:

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

The Haber process made it feasible to produce fertilisers with a high nitrogen content. This allowed for better crop yields in agriculture. Easy access to reasonably priced fertilisers has saved lives and reduced starvation 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 the World War I.

However, Haber's involvement in the production and use of chemical weapons by the German army in World War I made the award of a Nobel Prize controversial to many scientists who considered him to be guilty of war crimes.

You will learn more about the importance of Haber and his process in Chapter 11.

FIGURE 2.2.6 Fritz Haber (1868–1934) invented a process for producing ammonia from atmospheric nitrogen and hydrogen. He was awarded the Nobel Prize in Chemistry in 1918.

Increasing the amount of gas in a container of fixed volume or reducing the volume of the container will increase both the partial pressure and the concentration of the gas.

The changes that occur when nitrogen and hydrogen gas form an equilibrium mixture with ammonia gas can be described by measuring the partial pressures of the individual gases. At equilibrium, the partial pressures of the three gases will be constant.

DYNAMIC STATE OF EQUILIBRIUM

Chemical equilibrium can be described as a dynamic state because the forward and reverse reactions have not ceased. Instead, they occur simultaneously at the same rate.

During **dynamic equilibrium**:

- the **macroscopic properties** are constant. This means that the amount and concentrations of reactants and products, the pressure and the temperature are constant
- 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.

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

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 2.2.7 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.

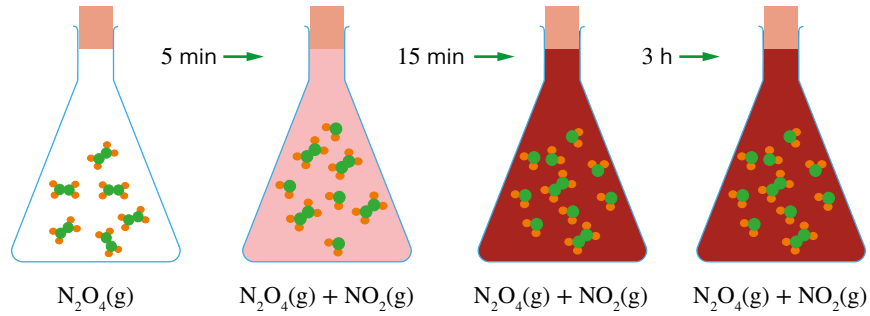


FIGURE 2.2.7 The decomposition of dinitrogen tetroxide produces the brown gas nitrogen dioxide. As the concentration of nitrogen dioxide increases, the colour deepens until equilibrium is reached. At equilibrium (after 8 seconds), there is no further change in colour regardless of how long the reaction is allowed to proceed.

EXTENSION

Investigating dynamic equilibrium

Chemists can use radioactive isotopes to investigate systems in dynamic equilibrium. Radioactive isotopes behave chemically in the same way as non-radioactive atoms of the same element, but their presence and location can be easily determined by a radiation detector.

When solid sodium iodide (NaI) is added to water, it dissolves readily at first. As the concentration of dissolved sodium iodide increases, a saturated solution forms and no further solid dissolves. The concentrations of the Na^+ ions and I^- ions in solution remain constant and some solid NaI is always present on the bottom of the test tube.

When solid sodium iodide containing radioactive iodide ions is added to a saturated solution, the subsequent movement of these 'labelled' ions can be traced. Figure 2.2.8 shows that although solid sodium iodide is still observed in the bottom of the flask, the solution quickly becomes radioactive.

The radioactivity of the solution shows that some of the radioactive sodium iodide has dissolved. The concentration of sodium iodide remains constant, so particles that were not radioactive must have crystallised from the solution at the same rate as the radioactive solid was dissolving (Figure 2.2.9).

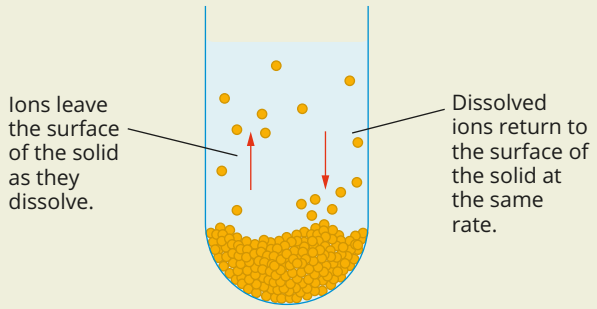


FIGURE 2.2.9 The cyclic dissolving and redepositing of ions in a saturated solution is an example of dynamic equilibrium.

Even though you see nothing happening, there must be continual activity at the surface of the solid. The process is a dynamic equilibrium:

$$NaI(s) \rightleftharpoons NaI(aq)$$

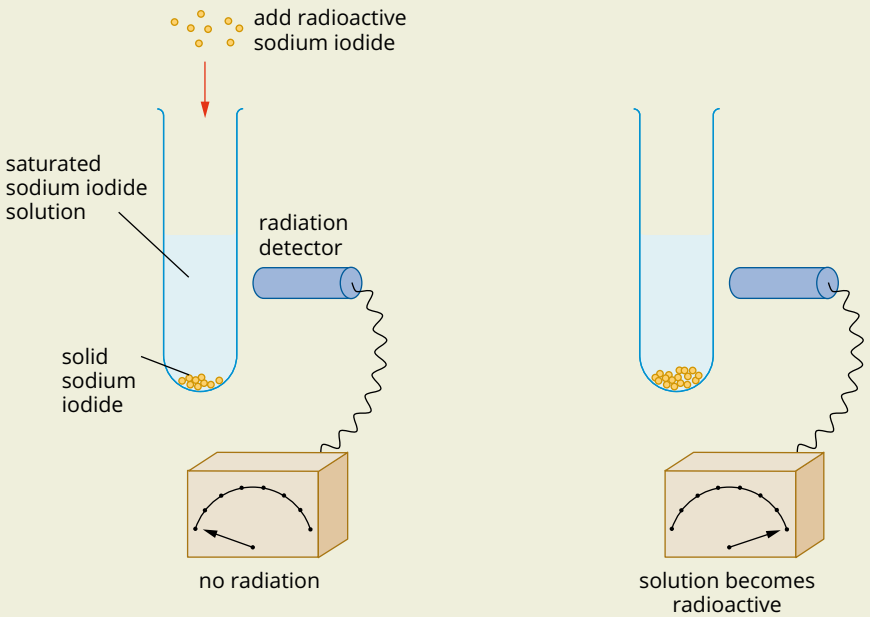


FIGURE 2.2.8 This experiment shows that a dynamic equilibrium between the solid and dissolved ions is present in a saturated solution.

EXTENT OF REACTION

You have seen that reactions are reversible, but not all reactions proceed to the same extent before they reach equilibrium. This can be shown with a simple experiment.

Both hydrogen chloride (HCl) and ethanoic acid (acetic) acid (CH_3COOH) react with water to form ions, according to the equations:

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

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 2.2.10 shows the results obtained from such an experiment. You can see that when hydrogen chloride dissolves in water, the solution formed (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 molecules to identical volumes of water.

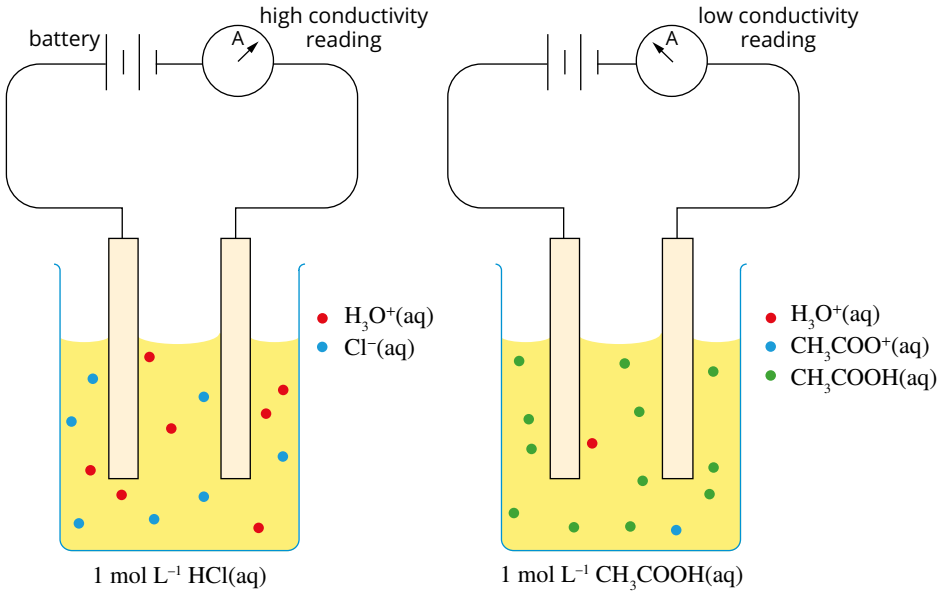


FIGURE 2.2.10 This experiment compares the electrical conductivity of 1 mol L^{-1} solutions of hydrogen chloride and ethanoic acid.

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 a better explanation of the idea of strong and weak acids by looking at the extent of the ionisation reaction.

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.

So, 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.

2.2 Review

SUMMARY

- At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction. This is called a state of dynamic equilibrium.
- Different reactions proceed to different extents.
- The relative ratios of reactants to products when equilibrium is reached are 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 concentration of the reactants and products with time.

KEY QUESTIONS

1 Which one of the following statements about the extent of reaction is true?

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.

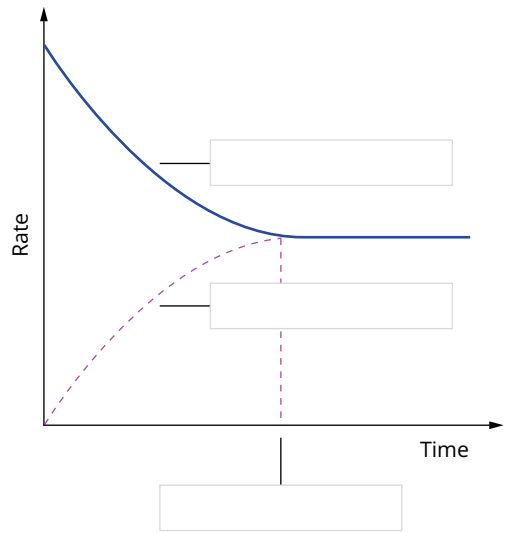
C The extent of reaction indicates how far the reaction has proceeded in the forward direction when equilibrium is achieved.

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.

2 Hydrogen gas is mixed with iodine gas in a sealed container. A reaction occurs according to the equation:

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

On the rate–time graph for this system shown below, label the lines for the forward and reverse reactions with the appropriate chemical equation. Also label the point when equilibrium is first established.

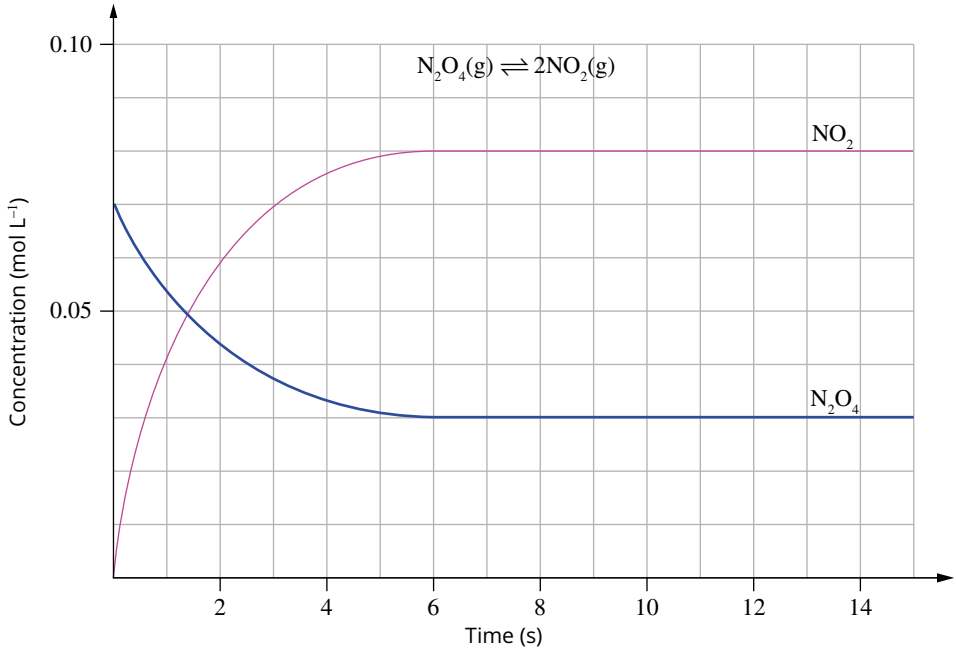


3 Fill in the blanks to complete the sentences about dynamic equilibrium.

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 backward reactions are _____ and the concentrations of all species do not change.

2.2 Review *continued*

4 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 answer the following questions.



a What is the initial concentration of N_2O_4 in the flask?
b What is the initial concentration of NO_2 in the flask?
c What is the concentration of N_2O_4 at equilibrium?
d What is the concentration of NO_2 at equilibrium?
e Over the course of the reaction, how many moles of N_2O_4 decompose?
f What do the horizontal regions of the graph indicate?
g How long does it take for equilibrium to be reached?
h A student studying this reaction records her observations over time. What will she observe as the reaction proceeds?

2.3 The equilibrium law

In this section, 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.

REACTION QUOTIENT

Consider the equilibrium system you were introduced to in section 2.2:

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

An unlimited number of different equilibrium mixtures of the three gases, nitrogen, hydrogen and ammonia, can be prepared. Table 2.3.1 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.

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 2.3.1 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	0.25	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 2.3.1, 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. Note that the coefficients of the reactants and products in the chemical equation above form the indices of the respective reactant and product concentrations used in the reaction quotient.

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.

CHEMFILE

Equilibria in biological systems

Although the principles you will learn in this section and the other sections in this chapter 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 2.3.1). If the populations change because of 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 2.3.1 The populations of zebras and lions in Africa can be understood by using the principles of equilibrium.

i K_c is the equilibrium constant for a reaction. The value of K_c is different for different reactions.

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 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 expression, the concentrations of the products are always on the top of the expression.

Worked example 2.3.1

DETERMINING THE EXPRESSION FOR THE EQUILIBRIUM CONSTANT FOR AN EQUILIBRIUM SYSTEM

The decomposition of N_2O_4 is a reversible reaction that occurs according to the equation:

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

Write the expression for the equilibrium constant K_c.

Thinking	Working
Identify the reactants and products. The reactants appear in the denominator of the expression and the products in the numerator.	N_2O_4 is a reactant, so it appears in the denominator of the expression. NO_2 is a product, so it appears in the numerator of the expression.
Write the expression for K_c. $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$ Remember that the index of each component concentration is the same as its coefficient in the balanced chemical equation.	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$

Worked example 2.3.1: Try yourself

DETERMINING THE EXPRESSION FOR THE EQUILIBRIUM CONSTANT FOR AN EQUILIBRIUM SYSTEM

Write the expression for K_c for the reversible reaction:

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

CHEMFILE

Equilibrium in the theatre

A yellow solution containing Fe^{3+} ions reacts with a colourless solution containing SCN^- ions to form a blood-red solution containing $FeSCN^{2+}$ ions, according to the equilibrium reaction:

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$
$$K_c = 9 \times 10^2 \text{ at } 25°C$$

An appreciable amount of the product $FeSCN^{2+}$ is present in an equilibrium mixture, so the mixture appears blood red in colour (Figure 2.3.3).

This equilibrium reaction is used in theatrical productions to make fake blood. A layer of colourless SCN^- solution can be painted onto an actor's hand prior to the scene. If a plastic knife that has been previously dipped in pale yellow Fe^{3+} solution is used to make a fake cut across the hand, a blood-red 'cut' appears due to the production of red $FeSCN^{2+}$.

FIGURE 2.3.3 Chemicals needed to make fake blood. From left to right: a solution containing Fe^{3+}, a solution containing SCN^-, and an equilibrium mixture of Fe^{3+}, SCN^- and $FeSCN^{2+}$.

HOMOGENEOUS AND HETEROGENEOUS EQUILIBRIA

The chemical reactions discussed so far have involved **homogeneous reactions**, in which all reactants and products are in the same state or phase. However, some equilibria involve **heterogeneous reactions**, in which reactants and products are in different states or 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 the value of 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 a 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:

$$K_c = [CO_2]$$

Since CaO and $CaCO_3$ are both solids, they do not appear in the equilibrium law.

The dissolution of a solid to form an aqueous solution is another example of a heterogeneous equilibrium system. Consider the dissociation of lead chloride ($PbCl_2$) into lead and chloride ions in solution:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

Because the concentration of the solid lead chloride is constant, it is assigned the value of 1 and not written in the expression for the equilibrium law. This results in the expression:

$$K_c = [Pb^{2+}][Cl^-]^2$$

2.3 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:
  $aW + bX \rightleftharpoons cY + dZ$
  is:
  $K_c = \frac{[Y]^c[Z]^d}{[W]^a[X]^b}$
- A reaction quotient, Q_c, can be calculated for any stage of a chemical reaction. The reaction quotient has the same mathematical expression as the equilibrium constant.
- When a reaction system at a particular temperature has reached equilibrium, the reaction quotient is equal to the equilibrium constant.
- An expression for the equilibrium law can be written for both homogeneous and heterogeneous systems. For heterogeneous systems, the concentration of a pure solid or a pure liquid is assigned as 1.

KEY QUESTIONS

1 Write an expression for the equilibrium constant for the reaction of hydrogen and chlorine with the equation:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

2 Match each of the terms in **a–d** with the appropriate statement (1–4).

1 a system where some of the species are in different states
2 is always equal to K_c
3 a system where all the species are in the same state
4 is equal to K_c at equilibrium

a homogeneous system
b heterogeneous system
c reaction quotient
d equilibrium constant

3 For each of the following reactions, write the correct expression for the equilibrium constant, K_c.

a $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$
b $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
c $2Ag^+(aq) + CO_3^{2-}(aq) \rightleftharpoons Ag_2CO_3(s)$
d $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$

4 Which one of the equations below has the following expression for the equilibrium constant?

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

A $4H_2(g) + 2CO(g) \rightleftharpoons 2CH_3OH(g)$
B $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$
C $2CH_3OH(g) \rightleftharpoons 4H_2(g) + 2CO(g)$
D $CH_3OH(g) \rightleftharpoons 2H_2(g) + CO(g)$

2.4 Working with equilibrium constants

In section 2.3, you learnt that an equilibrium law can be written for a chemical reaction at equilibrium. The mathematical expression for the equilibrium law is a fraction involving the concentrations of the reactants and products, which has a value equal to K_c, the equilibrium constant for the reaction at equilibrium.

The value of an equilibrium constant indicates the extent of a reaction or how far a reaction will proceed towards the products. In this section you will learn how to interpret these values in terms of the relative amounts of reactants and products present at equilibrium.

You will also discover how temperature affects an equilibrium constant and what happens to the value of an equilibrium constant when an equation is reversed or the coefficients of the equation are changed.

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 also given.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_c = \frac{[N_2O_4]}{[NO_2]^2}$$

$$2N_2O_4(g) \rightleftharpoons 4NO_2(g) \qquad K_c = \frac{[NO_2]^4}{[N_2O_4]^2}$$

$$\frac{1}{2}N_2O_4(g) \rightleftharpoons NO_2(g) \qquad K_c = \frac{[NO_2]}{[N_2O_4]^{\frac{1}{2}}}$$

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 amount 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 2.4.1.

TABLE 2.4.1 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. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_c = 0.52$ 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.

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.

Only a change in temperature will change the value of K_c for a given reaction.

Table 2.4.2 summarises the effect on K_c when temperature increases. The opposite is true when temperature decreases.

TABLE 2.4.2 The effect on the value of K_c when the temperature of the 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.

2.4 Review

SUMMARY

- The expression for the equilibrium constant, K_c, is dependent on the equation for the reaction.
- The value of K_c provides a measure of the extent of reaction and the relative concentrations of reactants and products at equilibrium (Table 2.4.3).
- As temperature increases, the value of K_c increases for endothermic reactions and decreases for exothermic reactions.

TABLE 2.4.3 Summary of the relationship between the value of K_c and the extent of a reaction

Value of K_c	Extent of reaction
Between about 10^{-4} and 10^{4}	Indicates significant reaction occurs
$>10^{4}$	Indicates an almost complete reaction occurs
$<10^{-4}$	Indicates negligible reaction occurs

KEY QUESTIONS

1 Complete the sentences to describe equilibrium by selecting terms from the box.

a significant	an extensive	equal to
greater than	the products	less than
negligible	the reactants	
both the reactants and the products		

Equilibrium occurs when the rate of the forward reaction is _____ the rate of the reverse reaction. The value of the equilibrium constant, K_c, is dependent upon the equilibrium concentrations of _____. If, at a particular temperature, K_c for a reaction is 10^{-6}, this reaction will produce _____ amounts of product at equilibrium.

2 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 Write an expression for the equilibrium constant for the equation:

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

b Based on the stated value of the equilibrium constant in the question, suggest why, at the same temperature, the value of the equilibrium constant for the equation in part **a** will be less than 1.

3 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}. Assuming no change in temperature, write the expression for the equilibrium constant for the following reactions:

a $H_2O(g) + Cl_2(g) \rightleftharpoons 2HCl(g) + \frac{1}{2}O_2(g)$

b $2HCl(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g) + Cl_2(g)$

4 A chemist investigated three different reactions and determined the value of the equilibrium constant for each. In which of the reactions would there 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: $K_c = 3.1 \times 10^{-3}$

5 State 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 $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \quad \Delta H = -564\ kJ\,mol^{-1}$

2.5 Le Châtelier's principle

FIGURE 2.5.1 The effect of changes on the equilibrium: $Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$. 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.

CHEMFILE

Henri Le Châtelier

Henri Le Châtelier (Figure 2.5.2), was a French chemist and engineer. He is best known for developing the principle of chemical equilibrium, which is now named after him.

Le Châtelier made an early attempt at synthesising ammonia from nitrogen and hydrogen, but an error in the design of the experiment resulted in an explosion that nearly killed one of his laboratory assistants. Le Châtelier also developed the oxyacetylene welding torch and the thermocouple for accurate temperature measurement.

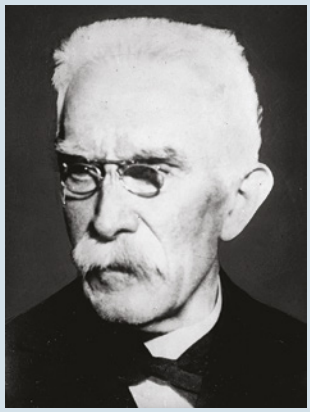


FIGURE 2.5.2 Henri Le Châtelier (1850–1936)

In this section, 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 shown in Figure 2.5.1.

The effect of changes on a chemical equilibrium is very important to the chemical industry. Conditions must be carefully selected to ensure that optimum yields of products are obtained within a reasonable timeframe.

CHANGES TO AN EQUILIBRIUM SYSTEM

Different reactions proceed to different extents. As a consequence, the relative amounts of reactants and products at equilibrium differ from one reaction to another. The relative amounts of reactants and products at equilibrium is called the **position of equilibrium** and it depends 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 (for equilibria involving gases)
- diluting (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).

i The position of equilibrium should not be confused with K_c. The value of K_c is only ever changed by a change in temperature.

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**.

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 that change.

When a change occurs to an equilibrium system so that it is momentarily no longer at equilibrium, a net reaction occurs that partially counteracts 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.

Adding extra reactant or product

A sealed reaction vessel of hydrogen and nitrogen gases at a particular temperature will establish an equilibrium with ammonia gas, 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 and partial pressures of the three gases are constant. If extra N_2 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 adjust to decrease the concentration (and partial pressure) of the added N_2, so a net forward reaction will occur.

It is important to note that, even though the concentration (and partial pressure) of N_2 gas decreases as the system moves to establish the new equilibrium, its final concentration (and partial pressure) 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

You can apply your knowledge of collision theory and reaction rates to understand 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 concentrations of N_2 and H_2 decrease 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 2.5.3 show the effects on the rate of the forward and reverse reactions as the composition of the mixture adjusts to form a new equilibrium.

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 with sufficient energy and the correct orientation. The more successful collisions that occur within a specified time period, the faster is the reaction rate.

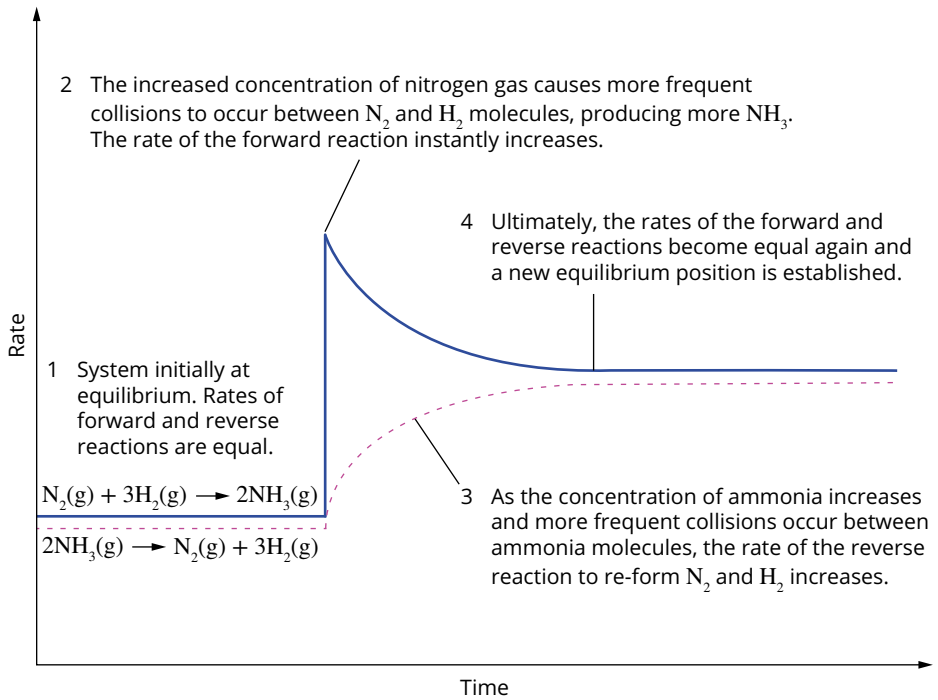


FIGURE 2.5.3 This rate–time graph shows the events that occur as a mixture of nitrogen and hydrogen gas returns to equilibrium after the addition of extra nitrogen gas.

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 and partial pressure of NH_3 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 or a pressure–time graph. Figure 2.5.4 illustrates the effect on the system when N_2 gas is added as described.

Note that the value of K_c for the equilibrium reaction remains unchanged as the temperature has not changed.

i Only temperature changes the value of K_c for an equilibrium system.

If you follow the same reasoning as for the addition of N_2, you can see that adding extra amounts of the other reactant, H_2, to the system will also increase the concentration and partial pressure of NH_3 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 and partial pressure of NH_3 as seen in Figure 2.5.5.

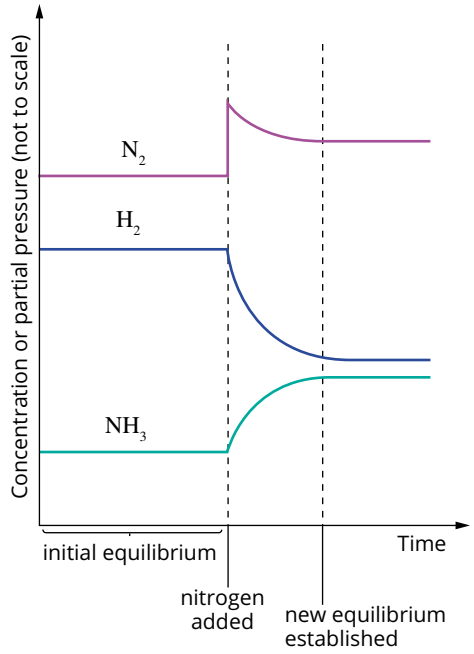


FIGURE 2.5.4 A representation of changes in concentrations and partial pressures that occur when additional nitrogen gas is added to the equilibrium:

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

Note that the vertical axis does not show the rate of reaction.

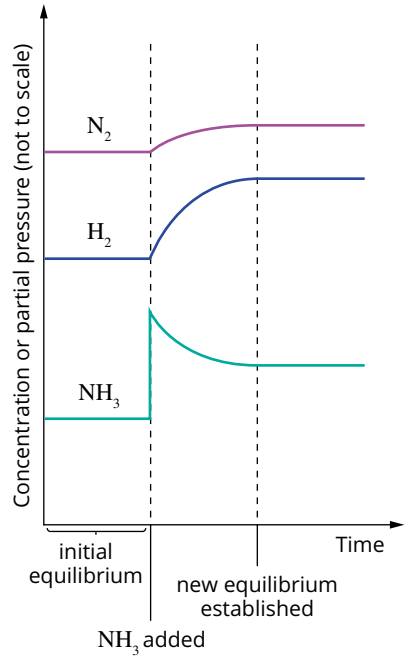


FIGURE 2.5.5 A representation of changes in concentrations and partial pressures that occur when additional ammonia gas is added to the equilibrium:

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

The reaction shifts to the left, forming more N_2 and H_2.

Table 2.5.1 summarises how an equilibrium system acts to oppose the addition or removal of reactants and products.

TABLE 2.5.1 The general effects of a change to a system at equilibrium

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

Worked Example 2.5.1 shows the use of collision theory to explain how an equilibrium system is affected by the addition of a reactant or product.

Worked example 2.5.1

USING COLLISION THEORY TO EXPLAIN THE EFFECT OF ADDITION OF A REACTANT OR PRODUCT ON AN EQUILIBRIUM SYSTEM

In solution, pink-coloured $Co(H_2O)_6^{2+}$ ions form an equilibrium with blue-coloured $CoCl_4^{2-}(aq)$ ions, as shown by the equation:

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

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.

Worked example: Try yourself 2.5.1

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.

CHEMISTRY IN ACTION

Competing eqilibria—carbon monoxide poisoning

Haemoglobin in red blood cells transports oxygen from your lungs to the cells in your body. The haemoglobin complex combines with oxygen to form an equilibrium system with oxyhaemoglobin:

haemoglobin + oxygen $\rightleftharpoons$ oxyhaemoglobin

In the lungs, oxygen from the air combines with haemoglobin. According to Le Châtelier's principle, the higher concentration of oxygen in this environment will cause a net forward reaction, producing greater amounts of oxyhaemoglobin. Most of the haemoglobin is converted to oxyhaemoglobin as a result of the continual addition of oxygen from each breath you take.

Carbon monoxide is a colourless, odourless and tasteless gas that is formed as a product in the incomplete combustion of fuels. Carbon monoxide is present in cigarette smoke and in the exhaust gases from car engines (Figure 2.5.6).

FIGURE 2.5.6 Carbon monoxide gas is formed when hydrocarbon fuels, such as petrol, are burnt in limited supplies of oxygen.

The high toxicity of carbon monoxide is a result of its reaction with haemoglobin:

haemoglobin + carbon monoxide $\rightleftharpoons$ carboxyhaemoglobin

The equilibrium constant for the reaction between carbon monoxide and haemoglobin is nearly 20 000 times greater than for the reaction between oxygen and haemoglobin. The larger equilibrium constant means that the forward reaction is much more likely to occur. Even small concentrations of carbon monoxide shift the position of equilibrium well to the right.

The formation of carboxyhaemoglobin reduces the concentration of haemoglobin, causing the reverse reaction of oxyhaemoglobin formation to occur. In extreme cases, almost no oxyhaemoglobin is left in the blood and carbon monoxide poisoning occurs.

Symptoms of carbon monoxide poisoning include drowsiness, dizziness, headaches, shortness of breath and loss of intellectual skills. Loss of consciousness and even death can result from carbon monoxide concentrations as low as 200 ppm.

The reactions of oxygen and carbon monoxide with haemoglobin are described as **competing equilibria**, because both oxygen and carbon monoxide 'compete' for the same substance, haemoglobin. The equilibrium reaction with the larger equilibrium constant has a significant effect on the extent of reaction of the other reaction.

2.5 Review

SUMMARY

- Le Châtelier's principle states that if an equilibrium system is subjected to change, the system will adjust itself to partially oppose the change.
- The effect of a change on an equilibrium can be predicted from Le Châtelier's principle. The effects of changes can also be explained by the use of collision theory and the equilibrium law (Table 2.5.2).

TABLE 2.5.2 Summary of effect of change on equilibrium using Le Châtelier's principle and collision theory

Change to system in equilibrium	Le Châtelier's principle prediction: effect of change on equilibrium position	Collision theory explanation: effect of change on equilibrium position
Adding extra reactant	Shifts to the right (net forward reaction)	Increased reactant concentration causes more frequent collisions, initially increasing the rate of the forward reaction. As reactants are consumed and more products form, the rate of the forward reaction decreases and the rate of the reverse reaction increases. A new equilibrium forms when the rates become equal. However, since the rate of the forward reaction was initially increased, this results in a net forward reaction.
Adding product	Shifts to the left (net reverse reaction)	Increased product concentration causes more frequent collisions, initially increasing the rate of the reverse reaction. As products are consumed and more reactants form, the rate of the reverse reaction decreases and the rate of the forward reaction increases. A new equilibrium forms when the rates become equal. However, since the rate of the reverse reaction was initially increased, this results in a net reverse reaction.

KEY QUESTIONS

1 Use Le Châtelier's principle to predict the effect on the position of equilibrium of adding more hydrogen gas to the following systems.

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

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

c $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

2 Use the concepts of rates of reaction and collision theory to explain the effect on the position of equilibrium of increasing the partial pressure of hydrogen by adding more hydrogen gas to the following systems.

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

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

3 Predict the effect of the changes on the position of each of the following 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:

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

4 Consider the equilibrium:

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq)$$

Which one of the following correctly describes a change that would cause an increase in the amount of $Cu(NH_3)_4{}^{2+}$ present?

A $OH^-(aq)$ is added, to react with Cu^{2+}, and the reaction shifts to the left.

B More NH_3 is added, and the reaction shifts to the right.

C $H^+(aq)$ is added, to react with the NH_3 and the reaction shifts to the left.

D None of the above reactions increase the amount $Cu(NH_3)_4{}^{2+}$.

2.6 Further applications of Le Châtelier's principle

FIGURE 2.6.1 Cuttlefish have an internal shell made of calcium carbonate. Cuttlefish and other marine animals could be affected by the decreasing pH of oceans.

Le Châtelier's principle can be used to understand how changes to chemical equilibria can affect many natural systems.

For example, in the oceans, carbon dioxide gas is involved in equilibria that provide the carbonate ions needed for the growth of seashells, 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 pH of the Earth's oceans. This will put marine ecosystems and organisms at risk, including the cuttlefish in Figure 2.6.1, whose shells are made of calcium carbonate.

In this section, 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.

Later in the course, you will learn how the principles of equilibrium can be applied to predict the optimum conditions for the industrial production of chemicals, by considering both rate and yield as well as costs and energy requirements.

CHANGING PRESSURE BY CHANGING VOLUME

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 the reverse reaction causes an overall increase in pressure of the system.

As you saw in the section 2.5, a change in the position of an equilibrium can be predicted by applying:

- Le Châtelier's principle
- your knowledge of collision theory and the rates of reactions.

> **i** Remember that 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 overall number of particles will change the pressure.

Predicting the effect of a 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.

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 2.6.2.

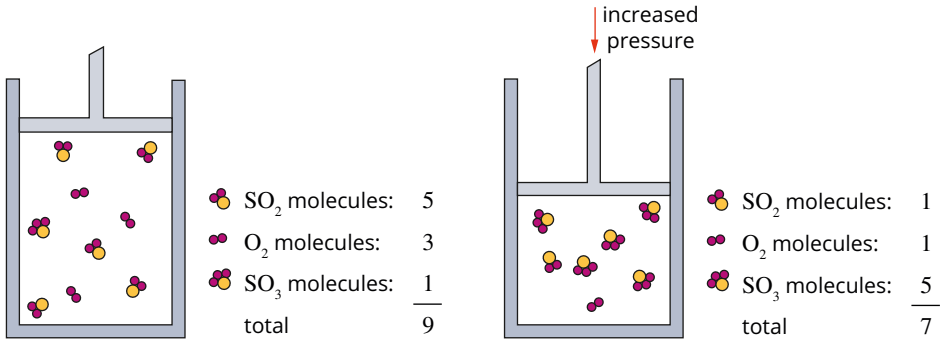


FIGURE 2.6.2 A representation of the effect of increased pressure on the equilibrium: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

The effect of the change can also be illustrated in a graph (Figure 2.6.3). When the system is initially at equilibrium and there is an increase in pressure, the partial pressures of all gases increase simultaneously, as do the concentrations.

As the system adjusts, there is a gradual change in concentration and partial pressure of each of the species until the new equilibrium is established. At the new equilibrium position, the individual partial pressures and concentrations are different from those at the first equilibrium. However, the equilibrium constant, K_c, has not changed. The ratio of products to reactants in the equilibrium law still equals K_c at the new equilibrium position.

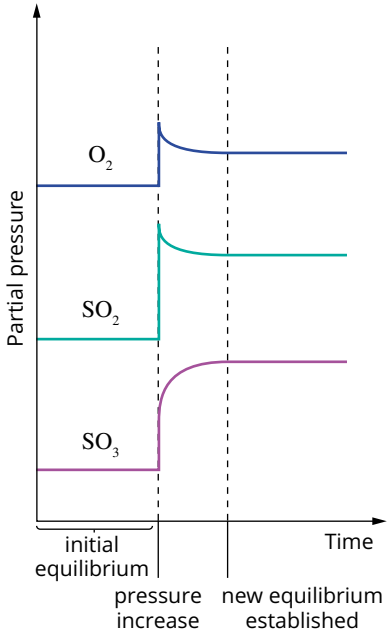


FIGURE 2.6.3 The effect of increased pressure on the equilibrium: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

An increase in pressure will favour the side of the reaction with the least number of particles.

Explaining the effect of a change using collision theory and rates of reaction

The effect of a reduction in volume on the equilibrium can also be understood by 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 concentration fraction.

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

CHEMFILE

Chickens lay eggs with thinner shells in the summer

Chickens, like dogs, do not perspire. Therefore, in hot weather chickens have to pant to try to maintain a healthy temperature. This means that they exhale more carbon dioxide gas than when they are breathing normally.

This affects the following series of competing equilibria, which produce eggshells made from calcium carbonate:

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

$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

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

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

Removing CO_2 gas shifts each equilibrium, in turn, to the left. This ultimately results in less $CaCO_3$ being made. So, in summer, chickens lay eggs with thinner shells (Figure 2.6.4). This means eggs are more easily broken, at great economic cost to farmers and supermarkets.

Scientists solved the problem by giving the chickens carbonated water to drink. This increases the concentration of aqueous carbon dioxide and pushes the equilibria to the right, increasing the amount of calcium carbonate.

Apparently the chickens like the carbonated water and they produce eggs with thicker, stronger shells. Another victory for chemistry and Le Châtelier!

FIGURE 2.6.4 The eggshell dilemma is solved with the aid of Le Châtelier's principle.

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 back reactions to be increased equally.

Worked example 2.6.1

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 particles, and vice versa for a volume increase.) Decide how the equilibrium will respond.	There are 2 molecules of gas on the reactant side and 4 molecules of gas on the product side, so the system will shift to the left. This decreases the amounts of the products, including CO. (Note that the concentration and partial pressure of the CO will still be higher than it was at the initial equilibrium. The shift in equilibrium position only partially compensates for the change.)

Worked example: Try yourself 2.6.1

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 (Figure 2.6.5).

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 or the equilibrium constant. Using collision theory, you can see that any collisions with inert gas molecules will not produce a reaction, so no net reaction occurs.

FIGURE 2.6.5 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 reactants or products, so there is no change to the reaction quotient according to the equilibrium law.

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. Le Châtelier's principle shows that 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:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$$
$$2 \text{ particles in solution} \qquad 1 \text{ particles in solution}$$

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 concentration of particles in solution.

Figure 2.6.6 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.

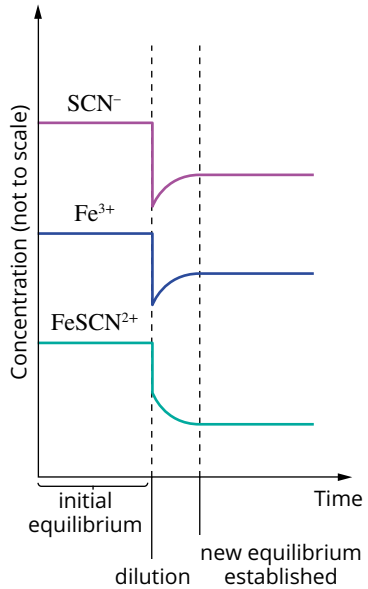


FIGURE 2.6.6 Effect of dilution on the equilibrium $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$. Although the equilibrium position shifts to the left, note that the concentrations of Fe^{3+} and SCN^{-} at the new equilibrium are lower than their concentrations prior to dilution, as the equilibrium shift only partially opposes the change.

Dilution of an aqueous equilibrium system has no effect on the value of K_c for the reaction.

CHANGING TEMPERATURE

In section 2.4, you saw that the effect of a temperature change on an equilibrium reaction depends upon whether the reaction is exothermic or endothermic, as shown in Table 2.6.1.

TABLE 2.6.1 The effect on the value of K_c when the temperature of a system is increased

ΔH	T	K_c
Exothermic (–)	Increase	Decrease
Endothermic (+)	Increase	Increase

Changing the temperature of an equilibrium in a closed system affects both the equilibrium position and the value of the equilibrium constant.

The overall effect on equilibrium position due to temperature can also be predicted from Le Châtelier's principle and explained using collision theory and rates of reaction.

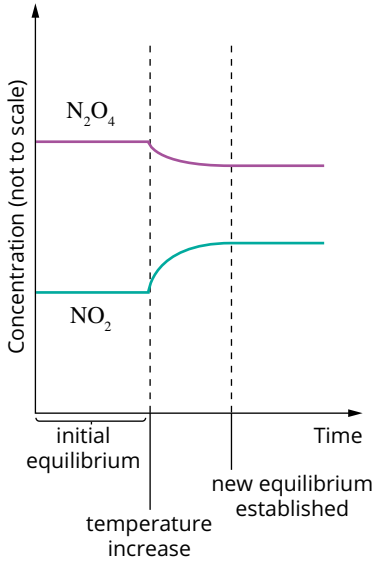


FIGURE 2.6.7 The effect of heating on the equilibrium $2NO_2(g) \rightleftharpoons N_2O_4(g)$

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 wouldn't 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 2.6.7 shows the gradual decrease in the concentration of N_2O_4 as the system moves to produce more reactants, NO_2. Note that with a change in temperature there is no instantaneous change in concentration.

Because the reactants and products of this 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 to be a darker brown (Figure 2.6.8).

FIGURE 2.6.8 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, and a decrease in K_c
- net forward reaction (more products) for endothermic reactions, and an increase in K_c.

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 activation energy 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 activation energy 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 2.6.9, 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. 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.

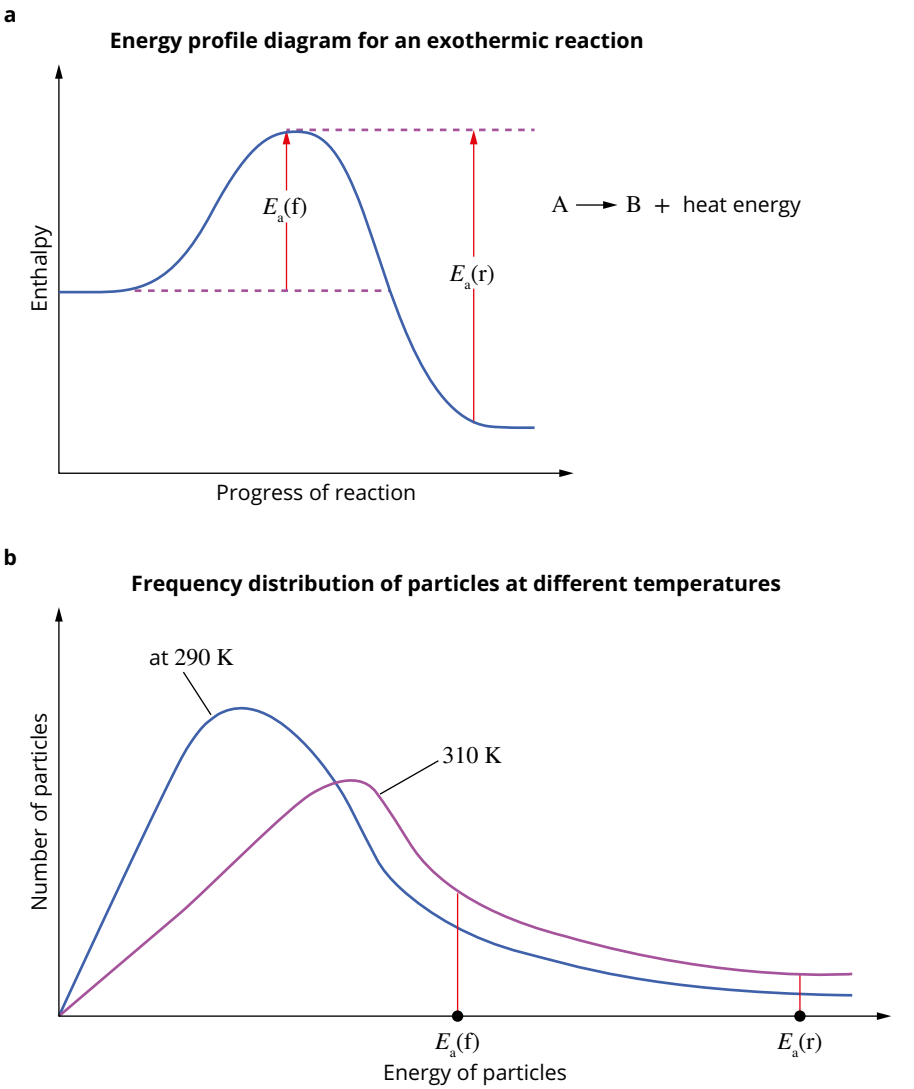


FIGURE 2.6.9 (a) Energy profile diagram for an exothermic reaction. The activation energy of the forward reaction, E_a(f), is less than the activation energy of the reverse reaction, E_a(r). (b) The frequency distribution of molecules at two different temperatures. At the higher temperature, a greater proportion of particles have the necessary activation energy for the endothermic reaction.

Worked example 2.6.2

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

Consider the equilibrium:

$$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

Explain, using collision theory, 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 activation energy 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.

Worked example: Try yourself 2.6.2

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

Consider the equilibrium:

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

Explain, using collision theory, the effect of an increase in temperature on this reaction.

EFFECT OF A CATALYST ON EQUILIBRIUM

A catalyst lowers the activation energy of both the forward and reverse reactions by providing an alternative reaction pathway (see Chapter 1). This can be seen in the energy profile diagram shown in Figure 2.6.10.

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.

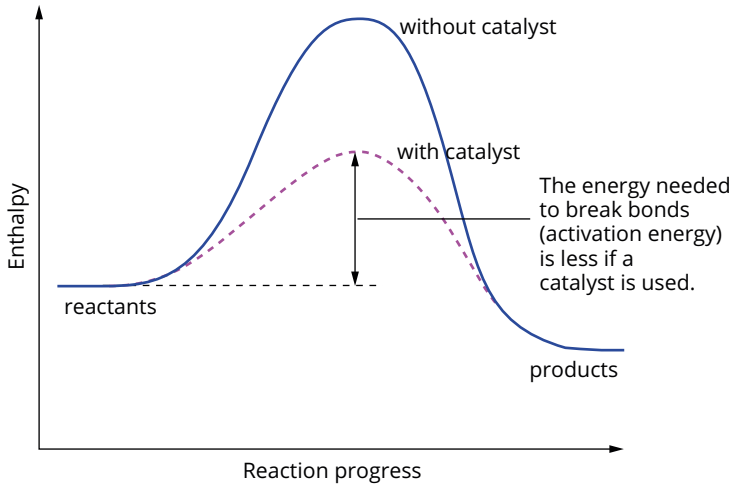


FIGURE 2.6.10 Energy changes in a catalysed and uncatalysed reaction.

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 at equilibrium. Consequently, the presence of a catalyst does not change the position of equilibrium or the value of the equilibrium constant, K_c. 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.

The addition of a catalyst does not change the position of equilibrium of a system, only how quickly equilibrium is attained.

OPTIMISING THE YIELD OF INDUSTRIAL PROCESSES

The chemical industry is central to the world economy. The companies in this sector convert raw materials (such as oil, natural gas, air, water, metals and minerals) into tens of thousands of different products, including dyes and pigments, ammonia, chlorine, caustic soda, sulfuric and nitric acids, and organic chemicals.

The extent of the reactions in these industrial processes and the rate of conversion of reactants to products are influenced by reaction conditions such as temperature, pressure and concentration. In order to avoid waste and reduce costs, conditions are carefully selected to ensure that acceptable yields of product are obtained.

It is essential to select the optimum conditions for an efficient reaction process to make the production of useful chemicals economically viable.

Later in the course, you will learn how industrial chemists maximise the rate and yield of chemical reactions by manipulating the position of equilibrium and by controlling reaction rate.

CHEMISTRY IN ACTION

Equilibria in a swimming pool

The water in swimming pools is used many times. Even though it is filtered, the water can quickly become contaminated with microscopic algae and bacteria. Some interesting chemistry involving chemical equilibria is involved in keeping swimming pools clean, clear and safe to swim in (Figure 2.6.11).

FIGURE 2.6.11 Chemical equilibria are responsible for keeping the water in backyard swimming pools hygienic and safe for swimmers.

Swimming pools are 'chlorinated' to prevent the growth of harmful microorganisms. Chlorination produces hypochlorous acid (HOCl), which is a very efficient antibacterial agent and algicide.

Commercially available 'pool chlorine' powder (Figure 2.6.12) consists of calcium hypochlorite ($Ca(OCl)_2$), which dissolves in water to release hypochlorite ions (OCl^-). The hypochlorite ions then react with hydronium ions in the water to form hypochlorous acid:

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

$$OCl^-(aq) + H_3O^+(aq) \rightleftharpoons HOCl(aq) + H_2O(l)$$

FIGURE 2.6.12 Commercial 'pool chlorine' contains the hypochlorite ion (OCl^-), which forms an equilibrium with H_3O^+ ions in water.

The H_3O^+ is available from the self-ionisation of water, another equilibrium reaction, this time between water molecules, forming H_3O^+ and OH^- ions:

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

The relative amounts of HOCl, OCl^- and H_3O^+ in a swimming pool need to be carefully controlled. This is done by monitoring the pH of the swimming pool and adding either more pool chlorine or more acid as needed to maintain a pH in the range 7.2–7.8. Figure 2.6.13 shows the relationship between the three substances. Remember, pH measures the concentration of H_3O^+ ions.

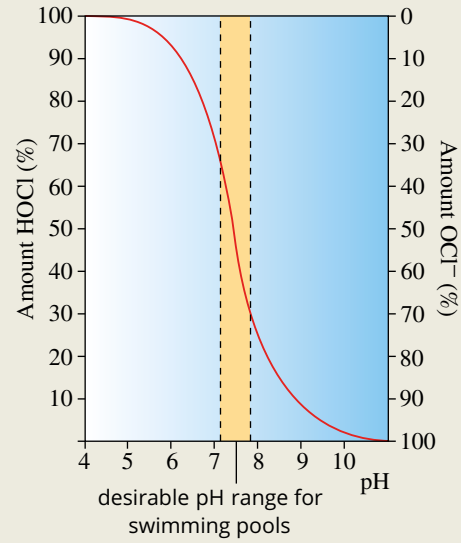


FIGURE 2.6.13 The effect of pH on the proportion of HOCl and OCl^- in water means that the position of the equilibrium can be monitored by changes in pH of the water.

As pH increases, the concentration of $H_3O^+(aq)$ decreases. Le Châtelier's principle tells you that the position of equilibrium will move to the left, consuming some of the HOCl. If the pH rises above about 7.8, the concentration of HOCl will be insufficient to control the growth of bacteria and algae.

On the other hand, as pH falls, the concentration of $H_3O^+(aq)$ increases. The position of equilibrium will move to the right and more HOCl will be formed. Although pH values below around 7.2 result in greater amounts of HOCl in the pool, if the pool is too acidic, the water can irritate eyes and skin.

Thus, maintaining a pool so that it is hygienic and comfortable for swimmers involves carefully maintaining an optimum equilibrium position in the reaction mixture.

2.6 Review

SUMMARY

- The effect of a change on an equilibrium can be predicted using Le Châtelier's principle and the equilibrium law (Table 2.6.2).
- Alternatively, the effects of changes on an equilibrium can be explained on the basis of collision theory and rates of reaction (Table 2.6.2).

TABLE 2.6.2 Summary of the effect of a change on equilibrium

Change on equilibrium	Le Châtelier's principle prediction: effect of change on equilibrium position	Collision theory explanation: 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 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.
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 forward and reverse reactions.
Adding water (dilution of solutions)	Shifts in the direction of the most dissolved particles	Less frequent collisions; the reaction that is less dependent on a collision (fewer particles reacting) occurs to a greater extent.
Increasing the temperature for exothermic reactions	Shifts to the left	All reactant and product molecules have more energy and move faster; increased temperature favours the 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	All reactant and product molecules have more energy and move faster; increased temperature favours the rate of an endothermic reaction; net reaction in direction of endothermic reaction, i.e. favouring the forward direction.

KEY QUESTIONS

1 In which one the following systems will the position of equilibrium be unaffected by a change of volume at constant temperature? Explain 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 $2C_2H_6(g) + 7O_2(g) \rightleftharpoons 4CO_2(g) + 6H_2O(g)$

2 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:

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

c Increasing the temperature of the endothermic equilibrium:

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

3 For the reactions in Question 2, explain the effect of the changes, in terms of collision theory and rates of reaction.

4 Consider the following equilibria:

i $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \quad \Delta H = +42\,kJ\,mol^{-1}$
ii $N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = +58\,kJ\,mol^{-1}$
iii $H_2(g) + F_2(g) \rightleftharpoons 2HF(g) \quad \Delta H = -536\,kJ\,mol^{-1}$

How would you alter the:

a temperature of each equilibrium mixture in order to shift the position of equilibrium to the right?
b volume of each equilibrium mixture in order to shift the position of equilibrium to the right?

5 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 Partial pressure of NO_2
b Mass of NO_2

6 The International Space Station uses waste hydrogen and the carbon dioxide released by astronauts during respiration to form water according to the reaction:

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

a How would you alter the temperature in order to increase the yield of the reaction?
b How would you alter the volume in order to increase the yield of the reaction?

Chapter review

02

KEY TERMS

activation energy
closed system
collision theory
competing equilibria
concentration fraction
dynamic equilibrium
endothermic
equilibrium
equilibrium constant
equilibrium law
equilibrium yield
exothermic
extent of reaction
heterogeneous reaction
homogeneous reaction
irreversible reactions
Le Châtelier's principle
macroscopic property
open system
partial pressure
position of equilibrium
rate of reaction
reaction quotient
reversible reaction
saturated solution
surroundings
system

Chemical systems

1 Which one of the following statements about an open system is correct?

- **A** In an open system, only energy can be exchanged with the surroundings.
- **B** In an open system, the reactants and products cannot be exchanged with the surroundings.
- **C** In an open system, matter and energy can be exchanged with the surroundings.
- **D** In an open system, some reactants and products must always remain when the reaction is complete.

2 Consider a saturated solution of salt in contact with undissolved salt crystals at a constant temperature. Which one of the following statements is correct?

- **A** It is an example of a closed system, which is non-reversible.
- **B** It is an example of an open system, which is non-reversible.
- **C** It is an example of a closed system, which is reversible.
- **D** It is an example of an open system, which is reversible.

3 **a** Draw an energy profile diagram for the theoretical exothermic reaction: $P + Q \rightleftharpoons R + S$. Label ΔH, activation energy of forward reaction, activation energy of reverse reaction, enthalpy of reactants and enthalpy of products.

b Use the diagram to explain why it is possible for the reverse reaction $R + S \rightleftharpoons P + Q$ to occur.

Dynamic equilibrium

4 What are the characteristics of a homogeneous reaction system at equilibrium?

5 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. Is this because of an equilibrium process? Explain your answer.

6 PCl_3 gas is mixed with Cl_2 gas in a sealed container. A reaction occurs according to the equation:

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

Sketch a graph to show how the rate of the forward reaction and the rate of the reverse reaction change with time. Label the lines for the forward and reverse reactions with the appropriate chemical equation. Also label the point when equilibrium is first established.

The equilibrium law

7 Write the expression for K_c for the following equilibrium system:

$$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + Sn^{4+}(aq)$$

8 Write balanced equations for the reactions with the following equilibrium laws:

a $K_c = \dfrac{[H_2]^2[CO]}{[CH_3OH]}$

b $K_c = \dfrac{[H_2S]^2}{[S_2][H_2]^2}$

c $K_c = \dfrac{[N_2O_4]^{\frac{1}{2}}}{[NO_2]}$

9 Write the expression for the equilibrium constant for the following chemical equations.

- **a** $Cu^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CuCO_3(s)$
- **b** $CuCO_3(s) \rightleftharpoons Cu^{2+}(aq) + CO_3^{2-}(aq)$
- **c** $P_4(s) + 10Cl_2(g) \rightleftharpoons 4PCl_5(g)$
- **d** $8PCl_5(g) \rightleftharpoons 2P_4(s) + 20Cl_2(g)$

10 Explain the difference between the terms 'reaction quotient' (Q_c) and 'equilibrium constant' (K_c).

Working with equilibrium constants

11 Complete the following statements about the equilibrium constant K_c.

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.

12 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 Explain whether a significant reaction would occur when solutions of tin(IV) chloride and iron(II) chloride are mixed.

b Explain whether a significant reaction would occur when solutions of tin(II) chloride and iron(III) chloride are mixed.

13 Consider the following equilibrium at 227°C:

$$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$$

Write the expression for K_c for the equilibrium system.

Le Châtelier's principle

14 State Le Châtelier's principle. Write an equilibrium equation in terms of reactants A and B in equilibrium with products C and D. Use the principle to explain what occurs when the products are gradually removed.

15 Predict the effect of the following changes on the position of equilibrium in the system:

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

a Addition of SO_2 to the equilibrium system

b Removal of O_2 from the equilibrium system

c Removal of SO_3 from the equilibrium system

16 The following equilibrium system is present in a sealed container of fixed volume:

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

What change in the partial pressure of hydrogen gas can cause the following changes to the system at constant temperature?

a The partial pressure of the product increased.

b There was a net reverse reaction.

Further applications of Le Châtelier's principle

17 The reaction represented by the following equation is exothermic:

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

At equilibrium at constant temperature, the volume is halved by increasing the pressure. Which one of the following statements is correct?

A The new equilibrium concentration of CO will be less than the initial concentration.

B The value of K_c will increase.

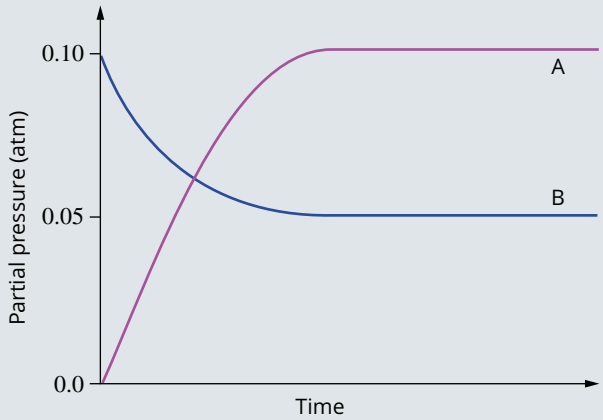
C The amount of $COCl_2$ will increase.

D A net reverse reaction will occur.

18 Dinitrogen tetroxide, N_2O_4, and nitrogen dioxide, NO_2, coexist according to the equilibrium reaction:

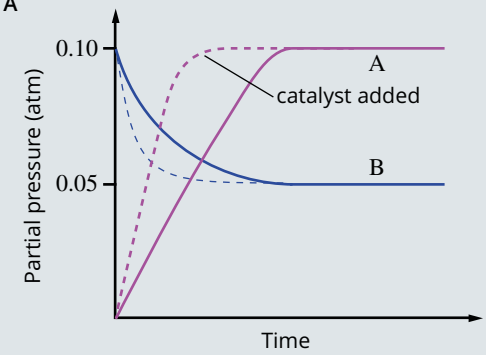
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

a The graph below shows the change of the partial pressures of the two gases with time as they reach equilibrium at constant temperature. Identify labels A and B as $N_2O_4(g)$ or $NO_2(g)$.

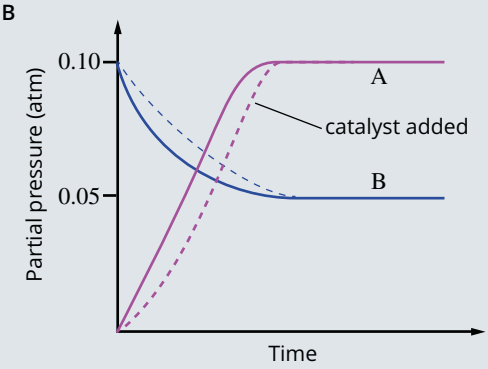


b Which one of the following graphs correctly shows the effect on the partial pressures of A and B when a catalyst is added? The dashed lines indicate their pressures when the catalyst is added.

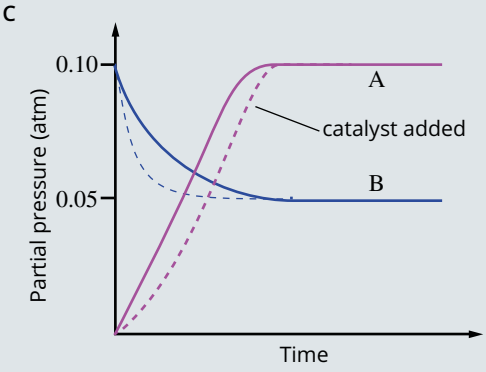
A



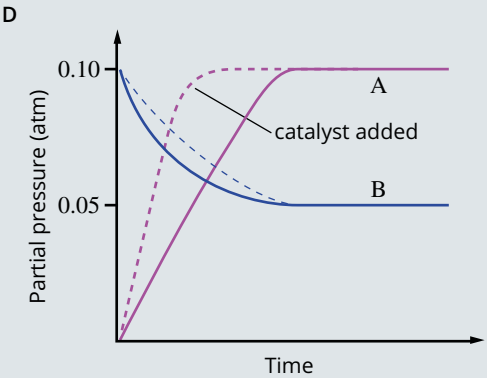
B



C



D



19 Which one of the following statements about equilibrium is true?

A A catalyst increases the rates of the forward and reverse reactions equally because it decreases the temperature.

B Dilution of an aqueous equilibrium system never causes any change to the position of equilibrium of the system.

C Increasing the pressure of a gaseous equilibrium system, by reducing the volume, causes the value of K_c to increase.

D An increase in temperature of an endothermic equilibrium system increases the value of K_c.

20 **a** Use Le Châtelier's principle to 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.

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

ii $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H = +208\,kJ\,mol^{-1}$

b Use collision theory to explain the effect of heating the equilibrium mixtures in part **a**.

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

22 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:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Use your understanding of equilibrium to explain why inefficient absorption of Ca^{2+} ions could cause weakness in bones.

23 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 addition of a catalyst

iii addition of more oxygen.

iv decreasing the partial pressure of carbon monoxide (at constant volume).

b 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, comment on the magnitude of the equilibrium constant for the reaction.

24 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 L container at 350°C. Copy the following table and, for each of the changes listed, indicate if the reaction mixture would become darker or lighter. Give a reason for your choice.

	Colour change (lighter or darker)	Explanation using Le Châtelier's principle and collision theory
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.		

Connecting the main ideas

25 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 Write a balanced chemical equation for the reaction.

b Write an expression for the equilibrium constant of the reaction.

c Predict how each of the following changes to an equilibrium mixture would affect the yield of CS_2.

i Decreasing the partial pressure of O_2 (at constant total volume)

ii Increasing the temperature

iii Adding a catalyst

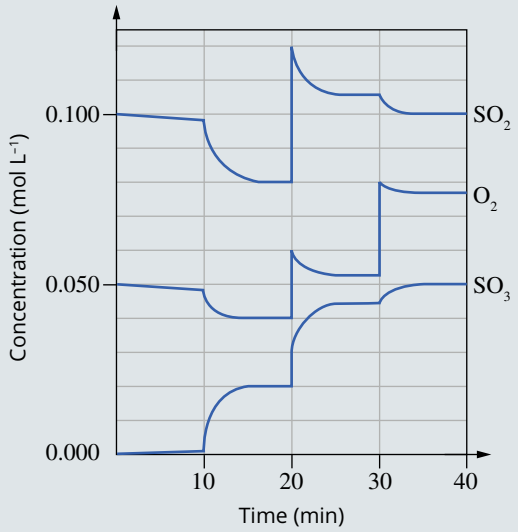
iv Increasing the pressure by decreasing the volume of the reaction vessel (at constant temperature)

v Increasing the pressure by introducing argon gas into the reaction vessel (at constant volume)

26 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 following graph shows how the concentrations of the three gases changed.



a Write an expression for the equilibrium constant, K_c, of the reaction.

b During which time intervals was the reaction at equilibrium?

c At what time was the catalyst added? Explain your reasoning.

d What change was made to the system at 20 minutes if temperature is constant?

e What change was made to the system at 30 minutes if temperature is constant?

CHAPTER

03 Equilibrium systems in the environment

Since the start of the Industrial Revolution in the 1760s, there has been a dramatic increase in the combustion of fossil fuels. This has resulted in significantly increased levels of carbon dioxide in the atmosphere. Scientists believe that the increase in atmospheric carbon dioxide is causing an increase in global warming and that it is also responsible for an increase in ocean acidity. The higher levels of ocean acidity are predicted to affect marine ecosystems involving coral reefs and other marine organisms.

In this chapter, you will apply your understanding of equilibrium to study the effects of increasing levels of atmospheric carbon dioxide. You will consider the chemistry and potential effects of increased ocean acidity on the natural and human environment.

In addition, you will learn about the Kyoto Protocol and other international agreements that have been developed in an attempt to reduce production of greenhouse gases and slow global warming and its consequences. Australia's role in the development and implementation of carbon targets is also described.

Science as a human endeavour

Levels of carbon dioxide in the atmosphere are rising and have a significant impact on global systems, including surface temperatures. The increasing level of carbon dioxide in the atmosphere causes more carbon dioxide to dissolve in the ocean, producing carbonic acid and leading to increased ocean acidity. This is predicted to have a range of negative consequences for marine ecosystems such as coral reefs. Calcification is the process that results in the formation of calcium carbonate structures in marine organisms. Acidification shifts the equilibrium of carbonate chemistry in sea water, decreasing the rate and amount of calcification among a wide range of marine organisms. The United Nations Kyoto Protocol and the Intergovernmental Panel on Climate Change aim to secure a global commitment to reducing greenhouse gas emissions over the next few decades.

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3.1 Carbon dioxide in the atmosphere

The atmosphere consists of a mixture of gases extending about 100 km above the 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.

The Earth has maintained its average temperature over time because of the balance between the radiation received from the Sun and the radiation reflected back into space. This section describes how suitable living conditions are maintained on Earth and considers the effects of changing the amounts of atmospheric carbon dioxide.

CARBON CYCLE

Equilibria involving carbon dioxide occur in a range of situations, including the production of glucose in plants, the formation of coral reefs and the process of respiration in cells and living things. Applying the principles of chemical equilibria to such systems allows the chemistry of these processes to be understood and hence the effects of changes to these systems can be predicted.

Carbon dioxide 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 3.1.1, carbon is exchanged between the atmosphere, oceans, rivers, lakes, soils and rocks.

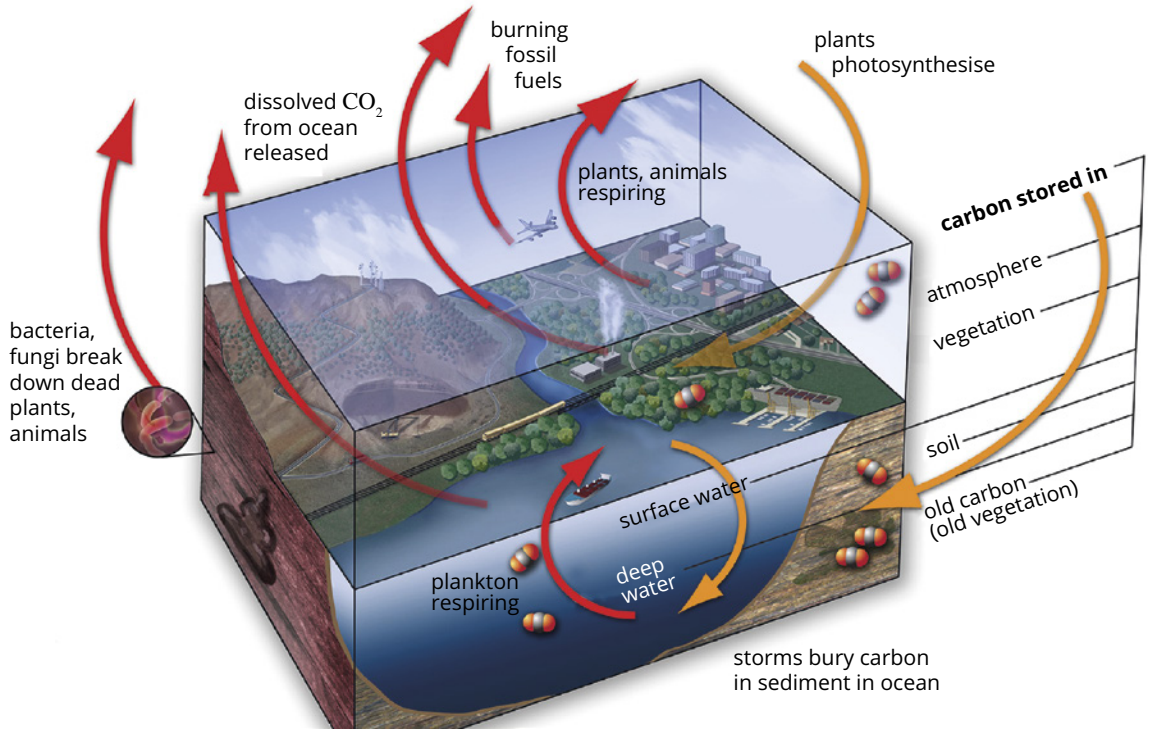

FIGURE 3.1.1 The carbon cycle. Carbon cycles between land, the atmosphere and the oceans in billions of tonnes each year. It takes about 100 years for half the available carbon atoms to leave and re-enter the atmosphere.

Photosynthesis

Plants take carbon dioxide from the atmosphere and, via **photosynthesis**, use it to make chemicals such as glucose ($C_6H_{12}O_6$), which act as an energy source. Plants can convert glucose into larger molecules that make up the structural parts within the plant. The process of photosynthesis can be summarised by the equation:

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

Photosynthesis involves an **endothermic** reaction that can only occur in the presence of sunlight and the pigment **chlorophyll**, found in the green parts of the plant. This process converts solar energy to chemical energy, which is used as an energy source by all living things in another process called **respiration**.

Respiration can be summarised by the equation below. The overall reaction is an **exothermic** reaction and can be regarded as being the reverse of photosynthesis:

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

As shown in Figure 3.1.1, carbon is released into the atmosphere through respiration and the decay of animal waste products and dead animals. Under some conditions, organisms do not fully decay and carbon is not returned to the atmosphere. The **non-renewable** energy resources coal, oil and natural gas were formed over a period of several million years from the remains of dead organisms. Carbon dioxide is released when these fuels are burnt.

The amount of carbon present at any particular stage of the carbon cycle depends on the rate at which it enters and leaves that stage. An equilibrium will exist when these rates are equal.

GREENHOUSE EFFECT

The Earth receives visible and ultraviolet radiation from the Sun. This energy can pass through the atmosphere to the Earth's surface. The Earth then radiates this energy back into space as lower-energy infrared radiation.

Gases such as carbon dioxide, water vapour, methane, nitrogen oxides and ozone are called **greenhouse gases**. They absorb some of the infrared radiation before it can reach space and can re-radiate it back towards the 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 Earth's surface in a similar way to how the Sun's energy heats a greenhouse.

i Atmospheric carbon dioxide and other greenhouse gases trap energy and re-radiate it back to Earth, maintaining the average surface temperature of the Earth.

Figure 3.1.2 shows how the greenhouse effect occurs naturally. 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.

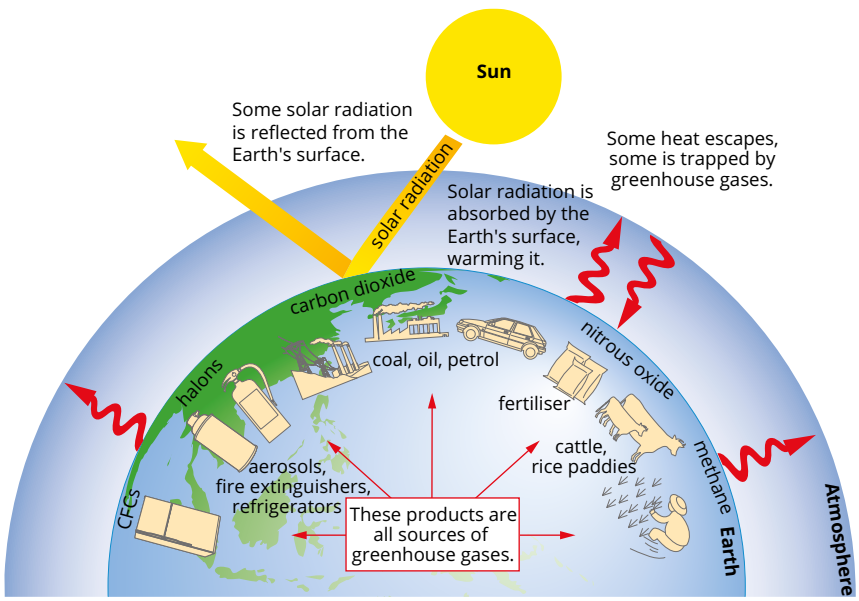

FIGURE 3.1.2 The greenhouse effect. Greenhouse gases help to maintain the temperature at the Earth's surface.

CHEMFILE

Temperatures without an atmosphere

Without an atmosphere, temperatures on Earth would be similar to temperatures on the Moon (Figure 3.1.3). During the day, it would be more than 100°C, and at night it would be less than –150°C. The average temperature of the Earth would drop from a pleasant 16°C to an estimated –18°C.

FIGURE 3.1.3 'Blue' Earth view from the Moon's surface. Note the contrast between the oceans and green areas on Earth with the craters and desert appearance of the Moon surface where temperatures are extreme.

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** (such as coal, crude oil and natural gas) has caused the average global concentration of carbon dioxide in the atmosphere to rise by more than 40% (Figure 3.1.4). The result is an increase in the infrared radiation absorbed and re-radiated back towards the Earth.

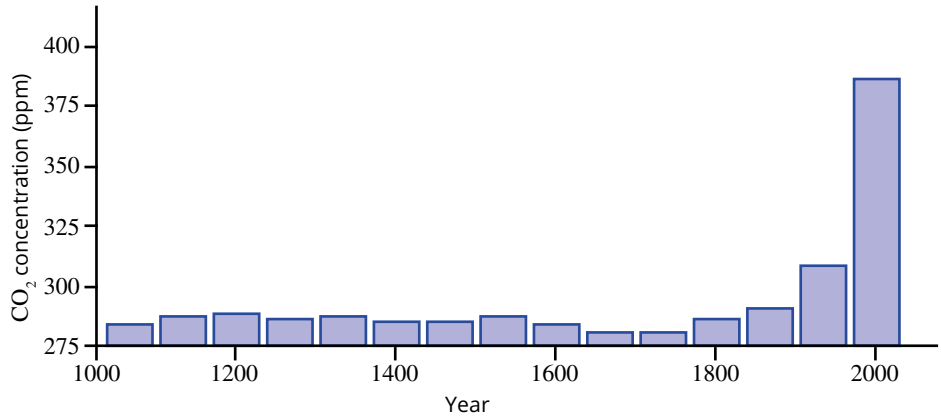

FIGURE 3.1.4 Concentrations of atmospheric carbon dioxide for the last 1000 years

Scientists are concerned that the increasing levels of greenhouse gases are influencing surface land and sea temperatures and causing **global warming**. This effect is referred to as the **enhanced greenhouse effect**. The higher global temperatures are thought to be 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.

The maps of Australia in Figure 3.1.5 show the present annual average temperatures and the temperatures in the late 21st century that are predicted from studies by the Commonwealth Scientific and Industrial Research Organisation (CSIRO). They indicate the change in climate that is expected due to global warming.

The enhanced greenhouse effect is sometimes referred to as 'global warming'. It is due to increased amounts of carbon dioxide and other greenhouse gases in the atmosphere causing more heat to be trapped, raising the average temperature of the Earth's surface.

The graph in Figure 3.1.6 shows the changes in average global surface temperatures over time. A comparison of Figures 3.1.4 and 3.1.6 shows the correlation between increasing levels of carbon dioxide and increasing surface temperatures.

Scientists use computer models of the Earth's climate system to understand the complex factors that affect the climate. The amount of future warming that is predicted by different models varies, but it is likely to be about 2°C by 2100, depending on the success of international action on climate change. You will learn more about climate modelling, projections for climate change and international action later in this chapter.

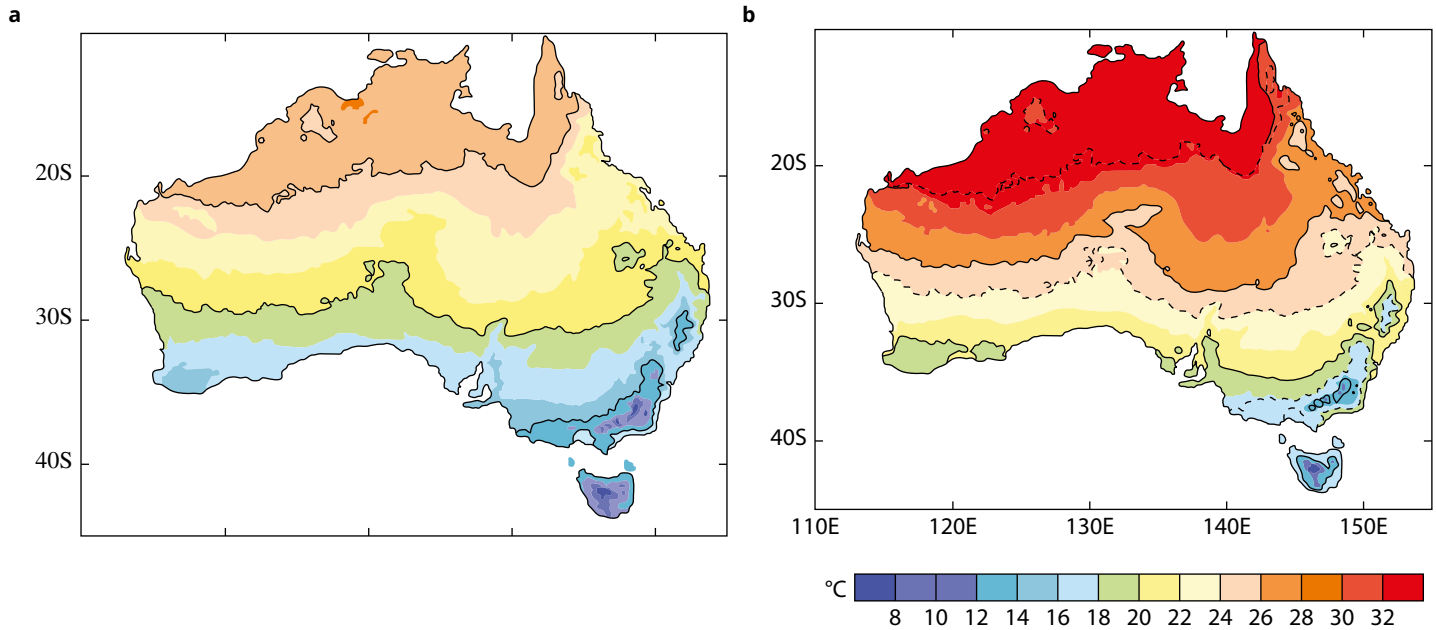

FIGURE 3.1.5 (a) Map showing the annual mean temperatures in Australia at present. (b) The annual mean temperature for the late 21st century. On each map the contour lines for 14°C, 20°C and 26°C are shown as solid lines. In order to show the shifts in climate, the original solid lines in map (a) are shown as dotted lines in map (b).

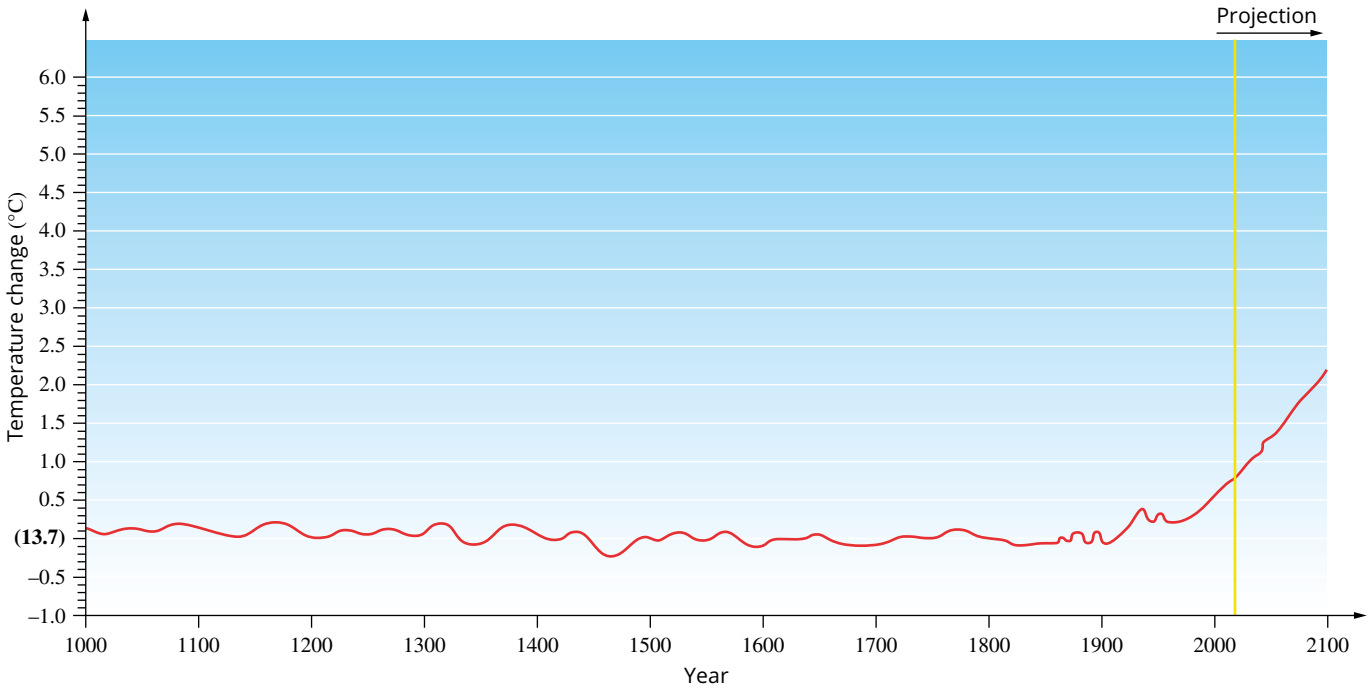

FIGURE 3.1.6 Change in the average surface temperature of the Earth from the year 1000 projected to 2100. Estimates of future temperatures vary, depending on what assumptions are made about future energy use.

3.1 Review

SUMMARY

- Photosynthesis is an endothermic process that converts solar energy into chemical energy in glucose and oxygen molecules, in the presence of chlorophyll.
- The equation for photosynthesis is:
  $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$
- Respiration can be described as the exothermic reverse reaction of photosynthesis.
- Greenhouse gases trap some solar energy and re-radiate some of it back towards Earth as heat.
- Carbon dioxide, methane, water vapour, nitrous oxide and ozone are greenhouses gases.
- The greenhouse effect warms the Earth's surface in a similar way to the heating of a greenhouse by the Sun.
- Higher global temperatures are predicted as a result of more greenhouses gases in the atmosphere.
- Global warming is referred to as the enhanced greenhouse effect.
- Some consequences of global warming are rising sea levels, the shifting of weather patterns and the occurrence of more extreme weather patterns.

KEY QUESTIONS

1 Which gas, present in small quantities in the atmosphere, is the basis of all food needed by plants and animals?

2 Write the equation for the process of photosynthesis.

3 Define a greenhouse gas and give three examples.

4 Briefly explain the term 'enhanced greenhouse effect', otherwise known as global warming.

3.2 Carbon dioxide in the oceans

Carbon dioxide is only slightly soluble in water. However, a series of interrelated equilibria involving the small concentration of dissolved carbon dioxide in sea water controls the pH and carbonate ion (CO_3^{2-}) concentration of the oceans. As a consequence, these equilibria provide marine organisms with the materials needed to develop their skeletons and shells. In the parts of the oceans where life exists, calcium carbonate minerals saturate the sea water, keeping it slightly alkaline.

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 will affect the coral reefs, fish stocks, algae and entire food chains upon which organisms in the oceans and coastal areas depend.

This section will examine the equilibria involving carbon dioxide in the oceans and the effects of increasing concentrations of carbon dioxide.

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 sea water 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 hydrogencarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}):

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

There are interrelated equilibria in sea water that involve carbon dioxide and the hydrogencarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}) ions.

These equilibria are illustrated in Figure 3.2.1.

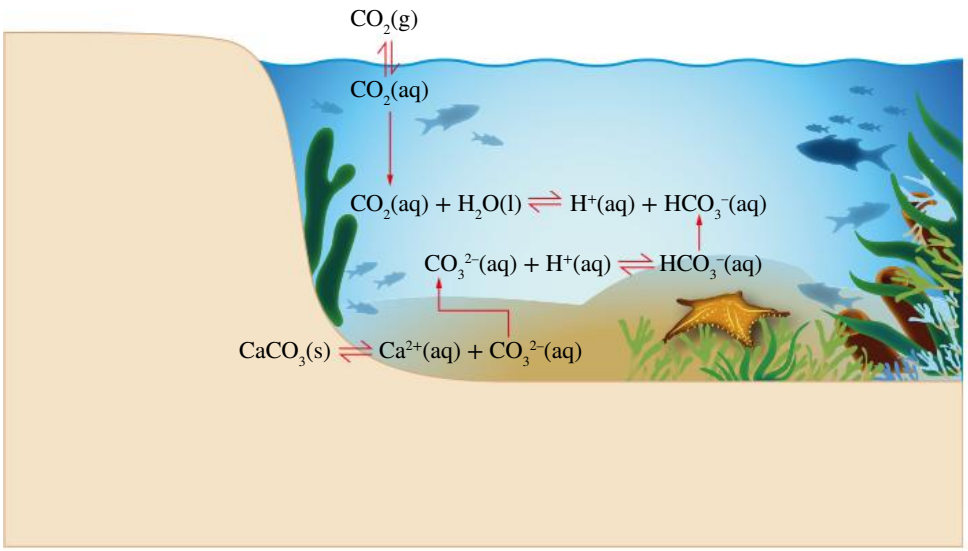

FIGURE 3.2.1 There is an interrelated set of reactions involving carbon in the ocean.

CHEMFILE

'Ocean acidity' does not mean a pH below 7

Sea water is slightly alkaline, with an average pH of 8.14. In the last 200 years, the pH of the oceans has dropped by 0.11. Because pH is a logarithmic scale ($pH = -\log[H^+]$, see Chapter 4), this is about a 30% increase in the concentration of hydrogen ions. If this trend continues, by 2100 it is estimated that this increase in concentration of H^+ will be 100%, resulting in a pH of about 7.85. Notice that the sea water will still be alkaline, but more acidic than it has ever been.

The alkalinity of sea water is due to the presence of limestone ($CaCO_3$) in the ocean. Solid $CaCO_3$ forms an equilibrium with Ca^{2+} ions and CO_3^{2-} ions. CO_3^{2-} ions then react with water to form an alkaline solution:

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

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

When carbon dioxide dissolves in water it forms the weak acid carbonic acid. This results in a decrease in alkalinity and an increase in acidity.

ACIDIFICATION

Applying Le Châtelier's principle to the previous equilibria, 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 $H_3O^+(aq)$ 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. The pH is currently 8.14 and predicted to fall to about 7.85 by 2100. Carbon dioxide gas, as with other gases, is more soluble in cold water. As a result, ocean acidification is greater in the polar regions (Figure 3.2.2) and, in some cases, these effects have been noted since the middle of the 1990s.

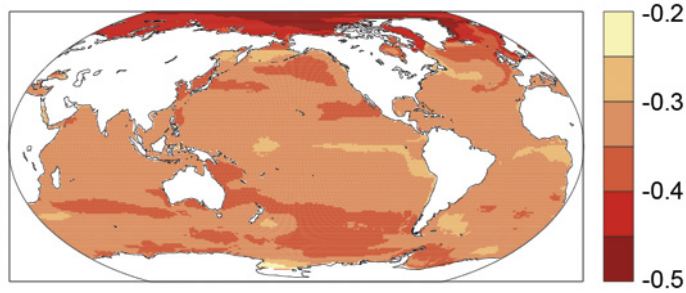

FIGURE 3.2.2 Changes in surface pH of the oceans predicted by 2100. Note the changes are greater in polar regions.

Ocean acidification is the decrease in pH that is occurring due to the absorption of carbon dioxide from the atmosphere.

The patterns of changes in pH and dissolved carbon dioxide predicted over time can be seen in the graph in Figure 3.2.3, which was produced by the US Institute of Climate Studies.

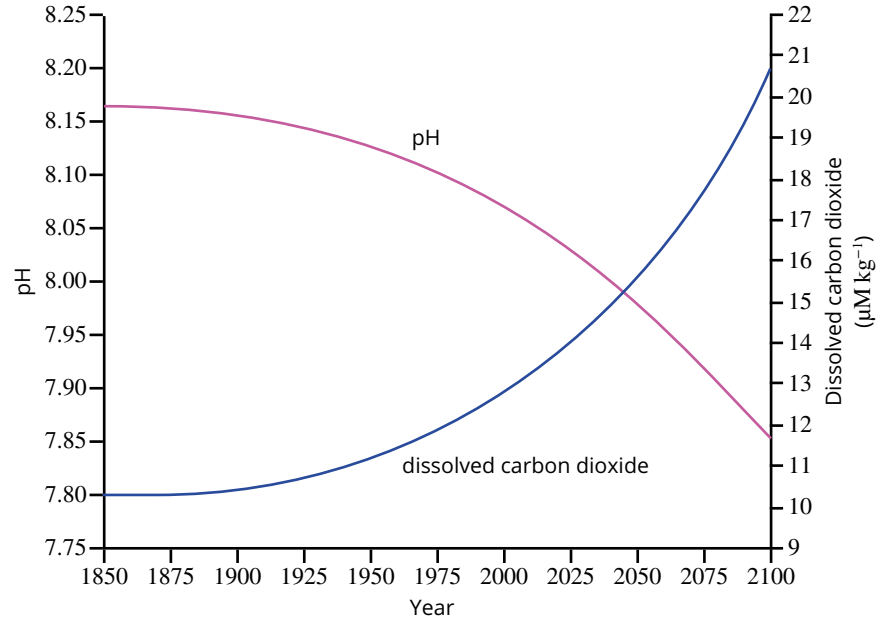

FIGURE 3.2.3 Historical (from 1850) and projected (to 2100) pH and dissolved CO_2 levels in the ocean

CHEMISTRY IN ACTION

Champagne sites

There are natural variations in the pH of sea water, depending on the season and region on Earth. Large amounts of carbon dioxide escape from undersea volcanoes, producing 'champagne sites' (Figure 3.2.4). By studying these regions, researchers can gain insight into the effects of future increases in levels of carbon dioxide. They are also able to see which plants and animals adapt to a lower pH and which cannot survive at all.

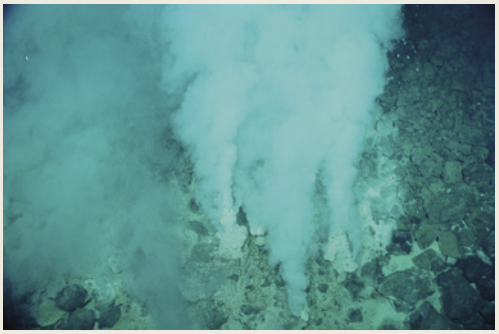

FIGURE 3.2.4 An underwater volcanic vent called a white smoker. The volcano is part of the Japanese volcano chain. Mineral precipitates of calcium, barium and silicon form white columns. Because the vent is pumping out significant amounts of carbon dioxide, they are called 'champagne sites'. Due to the pressure at these depths, the carbon dioxide is in a liquid, not gaseous, state.

CARBONATE EQUILIBRIA

Marine organisms such as corals, molluscs and crustaceans (Figure 3.2.5) use carbonate ions (CO_3^{2-}) to form protective coverings (exoskeletons) of calcium carbonate ($CaCO_3$), such as shells. The process is called **calcification**, and can be represented by the equation:

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

These organisms absorb calcium ions and carbonate ions from sea water to build and maintain the calcium carbonate structure essential for their survival.

Calcium carbonate is virtually insoluble in water and the oceans can be regarded as saturated solutions of calcium and carbonate ions. Once formed, calcium carbonate is usually quite stable. The health and growth of these marine organisms depend critically on the concentration of carbonate ions and therefore carbon dioxide in the oceans. Processes that disturb or change the CO_2 concentration, and therefore the concentration of CO_3^{2-}, will adversely affect these organisms.

Scientists have concluded that between one-third and one-half of the CO_2 emissions from human activity are absorbed by the oceans. Although this reduces the greenhouse effect of CO_2 in the atmosphere, it has decreased the pH of the oceans.

A decrease in pH (increase in H^+ concentration) affects the position of the following equilibrium with carbonate ions:

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

As the H^+ concentration increases, the equilibrium shifts to the right, consuming carbonate ions (CO_3^{2-}). This disturbs the following equilibrium with calcium ions, carbonate ions and solid calcium carbonate. A decrease in CO_3^{2-} drives the reaction to the left, causing calcium carbonate to dissolve:

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

This makes it more difficult for marine organisms to produce and maintain their skeletons.

FIGURE 3.2.5 The Ningaloo Reef in Western Australia 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.

As the level of dissolved CO_2 in the oceans increases, $[H^+]$ increases, pH decreases and solid $CaCO_3$ starts to dissolve.

Calcification involves the precipitation of dissolved calcium and carbonate ions as calcium carbonate in the form of shells and corals. If the concentrations of ions in the water change due to higher acidity levels, the formation of corals and shells is reduced.

EFFECTS OF INCREASED OCEAN ACIDITY

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 in turn, can affect the formation of calcium carbonate needed for many marine organisms.

Globally, coral reefs and their marine ecosystems support industries such as tourism and fisheries. Millions of people depend on these industries for their livelihoods. As a consequence, an increased concentration of carbon dioxide in the atmosphere would have environmental, social and economic effects.

Environmental impacts

Decalcification

As oceans become more acidic, the additional hydrogen ions react with carbonate ions:

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

This reaction has the effect of reducing the concentration of free CO_3^{2-} ions in sea water, making the formation of calcium carbonate structures more difficult for marine creatures. This process is called **decalcification**. Because the pH of the ocean is predicted to fall in future years, the rate and amount of calcification is likely to decrease.

Figure 3.2.6 shows the effect of decalcification in sea snails. These tiny free-swimming sea snails are an important food source for other marine animals. The snail on the left has a healthy, glass-like shell with smooth edges. The shell of the snail on the right has been affected by increased ocean acidity. Weak spots in the shell have an opaque, cloudy appearance and the shell edges are more ragged.

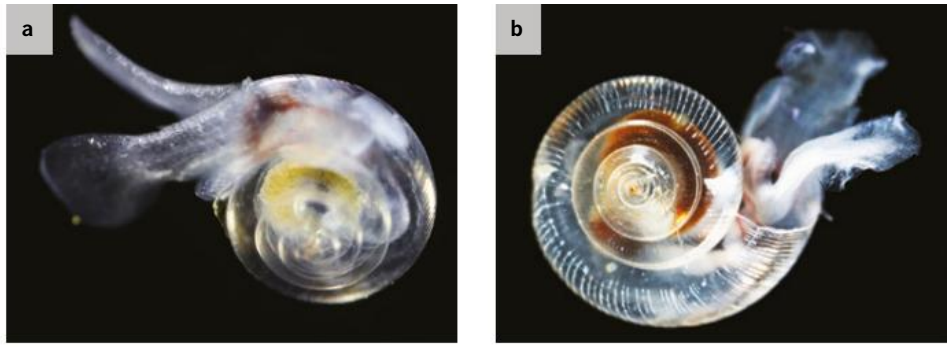

FIGURE 3.2.6 Free-swimming sea snails are an important food source for other marine animals. (a) A healthy specimen and (b) one that has been affected by increased ocean acidity.

Food chains

Increasing acidity has a detrimental effect on organisms, such as **plankton** and **krill** (Figure 3.2.7), which are at the bottom of the **food chain**.

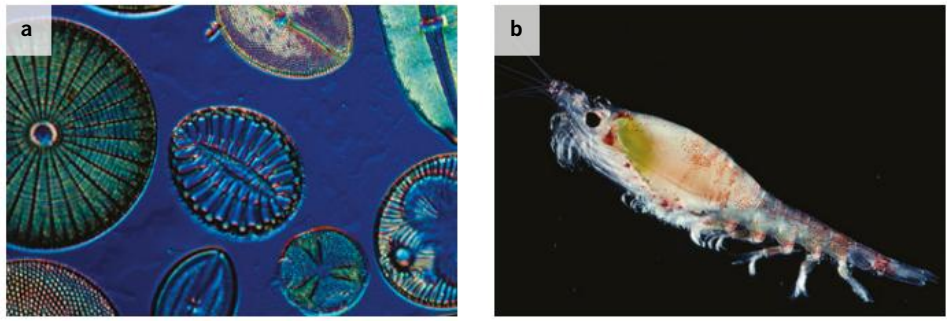

FIGURE 3.2.7 (a) Diatoms are single-celled algae that are an important component of plankton, which forms the base of marine and freshwater food chains. (b) Krill feed on plankton and can be found in swarms spanning kilometres across. They are a major food source for many marine organisms, from small fish such as sardines to huge mammals such as whales.

Plankton, such as diatoms, are a food source for krill, which, in turn, are consumed by animals higher up the food chain. An example of a food chain involving these organisms can be seen in Figure 3.2.8.

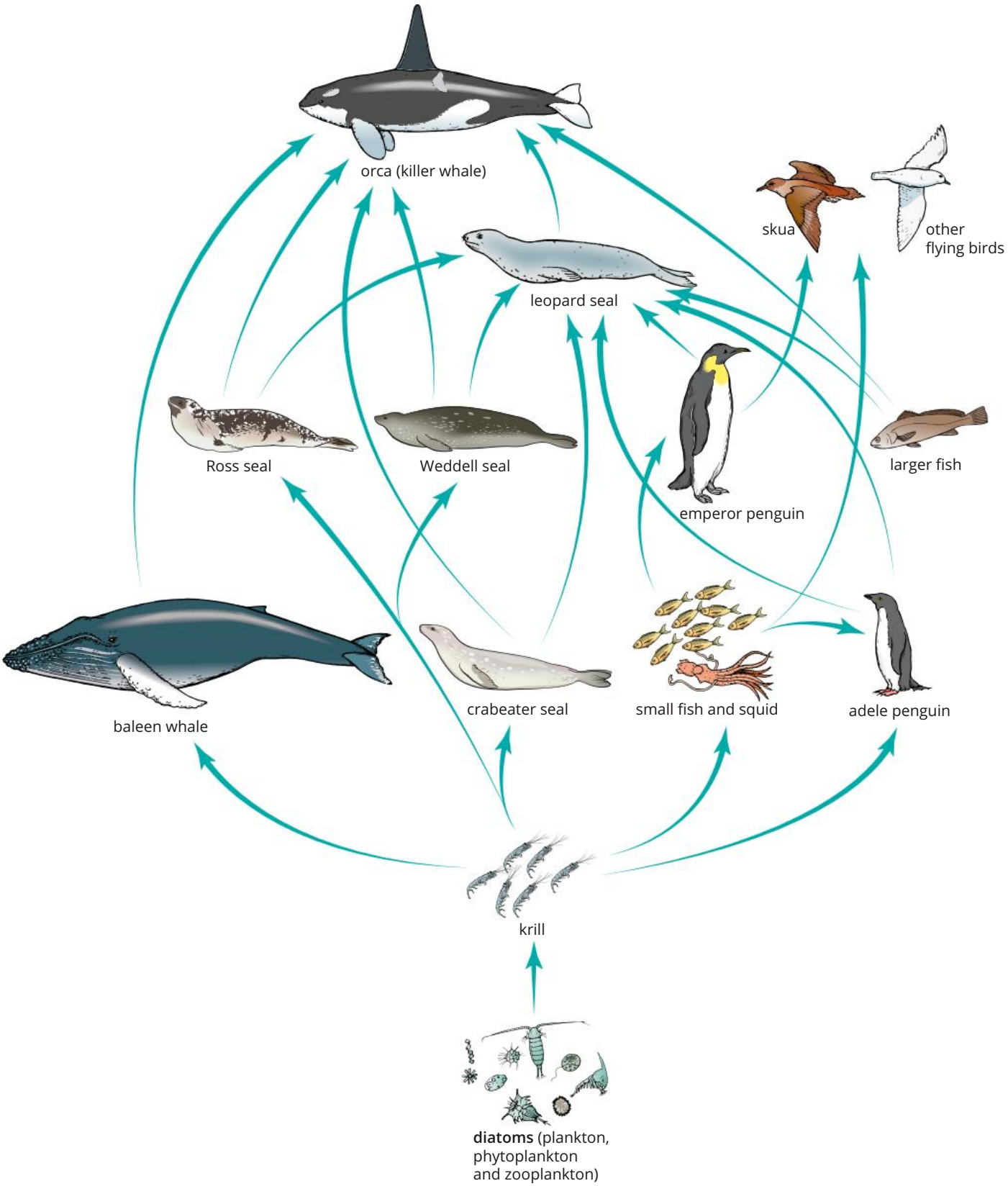

FIGURE 3.2.8 A food web showing the relationship between animals that live in Antarctic waters

Krill eggs will not hatch successfully at a lower pH. Therefore, 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 would have a disastrous effect on the **ecosystem** of the ocean.

Social and economic impacts

The environmental impact of increased ocean acidity is predicted to have social and economic impacts as well, particularly for people in coastal communities. Increased ocean acidity will potentially affect:

- food supplies
- coastal protection
- tourism.

These social and economic effects are illustrated in Figure 3.2.9.

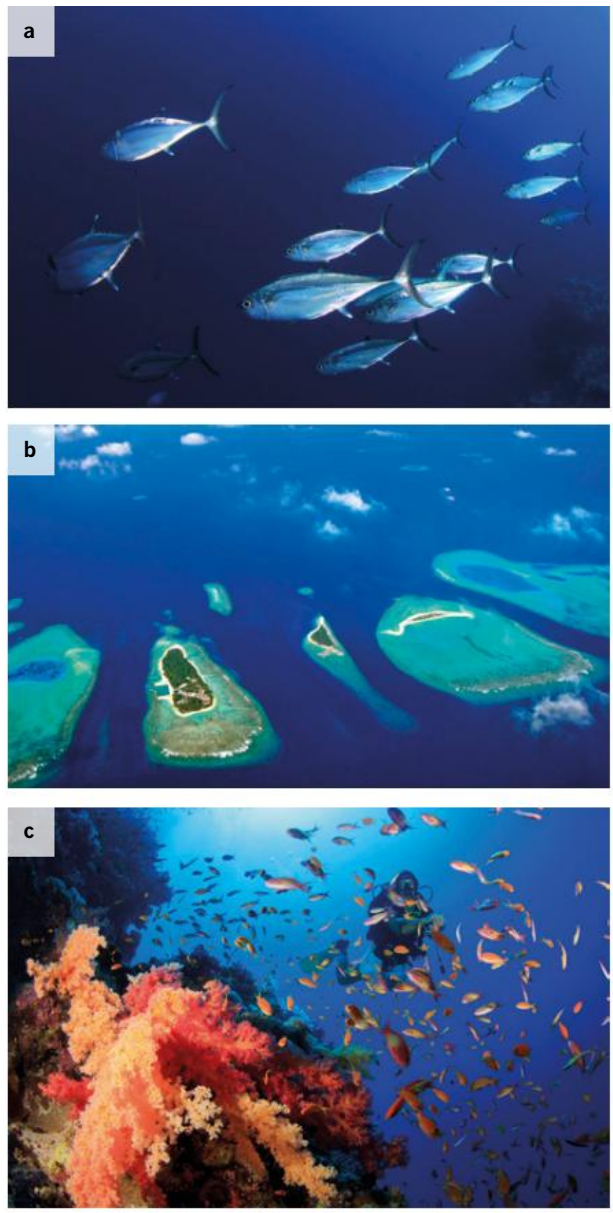

FIGURE 3.2.9 (a) Food supplies: The oceans provide a diverse range of food sources for human consumption. Increased ocean acidity may affect stocks of fish, molluscs and crustaceans that are consumed by humans. (b) Coastal protection: Coral reefs provide protection from storm and erosion. The destruction of coral reefs could threaten coastal communities. (c) Tourism: The colour and diversity of coral reefs make them a popular tourist attraction. Their destruction will affect the economies of communities that rely on tourism.

3.2 Review

SUMMARY

- Carbonic acid is a weak diprotic acid that reacts with water to produce hydronium ions, hydrogencarbonate ions and carbonate ions.
- An increased concentration of carbon dioxide in the atmosphere causes more carbon dioxide to dissolve in the oceans, producing more carbonic acid.
- Absorption of increased amounts of carbon dioxide increases the concentration of hydronium ions in sea water and lowers its pH. This process is called acidification.
- Calcification is the process that results in the formation of calcium carbonate structures such as coral reefs.
- An increase in ocean acidity causes some of the additional hydronium ions to react with carbonate ions according to the reaction: $H^+(aq) + CO_3^{2-}(aq) \rightarrow HCO_3^-(aq)$. This process is called decalcification.
- This reaction has the effect of reducing the concentration of free CO_3^{2-} ions in sea water.
- Some marine organisms use calcium ions and carbonate ions to protect themselves with layers of calcium carbonate. Reduced carbonate ion concentration impairs the ability of some marine organisms to build and maintain calcium carbonate structures.

KEY QUESTIONS

1 Write balanced equations for the two steps in which carbonic acid ionises to form hydrogencarbonate ions and carbonate ions.

2 A solution contains the following equilibria:
$CO_2(g) \rightleftharpoons CO_2(aq)$
$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$
$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$
$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$
Circle the correct answers from the alternatives provided, to complete the sentences about these equilibria.
If more CO_2 gas were to dissolve, the concentration of H_2CO_3 would increase/decrease and the pH would increase/decrease. The addition of a small amount of acid would cause the concentration of CO_3^{2-} ions to increase/decrease and the concentration of $CO_2(aq)$ to increase/decrease.

3 Write an equation to show how increased ocean acidity causes a decrease in the concentration of carbonate ions in sea water.

4 What is the name of the compound that forms a protective layer for many marine organisms? What is the name of the process for the formation of this layer?

5 Krill and plankton populations are expected to decrease with increasing ocean acidity.
a What is the direct effect of ocean acidity on krill?
b Why is the decrease of krill and plankton population numbers a concern for ecologists?

3.3 Modelling and responding to climate change

In this section, you will learn about some of the scientific research on **climate change** and the modelling that is being used to enhance our understanding of the effect of greenhouse gas emissions on weather patterns.

Figure 3.3.1 shows drought-affected country in Western Australia. Scientists report that extreme weather events, such as droughts, storms and floods, have become more widespread and have occurred more regularly over the last decade. There is considerable debate over the causes of climate change, although its existence is widely, although not universally, accepted.

FIGURE 3.3.1 A drought-affected sheep farm near York, Western Australia

The consensus among scientists is that human activity is the major influence on the warming of Earth that has been observed since the Industrial Revolution. Changes such as increasing temperatures of the atmosphere and oceans, reduction in snow and ice, rising sea levels and increasing concentrations of greenhouse gases have been observed since the mid-1800s.

An international response to these changes that involves nearly 200 countries has been negotiated to attempt to restrict temperature increases to less than 2°C above pre-industrial levels.

Most scientists agree that global warming is occurring and are near certain that human activity is the major influence.

MODELLING CLIMATE CHANGE

Climate models are mathematical models based on the laws of physics. The models are run on supercomputers. These mathematical representations simulate the way that the atmosphere, oceans, land surface and ice interact and affect the Earth's climate system.

The models consider the incoming energy from the Sun and the radiation of outgoing energy into space. The equilibrium that exists between the incoming and outgoing energy can be disturbed and any imbalance results in a temperature change. Models can vary from extremely complex mathematical equations that use tens of thousands of items of data, including measurements from satellites, to simple heat transfer models.

CHEMFILE

As ice melts more pollutants are released

Researchers from the National Aeronautics and Space Administration (NASA) in the United States have found that as the sea ice in the Arctic Ocean melts (Figure 3.3.2), deposits of mercury and bromine have been released. When there is a mix of salty ice, very low temperatures and sunlight, bromine is released into the air and this produces a complex series of chemical reactions. The reactions produce molecules of bromine monoxide (BrO), which then react with gaseous elemental mercury, producing mercury-containing pollutants that fall onto the Earth's surface.

FIGURE 3.3.2 The amount of sea ice has substantially reduced in the Arctic over the past decade. Conversely, the Antarctic sea ice has increased in area and thickness in recent years. Natural variations and wind changes are suggested as possible explanations.

More than 40 climate models have been developed by various scientific organisations around the world. The models vary in their ability to make successful predictions and are tested using simulations based on the recorded measurements of the climate in past decades, which develops confidence in the models and validates them.

Figure 3.3.3 shows the interaction of the factors in a model called a coupled climate change model. Coupled climate models link the exchange of energy and moisture to vegetation, soil, ice and the atmosphere.

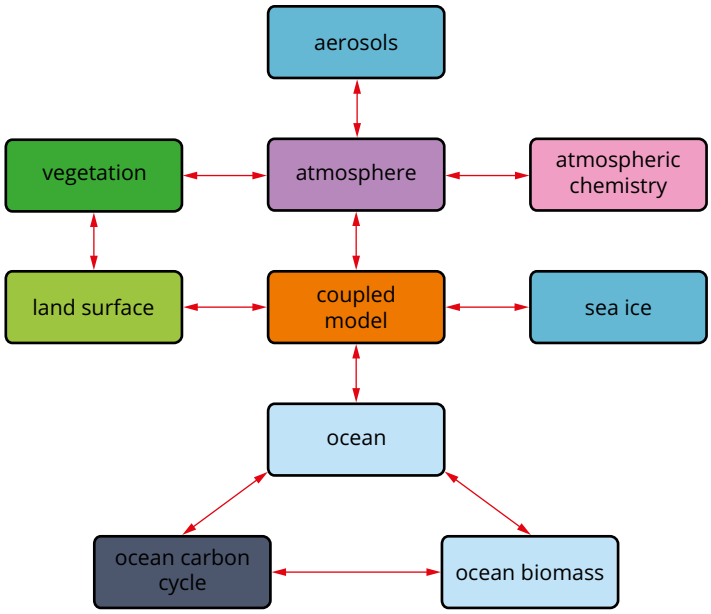

FIGURE 3.3.3 The components of a coupled climate change model. Modern climate models incorporate interactions between vegetation, soil, ice and land surface with the atmosphere.

These models allow scientists to predict the increase in temperature of both sea and land and future changes in ocean acidity. They also enable scientists to investigate the effects of the use of alternative fuels (such as biofuels) and other energy sources on the production of carbon dioxide. The research demonstrates that controlling the way these factors affect the equilibria in the carbon cycle, and particularly the cycling of carbon in the sea, will assist in slowing down the effects of climate change and global warming.

Some of the main predictions of climate models are as follows.

- The average global temperature is expected to rise by 0.3–4.8°C over the next century.
- The amount of rainfall everywhere, particularly in tropical and high-altitude regions, is expected to increase.
- Tropical storms are likely to increase in wind strength and amount of rainfall.
- The sea level is expected to rise by 0.3–1.2 metres in the next century.
- Amounts of sea ice and snow are expected to decrease.

Climate models predict increased global temperatures, increased rainfall, increased wind strength of tropical storms and rising sea levels.

CSIRO climate model

CSIRO climate scientists have developed a model called ACCESS (Australian Community Climate and Earth Simulator). You can see results from this model every time you look at the Bureau of Meteorology's Australian weather forecasts.

The model is used to make climate predictions for the coming century within Australia. More than 20 years of research and knowledge have been used to make these projections. ACCESS links models of the oceans, atmosphere, aerosols, chemistry, sea-ice, land surface and the global carbon cycle to simulate changes in the climate.

ACCESS involves researchers in CSIRO and Australian universities, and employs some of the most powerful supercomputers, enabling scientists to contribute to major international climate modelling and predictions. The results so far include:

- accurate forecasting of major weather events up to 3 days in advance, which allows greater certainty in planning
- tracking of tropical cyclones
- accurate forecasting of the weather conditions that produce extreme bushfire and flood conditions
- projections of the future greenhouse gas emissions for the 21st century.

POTENTIAL FUTURES

Figure 3.3.4 shows world energy production from different sources over time. There has been a marked increase in energy consumption since the 1800s.

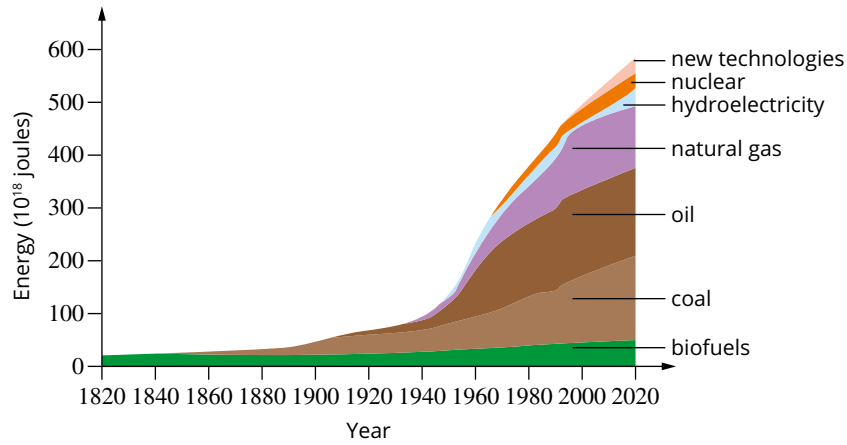

FIGURE 3.3.4 The increase in world energy production from different sources. Many countries, including Australia, are increasing their use of renewable energy in preference to fossil fuels.

Given the limited reserves of fossil fuels and evidence that the use of these fuels is linked to climate change, there is considerable interest in identifying and developing new energy sources that have less environmental impact. The development of alternative sources for large-scale energy production is not a simple task, as replacement energy sources need to meet a range of requirements, such as being reliable, sustainable and cost-effective. To be **sustainable**, an energy source must be able to meet increasing human needs, without compromising future demands.

Governments and industries are exploring alternatives to fossil fuels to ensure that future energy needs can be met and to limit the impact of these fuels on the environment. Ideally, new sources of energy will be both sustainable and renewable. A **renewable** energy source needs to be widely available, naturally replaced and have a small environmental impact.

Biofuels are examples of renewable sources of energy. Biofuels are fuels derived from plant materials such as grains (maize, wheat, barley or sorghum), sugar cane or vegetable waste, and vegetable oils. The three main biofuels are **biogas**, **bioethanol** and **biodiesel**. Bioethanol and biodiesel can be used alone or blended with fossil fuels, such as petrol and diesel, and used as transport fuels. Biogas can be used for small-scale electricity generation.

As well as their advantage of being renewable, there is potential for biofuels to have less impact on the environment than fossil fuels. The plant materials used in the generation of biofuels are produced by photosynthesis, which removes carbon dioxide from the atmosphere and produces glucose ($C_6H_{12}O_6$) in the following reaction:

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

Plants convert the glucose into cellulose and starch. Carbon dioxide is released back into the atmosphere when the biofuel is burnt. The carbon dioxide can then be used to make more plant material, which in turn can be used as fuel, and so the cycle continues.

A fuel is described as **carbon neutral** if its use results in no overall release of carbon into the atmosphere. In practice, biofuels are not strictly carbon neutral. For example, bioethanol is not carbon neutral because energy is required, and emissions produced, in growing crops, transport and refining of the fuel. However, it is argued that the use of biofuels has the potential to produce less carbon dioxide than fossil fuels, depending on how they are produced.

Future changes in the use of renewable energy sources rather than fossil fuels are factors that scientists try to take into account with projections from climate modelling. In Australia, the CSIRO predicts that alternative fuels will comprise 35% of the fuels used for transport by 2030.

EXTENSION

Food versus fuel

The growing of crops for the production of biofuels, such as bioethanol (Figure 3.3.5), involves energy expenditure and the use of resources, such as water and fertiliser. Intensive farming can also lead to erosion and pollution. These issues are more significant if crops are grown solely to produce ethanol, but of less concern if waste from food crops is used as a raw material.

FIGURE 3.3.5 Harvesting sugar cane in Queensland. Sugar cane can be used as a source of the raw materials for the production of bioethanol.

Biofuels are a renewable source of energy and current production levels are sustainable. However, biofuels produce only a small percentage of Australia's fuel needs. If biofuel production is to increase significantly, crops would need to be grown specifically for this purpose.

The use of land to grow crops for fuel production presents a number of issues, including land degradation and the widespread destruction of forests and bushland, which convert carbon dioxide into plant material more effectively than crops such as sugar cane.

Perhaps the most significant issue that arises is the use of agricultural land to grow fuel crops rather than food crops. If the use of biofuels increases, ensuring that low-cost food supplies are maintained while meeting the demand for fuel will be a challenge.

CHEMFILE

More CO_2—more photosynthesis

For marine plants that do not have shells, such as phytoplankton, seagrasses and kelp (Figure 3.3.6), an increase in the concentration of carbon dioxide in sea water due to climate change does not have an immediate negative consequence. Higher carbon dioxide levels increase the plants' ability to photosynthesise. This can lead to increased growth and also increase the food (glucose and therefore starch and cellulose) and oxygen in the surrounding waters, to the benefit of other nearby marine organisms.

FIGURE 3.3.6 Kelp forests underwater. With increased CO_2 concentrations, kelp and similar marine plants undergo more photosynthesis.

INTERNATIONAL RESPONSE

In 1988, member nations of the United Nations requested the establishment of a scientific body called the Intergovernmental Panel on Climate Change (IPCC). The IPCC supports the main international treaty on climate change, known as the United Nations Framework Convention on Climate Change (UNFCCC), which was negotiated in 1992.

The main objective of the IPCC is to 'stabilise greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous human-induced interference with the climate system'. The IPCC is the authority on climate change and produces reports (Figure 3.3.7) that are accepted by leading climate scientists and participating governments. Different models, shown in Figure 3.3.7, and labelled A1FI, B2 etc., give different estimates of the expected temperature changes. The models predict an increase in temperature of 2–4°C by 2100.

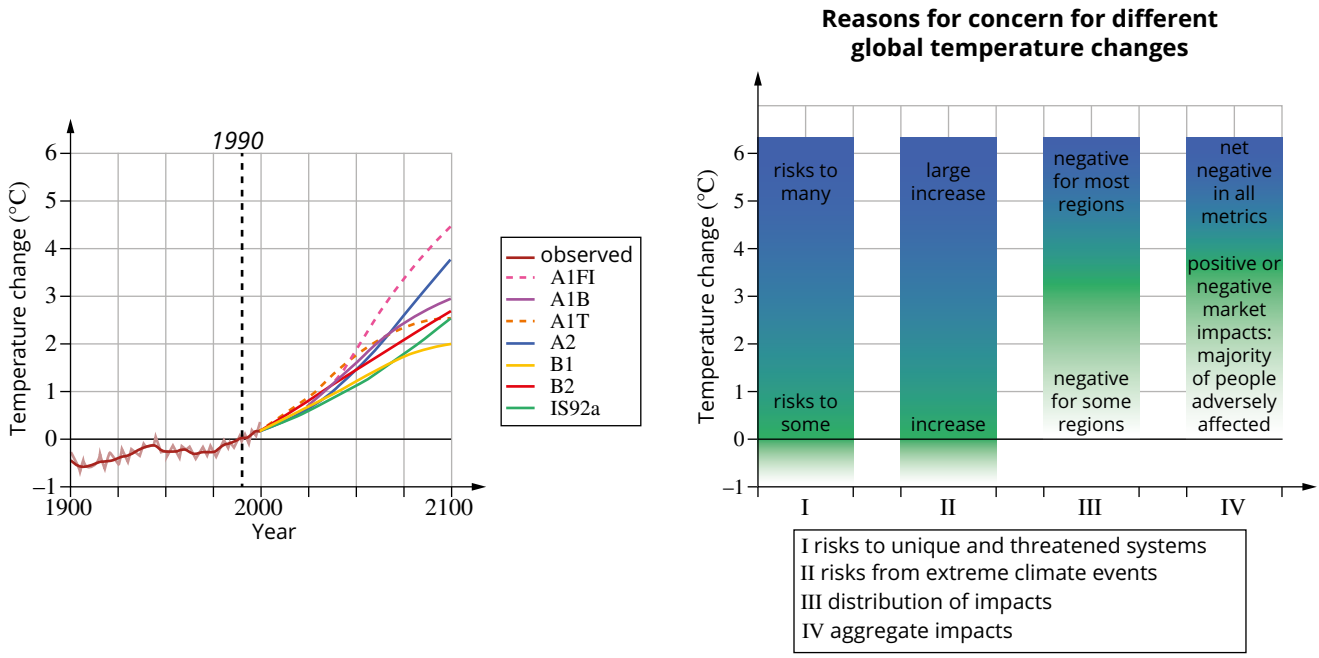

FIGURE 3.3.7 Risks and impacts of climate change. This assessment of global warming based on different models and the associated risks was initially published in 2001 by the IPCC and has been subsequently updated.

United Nations Kyoto Protocol

The Kyoto Protocol is an international agreement negotiated in 1997 that extended the UNFCCC. It established a commitment by 192 countries, including Australia, to binding reductions in greenhouse gas emissions to specified levels during the commitment period 2008–2012. The overriding aim of the protocol was to reduce the collective emissions of the countries by at least 5% from 1990 levels.

The achievements of the Kyoto Protocol were the:

- stimulation of many national policies
- creation of an international market for carbon
- development of emissions trading schemes.

Many countries developed their own methods to attempt to comply with the Kyoto Protocol and to address this environmental issue. The aim was to secure global commitment. This was difficult because the protocol is restricted by the:

- modest emission reduction limits
- lack of measures to achieve greater reductions
- absence of penalties for countries not achieving targets.

Paris Agreement

In 2015, the Kyoto Protocol was further strengthened when 72 countries, including the world's two largest greenhouse gas emitters, China and the United States, ratified an agreement for action on climate change called the Paris Agreement. The agreement requires countries to submit increasingly stringent pledges every 5 years. Unlike the Kyoto Protocol, which set commitment targets that have legal force, the Paris Agreement allows each country to determine their national targets. Nearly 200 countries, including Australia, have signed the treaty. However, in June 2017, President Donald Trump withdrew the United States from the Agreement, potentially weakening its power to ensure long-term reductions in greenhouse gas emissions across the globe.

Under the Paris Agreement, there is a goal to keep the increase in the global average temperature to below 2°C above pre-industrial levels and pursue efforts to keep warming below 1.5°C above pre-industrial levels.

AUSTRALIAN RESPONSE

Scientists predict that changes in Australia's climate will have significant economic, social and environmental impacts on the nation.

The Australian Climate Change Science Program (ACCSP) is the basis for the Australian Government's response to climate change. It is a partnership between CSIRO, the Department of the Environment, the Bureau of Meteorology and other agencies.

The specific areas of research for ACCSP include:

- understanding the influence of the Southern Ocean on global climate (Figure 3.3.8)
- increasing our understanding of atmospheric processes such as aerosol behaviour and cloud properties
- developing a greater knowledge of Australia's unique biosphere
- assessing the climate variability in the Australian region
- improving projections through more sophisticated climate models
- improving communication of regional projections of future climate change.

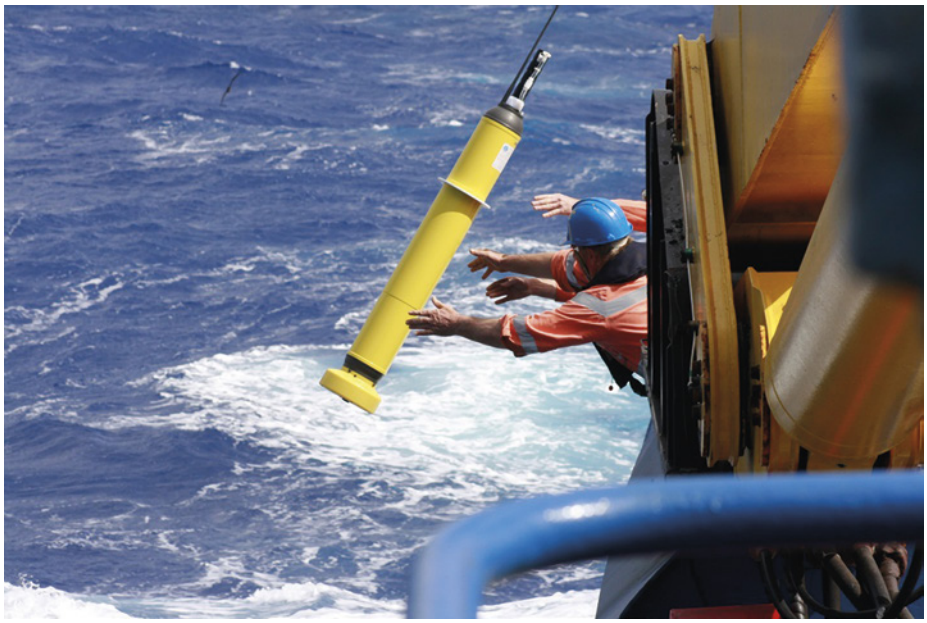

FIGURE 3.3.8 Researchers launch an Argo robotic float from *Southern Surveyor*. Argo is a collection of 3800 freely drifting floats that measure the temperature, salinity and speed of the ocean. CSIRO and other organisations use data from these floats for climate modelling.

Australian climate change targets

Australia is responsible for 1.3% of total global carbon emissions. While Australia is meeting its current climate change targets and supporting international agreements, there is considerable public and political debate over the most appropriate policies for reducing emissions and slowing down global warming.

The Australian Government has announced a target to reduce emissions by 26–28% by 2030 on the 2005 levels. This represents a 50–52% reduction in emissions per person between 2005 and 2030. The target being aimed for is similar to those agreed to by countries such as the United States, the European Union (EU), Canada, New Zealand and Japan (Figure 3.3.9).

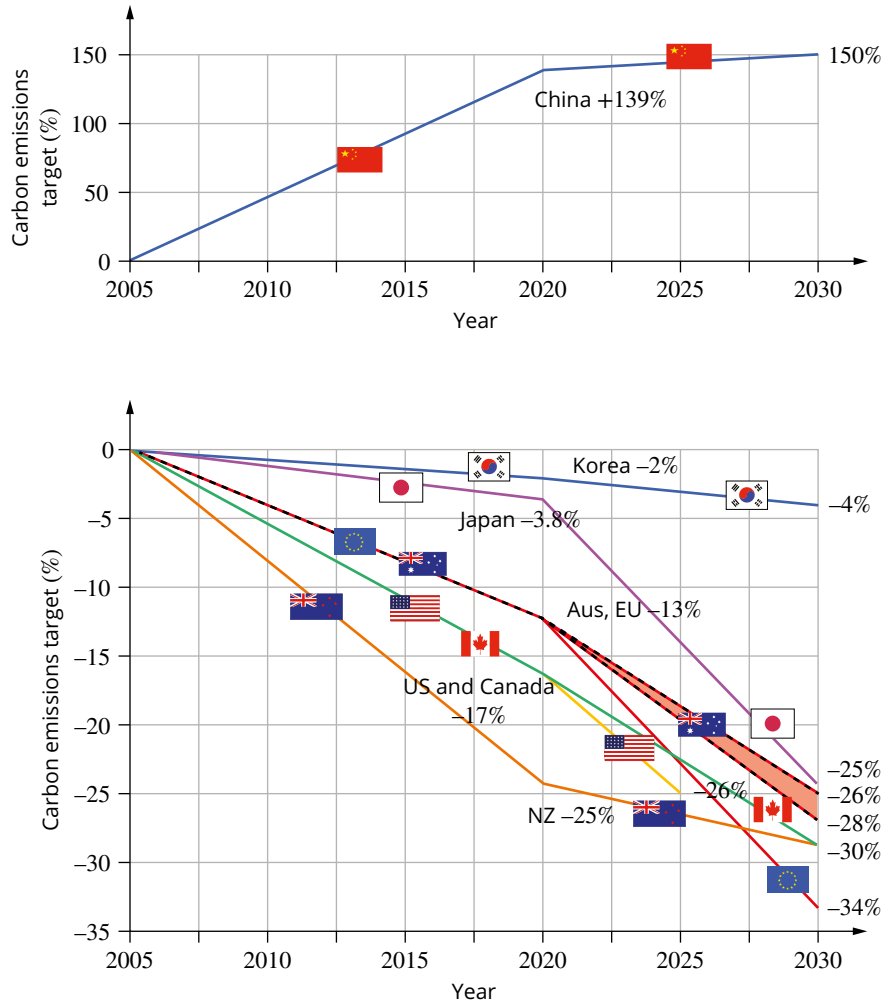

FIGURE 3.3.9 A comparison of Australia's carbon emissions target with other countries, against a common base year (2005).

The government aims to reduce carbon dioxide emissions by:

- using energy-efficient technologies such as innovative building design, LED lighting and electric cars
- phasing out inefficient energy producers of greenhouse gases, such as coal-fired power stations
- investing in low-emissions technologies and practices, such as the use of solar energy.

3.3 Review

SUMMARY

- Climate models are mathematical models based on the laws of physics and run on supercomputers. Scientists use these models to simulate the way that the atmosphere, oceans, land surface and ice interact and affect the Earth's climate system.
- Member nations of the United Nations have established a scientific body called the Intergovernmental Panel on Climate Change (IPCC) to secure a global commitment to reducing greenhouse gas emissions over the next few decades.
- The Kyoto Protocol is an international agreement that established a commitment by 192 countries, including Australia, to reduce greenhouse gas emissions to 5% from 1990 levels during the period 2008–2012.
- The Kyoto Protocol has stimulated national emissions policies, created an international market for carbon and developed emissions trading schemes.
- In 2015, the Paris Agreement required participating countries to submit increasingly stringent pledges every 5 years. The main goal of the Paris Agreement is to hold the increase in the global average temperature to below 2°C above pre-industrial levels.

KEY QUESTIONS

1 List three predictions of climate models.

2 Many countries have agreed to reduce greenhouse gas emissions in order to slow global warming. What is the target for the maximum temperature rise?

A 1°C
B 2°C
C 5°C
D 10°C

3 The Kyoto Protocol is an international agreement negotiated in 1997. State two achievements of the Kyoto Protocol.

4 **a** What is the full name of the United Nations organisation known as the IPCC?
b What are the main goals of the IPCC?

5 Complete the following paragraph about Australia's climate change goals and targets using terms from the list. Terms are used only once, although some may not be used at all:
natural gas, greenhouse gas, reduce, increase, London Declaration, Kyoto Protocol, greenhouse emissions, 26–28%, 50–52%, 2030, 2040, stabilised, solar energy.

Australia has signed the _____ _____ and the Paris Agreement. The country has pledged to _____ emissions so that the _____ _____ concentrations in the atmosphere can be _____. The aim is to reduce _____ _____to _____% below the 2005 levels by the year _____. The Australian government intends to achieve its target by using energy efficient technologies, phasing out inefficient energy producers and investing in low emission technologies such as _____ _____.

6 The 2015 Paris Agreement was an international response to global warming in which all nations were asked to commit to keeping the global average temperature rise to below 2°C, through reductions in greenhouse gas emissions.

a What impact would adoption of the Paris Agreement have on Australia?
b Discuss the role that biofuels could play in helping Australia meet its targets for reducing greenhouse gas emissions.

Chapter review

03

KEY TERMS

acidification
biodiesel
bioethanol
biofuel
biogas
calcification
carbon cycle
carbon neutral
chlorophyll
climate change
decalcification
diprotic acid
ecosystem
endothermic
enhanced greenhouse effect
exothermic
food chain
fossil fuel
global warming
greenhouse effect
greenhouse gas
krill
non-renewable
ocean acidity
photosynthesis
plankton
renewable
respiration
sustainable

Carbon dioxide in the atmosphere

1 List two ways in which carbon dioxide is returned to the atmosphere in the carbon cycle.

2 **a** What is the 'greenhouse effect'? Why has it been important in the evolution of life on Earth?

b What are the main greenhouse gases?

3 The combustion of fossil fuels adds carbon dioxide to the atmosphere. Write an equation for the combustion of octane (C_8H_{18}) in excess oxygen.

4 Briefly explain the concept of the enhanced greenhouse effect and its effect on climate.

Carbon dioxide in the oceans

5 Carbon dioxide levels are increasing in the atmosphere. Which one of the following statements about the impact on oceans is correct?

A As [CO_2] increases, the oceans become more acidic and marine animals have less difficulty producing shells.

B As [CO_2] increases, the oceans become less acidic and coral reefs are at risk.

C As [CO_2] increases, the oceans become less acidic and coral reefs will spread more rapidly.

D As [CO_2] increases, the oceans become more acidic and there is a reduction in [CO_3^{2-}].

6 Which one of the following species is present in highest concentration in sea water?

A $CO_3^{2-}(aq)$
B $HCO_3^-(aq)$
C $H_2CO_3(aq)$
D $CO_2(aq)$

7 When excess amounts of CO_2 gas dissolve in the oceans, causing corals to dissolve, which one of the following equilibria is not disturbed?

A $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$
B $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$
C $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$
D $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

8 The following four equibrium systems occur in the ocean:

1 $CO_2(g) \rightleftharpoons CO_2(aq)$
2 $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$
3 $H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$
4 $HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$

Using the equations above, explain how increased carbon dioxide levels in the atmosphere reduce the pH of the oceans.

9 Classify the following statements as describing aspects of acidification or calcification.

a Results in the destruction of coral reefs
b Results in calcium carbonate structures such as coral reefs
c Is decreased by increased ocean acidity
d Is caused by a decrease in pH
e Results in more calcium carbonate dissolving

10 Which one of the following is not associated with the problem that ocean acidification is predicted to cause for marine organisms?

A Calcium carbonate will tend to dissolve.
B The ocean pH will decrease.
C The concentration of hydrogencarbonate ions will decrease.
D More carbon dioxide gas will dissolve in the ocean.

11 Choose the correct alternatives from the pairs of terms listed to complete the sentences about carbon dioxide emissions.

A significant proportion of the carbon dioxide emissions from human activity is released/absorbed by the oceans. This reduces/increases the greenhouse effect in the atmosphere. The increased acidity of the oceans changes the position of the carbonate equilibrium:

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

As the H^+ concentration increases, the pH increases/decreases and the equilibrium shifts to the left/right, consuming carbonate ions. As a consequence, the equilibrium:

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

is disturbed.

The higher/lower concentration of CO_3^{2-} ions causes solid $CaCO_3$ to precipitate/dissolve and the reaction shifts to the left/right, increasing/decreasing the rate of calcification and making it more difficult for marine creatures to produce shells and coral.

12 As ocean acidity increases, corals become more at risk.

a What is this process called?

b Explain this process using appropriate equations.

Modelling and responding to climate change

13 Which one of the following statements about the Intergovernmental Panel on Climate Change (IPCC) is false?

A The IPCC aims to stabilise greenhouse gas concentrations in the atmosphere.

B The IPCC produces reports for climate scientists and governments.

C The IPCC aims to reduce the levels of atmospheric carbon dioxide.

D The IPCC was established by the United Nations.

14 Which one of the following statements regarding the Kyoto Protocol and associated agreements is true?

A Successful emission targets have been achieved.

B Penalties are in place for countries that do not comply.

C Some countries have agreed to cut emissions by 5% below 1990 levels.

D Global commitment by all nations has been achieved.

15 Complete the following sentences by choosing words from the list: stabilise, climate, atmosphere, human-induced, concentrations.

The United Nations Framework Convention on Climate Change is supported by reports from the IPCC (Intergovernmental Panel on Climate Change). The ultimate objective is 'to _____ greenhouse gas _____ in the _____ at a level which prevents _____ interference with the_____'.

Connecting the main ideas

16 **a** List three possible global consequences of the increasing levels of carbon dioxide in the atmosphere.

b Describe two strategies for reducing the levels of greenhouse gases in the atmosphere.

17 A calcium carbonate/carbon dioxide equilibrium exists in the oceans and between the carbon dioxide in the atmosphere. Write the following equations in the correct order to show the sequence of reactions involved in the formation of calcium carbonate from carbon dioxide.

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$$
$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$
$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$
$$CO_2(g) \rightleftharpoons CO_2(aq)$$

CHAPTER

04 Acids and bases

This chapter builds on the acid–base chemistry you studied in Year 11. You will examine the nature of acids and bases from the point of view of proton exchange. The role of water in acid–base chemistry will be discussed, as will the concept of pH as a measure of acidity.

You will learn to carry out calculations involving pH. The ideas about equilibrium systems that you explored in Chapter 2 will be applied to your understanding of acid–base chemistry.

Science as a human endeavour

Models and theories are contested and refined or replaced when new evidence challenges them, or when a new model or theory has greater explanatory scope. Davy initially proposed that acids were substances that contained replaceable hydrogen (hydrogen that could be partly or totally replaced by metals), and bases were substances that reacted with acids to form salts and water. The Arrhenius model, which includes only soluble acids and bases, identified acids as substances which produce hydrogen ions in solution and bases as substances which produce hydroxide ions in solution. Subsequently, the Brønsted–Lowry model describes acid–base behaviour in terms of proton donors and proton acceptors. This approach includes a wider range of substances and can be more broadly applied.

Science understanding

- observable changes in chemical reactions and physical changes can be described and explained at an atomic and molecular level
- 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 available for donation
- the strength of acids is explained by the degree of ionisation at equilibrium in aqueous solution, which can be represented by chemical equations and acidity constants (K_a)
- 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 protons between conjugate acid-base pairs
- the hydrolysis of salts of weak acids and weak bases can be represented using equations; the Brønsted–Lowry model can be applied to explain the acidic, basic and neutral nature of salts derived from bases and monoprotic and polyprotic acids
- water is a weak electrolyte; the self-ionisation of water is represented by $K_w = [H^+][OH^-]$ where $K_w = 1.0 \times 10^{-14}$ at 25°C
- K_w can be used to calculate the concentration of hydrogen ions or hydroxide ions in solutions of strong acids or bases
- 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 $pH = -\log_{10}[H^+]$

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4.1 Introducing acids and bases

Acids and **bases** make up some of the most commonly used products in our daily lives (Figure 4.1.1). They are important industrial and agricultural chemicals and are significant in a biological and environmental context. Acids and bases are found in many household products. Bases, in particular, sodium hydroxide (caustic soda) and sodium carbonate (soda ash), are used in many cleaning products for their ability to react with oils and grease.

In this section, you will be introduced to a theory that explains the chemical properties of acids and bases, helping you to understand their usefulness within the home and industry as well as their role in the environment. You will also look at how to measure the **acidity** of a solution, therefore defining the level of acidity or basicity of a solution.

FIGURE 4.1.1 Common household products that are acids, bases or salts

ACIDS AND BASES

Acids are used in our homes, in agriculture and in industry. They also play an important role in our bodies. Table 4.1.1 gives the names, chemical formulae and uses of some common acids.

TABLE 4.1.1 Common acids and their everyday uses

Name	Formula	Uses
Hydrochloric acid	HCl	Present in stomach acid to help break down proteins. Used as a cleaning agent for brickwork
Sulfuric acid	H_2SO_4	One of the most common chemicals manufactured. Used in car batteries and in the manufacture of fertilisers and detergents
Nitric acid	HNO_3	Used in the manufacture of fertilisers, dyes and explosives
Ethanoic (acetic) acid	CH_3COOH	Found in vinegar. Used as a preservative
Carbonic acid	H_2CO_3	Found in carbonated soft drinks and beer
Phosphoric acid	H_3PO_4	Used in some soft drinks and in the manufacture of fertilisers
Citric acid	$C_6H_8O_7$	Found in citrus fruits
Ascorbic acid	$C_6H_8O_6$	Found in citrus fruits (vitamin C)

CHEMFILE

Saving the Nobel Prize gold medal

George de Hevesy (1885–1966) worked for the Niels Bohr Institute in Denmark during World War II. The Institute was looking after a number of valuable gold medals that had been awarded to recipients of the Nobel Prize. The Nobel Prize is awarded for outstanding contributions to the fields of physics, chemistry, literature, peace, physiology or medicine, and economics.

When Germany invaded Denmark at the beginning of World War II, de Hevesy was concerned that the Germans would confiscate the gold medals. He dissolved the gold medals in aqua regia, which is a mixture of concentrated hydrochloric and nitric acids. Aqua regia is strong enough to dissolve gold, a metal known for its lack of chemical reactivity.

He hid the bottle containing the gold solution among the hundreds of other bottles on his laboratory shelves. The bottle was never found by the German occupiers and after the war de Hevesy retrieved the precious bottle and precipitated the gold out of solution. The gold was sent to the Nobel foundation where the medals were recast into duplicates of the originals and returned to their rightful owners (Figure 4.1.2).

FIGURE 4.1.2 Recipients of the Nobel Prize are given a sum of money and a gold medal weighing about 175 g.

Many cleaning agents used in the home, such as washing powders and oven cleaners, contain bases. **Solutions** of ammonia are used as floor cleaners, and sodium hydroxide is the major active ingredient in oven cleaner. Bases are effective cleaners because they react with fats and oils to produce water-soluble soaps. A soluble base is referred to as an **alkali**.

Table 4.1.2 gives the names, chemical formulae and uses of some common bases.

TABLE 4.1.2 Common bases and their uses

Name	Formula	Uses
Sodium hydroxide (caustic soda)	NaOH	Used in drain and oven cleaners, and in soap making
Ammonia	NH_3	Used in household cleaners, fertilisers and explosives
Calcium hydroxide	$Ca(OH)_2$	Found in cement and mortar. Used in garden lime to adjust soil pH
Magnesium hydroxide	$Mg(OH)_2$	Key ingredient in some antacids, such as milk of magnesia, used to overcome indigestion
Sodium carbonate	Na_2CO_3	Used in the manufacture of washing powder and glass

PROPERTIES OF ACIDS AND BASES

All acids have some properties in common. Bases also have common properties. The properties of acids and bases are summarised in Table 4.1.3.

TABLE 4.1.3 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

CHANGING IDEAS ABOUT THE NATURE OF ACIDS AND BASES

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 their taste, effect on indicators and reactions with other substances. (You will learn more about indicators in Chapter 6.)

In the late 18th century, attempts were made to define acids and bases on the basis of the nature of their constituent elements. Antoine Lavoisier, a French chemist, thought that acidic properties were due to the presence of oxygen. While this explanation applied to sulfuric acid (H_2SO_4), nitric acid (HNO_3) and phosphoric acid (H_3PO_4), it did not explain why hydrochloric acid (HCl) was an acid.

In about 1810, Humphrey Davy suggested that the acid properties of substances were associated with hydrogen and not oxygen. He came to this conclusion after producing hydrogen gas by reacting acids with metals. Davey also suggested that acids react with bases to form salts and water.

Aqueous solutions of bases are called alkalis. Calcium carbonate will react with acids. However, it is not considered an alkali because it is insoluble in water.

CHEMFILE

Handle strong bases with care

Bases feel slippery to the touch because they react with fats in your skin to produce soap. Strong bases should be handled with care. Oven cleaners contain about 4% of the strong base sodium hydroxide. A common name of sodium hydroxide is caustic soda.

Figure 4.1.3 shows the safety instructions on a can of oven cleaner.

FIGURE 4.1.3 Oven cleaner removes fatty deposits by turning them into soap. Note the safety instructions.

CHEMISTRY IN ACTION

Naturally occurring acids

Rainwater has a pH of about 6. Rainwater is naturally acidic because of the presence of carbon dioxide in the atmosphere. Carbon dioxide dissolves in water in the atmosphere and oceans, forming carbonic acid:

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

The pH of rain can drop below 6 when other gases, particularly oxides of non-metals such as sulfur and nitrogen, combine chemically with water and oxygen in the atmosphere and oceans, producing acids.

Sulfur dioxide and sulfur trioxide are both released in large quantities by volcanoes and combine with water in the atmosphere to produce sulfuric and sulfurous acids. Nitrogen oxides are produced when nitrogen combines explosively with oxygen during lightning strikes. The gases dissolve in atmospheric water to produce nitrous and nitric acid.

These gases and corresponding acids are an important part of the natural cycles of the Earth. However, their production from the combustion of fossil fuels and other industry is causing an imbalance that is contributing to large-scale problems such as acid rain and ocean acidification. Acid rain affects food chains at the decomposer level by disrupting the recycling of nutrients and killing aquatic plants and animals. It also affects the surfaces of plant leaves, reducing their ability to prevent water loss, which leads to deforestation. Increased acidity in the oceans, mainly due to increased atmospheric carbon dioxide levels, reduces the capacity of marine organisms such as shellfish and coral reef organisms to remove calcium carbonate from the water for shell and reef building. Table 4.1.4 shows the major gaseous non-metal oxides produced from the combustion of fossil fuels and the corresponding acids that they form.

TABLE 4.1.4 Non-metal oxides and the acids that they form

Oxide	Acid produced in the environment
CO_2	H_2CO_3 (carbonic acid)
SO_2, SO_3	H_2SO_3 (sulfurous acid) H_2SO_4 (sulfuric acid)
NO, NO_2	NO_2 reacts to form: HNO_2 (nitrous acid) HNO_3 (nitric acid

Figure 4.1.4 shows the damage caused to forests by acid rain.

FIGURE 4.1.4 Forest with dead trees destroyed by pollution and acid rain

This theory was further developed by the Swedish scientist Svante Arrhenius. In 1887, he defined acids and bases as follows.

- Acids are substances that **dissociate** (break apart) and **ionise** (form ions) in water. They produce hydrogen ions (H^+).
- Bases dissociate in water to produce **hydroxide ions** (OH^-).

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 theory 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.

BRØNSTED–LOWRY THEORY OF ACIDS AND BASES

According to the **Brønsted–Lowry theory**, 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 highly 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.

In this reaction, each HCl molecule has donated a proton to a water molecule, forming the **hydronium ion** ($H_3O^+(aq)$). According to the Brønsted–Lowry theory, 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 4.1.5.

The hydronium ion can be represented as either $H_3O^+(aq)$ or $H^+(aq)$. Therefore, the reaction of HCl(g) with water can be written as either a **hydrolysis reaction**:

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

or a dissociation reaction:

$$HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$$

A hydrolysis reaction occurs when a molecule or ion in aqueous solution reacts with water, either accepting or donating a proton. Writing the hydronium ion as $H^+(aq)$ in a dissociation equation makes it harder to see that a proton transfer has occurred. Therefore, the hydronium ion is usually written as $H_3O^+(aq)$ in this chapter.

The structural formulae of the hydronium ion and the water molecule are shown in Figure 4.1.6.

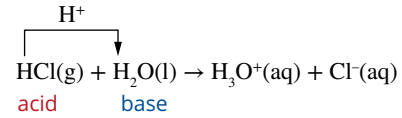

FIGURE 4.1.5 The reaction between hydrochloric acid and water is an example of an acid–base reaction, which involves a transfer of protons from an acid to a base.

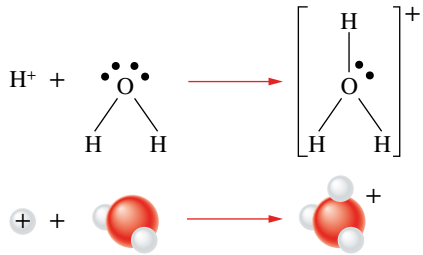

FIGURE 4.1.6 Formation of the hydronium ion

Remember that $H^+(aq)$ is often used interchangeably with $H_3O^+(aq)$ when discussing acids donating protons.

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.

Figure 4.1.7 shows the gaseous acid–base reaction between hydrogen chloride gas and ammonia gas.

FIGURE 4.1.7 A gaseous acid–base reaction between hydrogen chloride gas and ammonia gas. Fumes of solid ammonium chloride are formed.

Limitations of the Brønsted–Lowry model

Like all theories, the Brønsted–Lowry model has some limitations. For example, it cannot be applied to the reaction between acidic and basic oxides. Under certain conditions solid calcium oxide, a basic oxide, reacts with gaseous carbon dioxide, an acidic oxide, to produce the salt calcium carbonate:

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

CONJUGATE ACID–BASE PAIRS

A solution of hydrochloric acid is produced when hydrogen chloride ionises in water:

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

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 are two species that differ by a proton, i.e. H^+. There are two conjugate acid–base pairs in an acid–base reaction. 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 4.1.8.

In the reaction between NH_3 and H_2O (shown in Figure 4.1.9), 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.

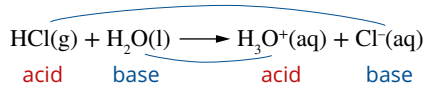

FIGURE 4.1.8 Conjugate acid–base pairs are formed when an acid donates a proton to a base.

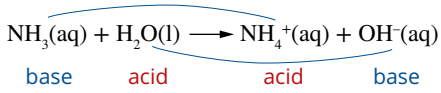

FIGURE 4.1.9 The reaction between ammonia and water, showing the conjugate acid–base pairs

Figure 4.1.10 shows the formulae of some common acids and bases and their conjugates.

Acids donate a proton to form:

HCl		Cl^-
H_2SO_4		HSO_4^-
HNO_3		NO_3^-
H_3O^+		H_2O
CH_3COOH	$-H^+$	CH_3COO^-
H_2CO_3		HCO_3^-
H_3PO_4		$H_2PO_4^-$
NH_4^+		NH_3
HCO_3^-		CO_3^{2-}
H_2O		OH^-

Bases accept a proton to form:

OH^-		H_2O
NH_3		NH_4^+
CO_3^{2-}		HCO_3^-
PO_4^{3-}	$+H^+$	HPO_4^{2-}
CH_3COO^-		CH_3COOH
O^{2-}		OH^-

FIGURE 4.1.10 Some common acid–base conjugate pairs

When acids react with water, hydronium (H_3O^+) ions are produced. When bases react with water, hydroxide (OH^-) ions are produced.

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 following reaction, water donates a proton to NH_3 and acts as an acid:

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

These reactions are represented in Figure 4.1.11.

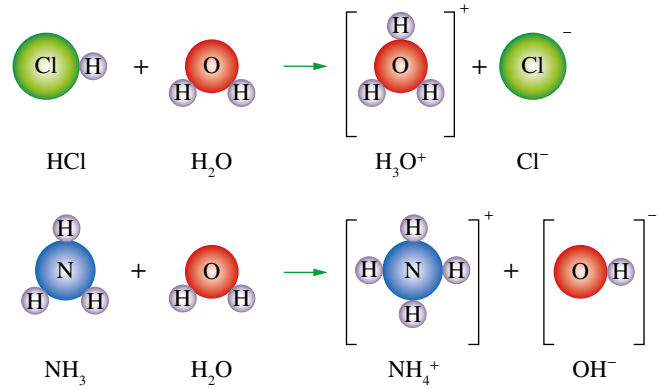

FIGURE 4.1.11 The amphiprotic nature of water is demonstrated by its reactions with HCl and NH_3.

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 listed in Figure 4.1.12.

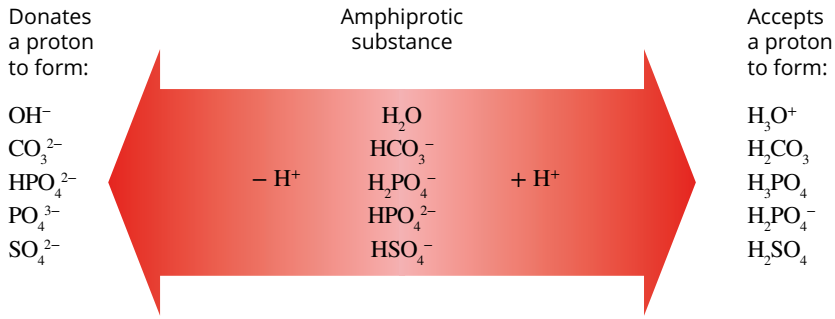

FIGURE 4.1.12 Substances that are amphiprotic

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^-) can act as both an acid and a base according to the equations:

$$\underset{\text{acid}}{HCO_3^-(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

$$\underset{\text{base}}{HCO_3^-(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

Although both reactions are possible for all amphiprotic substances in water, generally one reaction dominates. The dominant reaction can be identified by measuring the pH (a measure of the amount of hydronium ion in solution) of the solution. (You will look more closely at pH in section 4.3.)

MONOPROTIC ACIDS

Monoprotic acids can donate only one proton per molecule. These acids include hydrochloric acid (HCl), hydrofluoric acid (HF), nitric acid (HNO_3) and ethanoic (acetic) 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 it 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** (Figure 4.1.13).

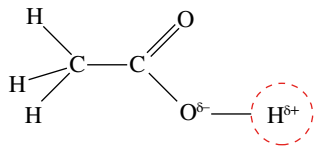

FIGURE 4.1.13 The structure of ethanoic acid. Each molecule can donate only one proton to a water molecule when ethanoic acid reacts with water.

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 can donate two protons. Sulfuric acid (H_2SO_4) and carbonic acid (H_2CO_3) are diprotic acids.

A diprotic acid, such as sulfuric acid, ionises in two stages:

Stage 1: $H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$

Stage 2: $HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$

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.

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 ionised. A double (reversible) arrow ($\rightleftharpoons$) indicates that an incomplete reaction occurs and an equilibrium is formed. (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. Phosphoric acid (H_3PO_4) and boric acid (H_3BO_3) are triprotic acids.

A triprotic acid, such as phosphoric acid, ionises 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 **ionisation** stage. The extent of the ionisation decreases progressively from stage 1 to stage 3.

4.1 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 an H^+ ion.
- A proton or hydrogen ion in solution can be represented by the hydronium 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 ionisation of a diprotic acid occurs to a greater extent than the second ionisation. In a triprotic acid, the third ionisation occurs to the least extent.

KEY QUESTIONS

1 An acidic solution is formed when hydrogen bromide gas (HBr) is mixed with water (H_2O). Write an equation for this reaction.

2 In the following reaction, what are the two acid–base conjugate pairs?

$H_2SO_4(aq) + HNO_3(aq) \rightarrow HSO_4^-\,aq) + H_2NO_3^+(aq)$

3 For each equation, give the conjugate of the acid or base that is written in bold.

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 $CH_3NH_2(aq) + HCl(aq) \rightarrow \mathbf{CH_3NH_3^+(aq)} + Cl^-(aq)$

4 Write the formulae of the conjugate acids of the following bases.

a NH_3

b CH_3COO^-

c HPO_4^{2-}

d CO_3^{2-}

5 Show, using an equation, that the reaction between a solution of sodium hydroxide and a solution of hydrochloric acid is a Brønsted–Lowry acid–base reaction.

6 Write an equation to show each of the following species acting as an acid and as a base with water.

a HCO_3^-

b HPO_4^{2-}

c HSO_4^-

d H_2O

4.2 Strength of acids and bases

The acid solutions in the two beakers shown in Figure 4.2.1 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 acid on the right.

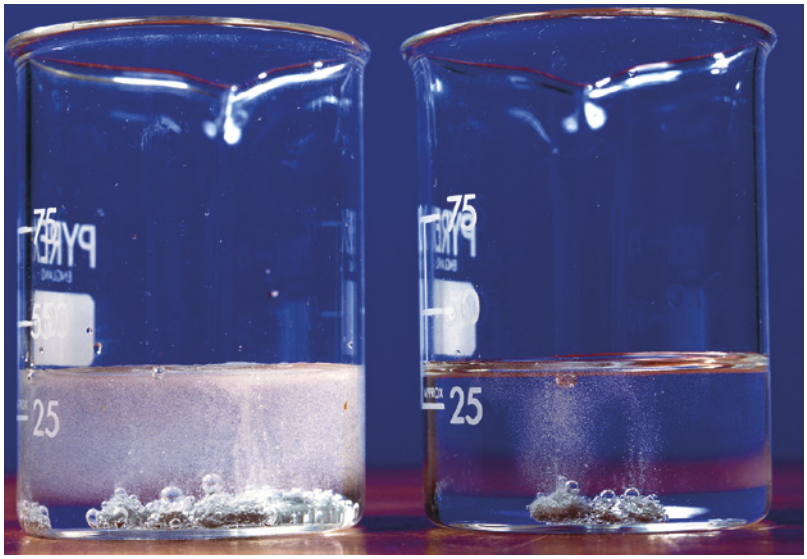

FIGURE 4.2.1 Zinc reacts more vigorously with a strong acid (left) than with a weak acid (right). The acid solutions are of equal concentration and volume.

In section 4.1, you learnt that the Brønsted–Lowry theory defines acids as proton donors and bases as proton acceptors. In this section, 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 concentrations of hydronium ions.

Some acids can donate a proton more readily than others. The Brønsted–Lowry theory 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.

Because 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 4.2.1 gives the names and chemical formulae of some strong and weak acids and bases.

TABLE 4.2.1 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 (Figure 4.2.2a). 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 ionisation 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 ionises in water to produce hydrogen ions and ethanoate (acetate) ions. In a $1.0\,mol\,L^{-1}$ solution of ethanoic acid (CH_3COOH), only a small proportion of ethanoic acid molecules are ionised at any one time (Figure 4.2.2b). A $1.0\,mol\,L^{-1}$ solution of ethanoic acid contains a high proportion of CH_3COOH molecules and only some hydronium 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 ionisation of a weak acid is shown in an equation using reversible (double) arrows:

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

The double reaction arrow $\rightleftharpoons$ in the equation above indicates that reaction is reversible and the ethanoic acid partially ionises. All reactant and product species are present in solution and the reaction is in a state of equilibrium.

Therefore, ethanoic acid is described as a weak acid in water (Figure 4.2.2b).

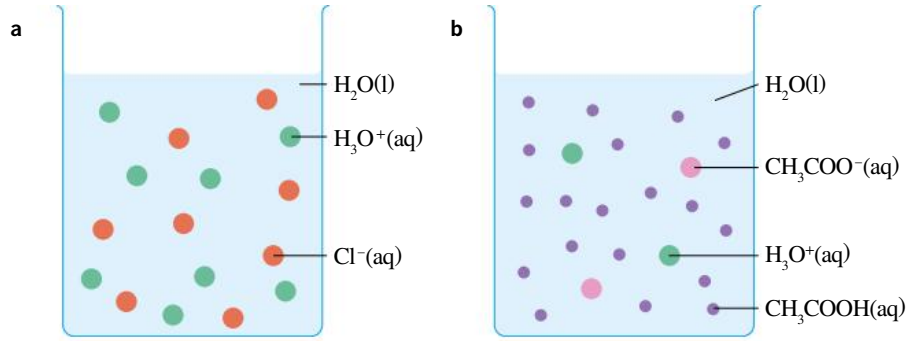

FIGURE 4.2.2 (a) In a $1.0\,mol\,L^{-1}$ solution of hydrochloric acid, the acid molecules are completely ionised in water. (b) However, in a $1.0\,mol\,L^{-1}$ solution of ethanoic acid, only a small proportion of the ethanoic acid molecules are ionised.

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Differences in conductivity

Acids of equal concentrations can have different abilities to conduct an electric current. When copper electrodes are immersed in a solution of $1.0\,mol\,L^{-1}$ hydrochloric acid and connected to an electric circuit containing a light globe, the globe glows brightly. When the hydrochloric acid is substituted with $1.0\,mol\,L^{-1}$ 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 that there are more ions present in a solution of hydrochloric acid than in ethanoic acid.

Strong bases

The ionic compound sodium oxide (Na_2O) dissociates 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^-):

$$\underset{\text{base}}{O^{2-}(aq)} + \underset{\text{acid}}{H_2O(l)} \rightarrow OH^-(aq) + OH^-(aq)$$

The oxide ion is an example of a **strong base**. Strong bases accept protons easily.

Sodium hydroxide (NaOH) is often referred to as a strong base. However, according to the Brønsted–Lowry definition of acids and bases, it is more correct to say that sodium hydroxide is an ionic compound that is a source of the strong base OH^-. That is, it is the OH^- that is acting as the base; the sodium ion is not involved in the acid–base reaction.

Weak bases

Ammonia is a covalent molecular compound that ionises in water by accepting a proton. This ionisation can be represented by the equation:

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

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 ionised 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 section 4.1 that conjugate acids and bases differ by one proton (H^+). The ionisation of HF can be 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 4.2.3.

Acid ionisation constants

The strength of an acid or a base can be described in terms of the position of equilibrium when the substance donates a hydrogen ion to, or accepts a hydrogen ion from, water. This type of reaction with water is called a hydrolysis reaction.

Ethanoic acid (CH_3COOH) is classified as a weak acid because the equilibrium constant for the hydrolysis reaction is small:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$

In this equation, ethanoic acid is behaving as a Brønsted–Lowry acid. K_a is the symbol given to the equilibrium constant for a hydrolysis reaction of an acid. This equilibrium constant is called the **acidity constant**. For the hydrolysis reaction of ethanoic acid, the acidity constant expression would be written as:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Note that the concentration of water does not appear in the denominator of the expression for K_a. This is because water is the solvent and its concentration is virtually constant.

> **i** Square brackets [ ] are often used to represent molar concentration.

An equilibrium mixture of ethanoic acid and water contains very few hydronium ions or ethanoate ions compared to the number of ethanoic acid molecules. For example, in a $0.1\,mol\,L^{-1}$ ethanoic acid solution, approximately 99% of the ethanoic acid molecules are un-ionised.

Ammonia is classified as a weak base because the equilibrium constant for its hydrolysis reaction is small:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

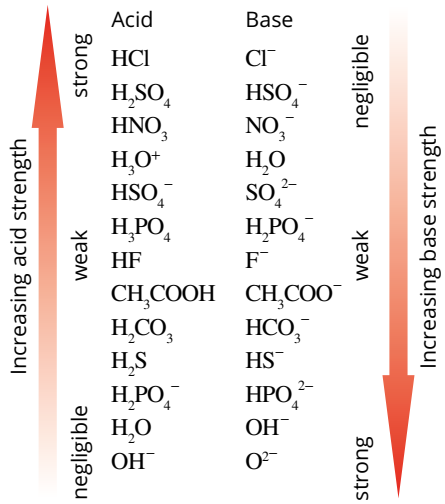

FIGURE 4.2.3 The relative strength of some conjugate acid–base pairs

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Super acids

Fluorosulfuric acid (HSO_3F) is one of the strongest acids known. It has a similar geometry as the sulfuric acid molecule (Figure 4.2.4). 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.

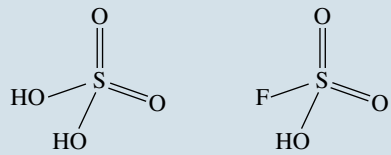

FIGURE 4.2.4 Structure of sulfuric acid (left) and fluorosulfuric acid (right) molecules

Fluorosulfuric acid is classified as a **super acid**. Super acids are acids that have acidity greater than the acidity of pure sulfuric acid.

Super acids, such as fluorosulfuric acid and triflic acid (CF_3SO_3H), are about 1000 times stronger than sulfuric acid. Carborane acid ($H(CHB_{11}Cl_{11})$) is a million times stronger than sulfuric acid. The strongest known super acid is fluoroantimonic acid (H_2FSbF_6), which is 10^{16} times stronger than 100% sulfuric acid.

Super acids are used in the production of plastics and high-octane petrol, in coal gasification and in research.

In this equation, ammonia is behaving as a Brønsted–Lowry base. K_b is the symbol given to the equilibrium constant for a hydrolysis reaction of a base. This equilibrium constant is called the basicity constant.

(It is only a coincidence that the values for K_a for ethanoic acid and K_b for ammonia are the same. These values indicate that the extent of hydrolysis in solution is approximately the same for both compounds.)

Table 4.2.2 lists the hydrolysis reactions for several weak acids and bases, together with the equilibrium constant values for these reactions.

TABLE 4.2.2 Some weak acids and bases and their aqueous solution equilibria. The size of the equilibrium constant indicates the extent of the reaction; strong acids and bases have larger equilibrium constants that weak acids and base

Weak acid or base	Hydrolysis equation	Equilibrium constant
Phosphoric acid	$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$	$K_a = 7.5 \times 10^{-3}$
Carbonic acid	$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$	$K_a = 4.3 \times 10^{-7}$
Ammonium ion	$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$	$K_a = 5.6 \times 10^{-10}$
Carbonate ion	$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$	$K_b = 1.8 \times 10^{-4}$
Ethanoate ion	$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$	$K_b = 5.6 \times 10^{-10}$

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, because it is partially ionised, it is a weak acid (Figure 4.2.5).

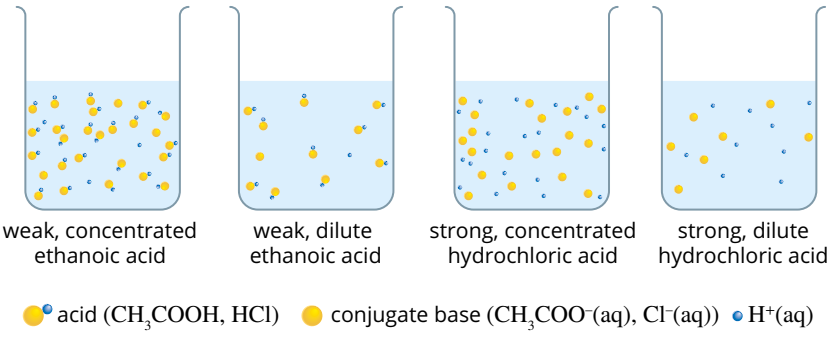

FIGURE 4.2.5 The concentration of ions in an acid solution depends on both the concentration and strength of the acid.

Terms such as 'weak acids', 'strong acids', 'dilute solutions' and 'concentrated solutions' are qualitative (or descriptive) terms. You can describe a solution accurately and quantitatively by stating concentrations in $mol\,L^{-1}$ or $g\,L^{-1}$.

4.2 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 is its conjugate base. The stronger a base, the weaker is its conjugate acid.
- The value of the equilibrium constant for the ionisation of an acid in aqueous solution (K_a) indicates the strength of the acid.

KEY QUESTIONS

1 Write 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.

2 Write balanced equations for the three ionisation stages of arsenic acid (H_3AsO_4).

3 Which one of the following equations represents the reaction of a strong acid with water?
- **A** $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$
- **B** $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
- **C** $LiOH(s) \rightarrow Li^+(aq) + OH^-(aq)$
- **D** $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

4 Perchloric acid is a stronger acid than ethanoic acid. Given 1.0 mol L^{-1} solutions, which acid would you expect to be a better conductor of electricity? Explain why.

5 Write expressions for the equilibrium constants (K_a) for the following weak acids.
- **a** hydrofluoric acid (HF)
- **b** hypochlorous acid (HClO)
- **c** hydrogen sulfide (H_2S)
- **d** ammonium ion (NH_4^+)

4.3 Acidity of solutions

In previous sections, you were introduced to the Brønsted–Lowry theory that defines an acid as a proton donor and a base as a proton acceptor. You also learnt that acids and bases can be classified as strong or weak, depending on how well they donate or accept protons.

In this section, you will learn about the pH scale, which is a measure of acidity. You will also learn about the relationship between the concentration of hydronium and hydroxide ions in different solutions.

IONIC PRODUCT OF WATER

Water molecules can react with each other to form the equilibrium 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 4.3.1.

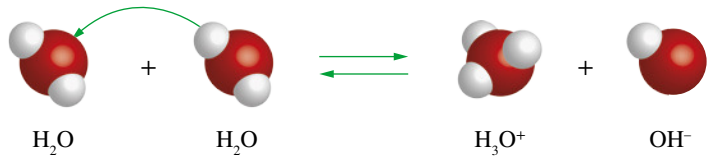

FIGURE 4.3.1 The ionisation of water molecules

Pure water undergoes this **self-ionisation** to a very small extent. In this reaction, water behaves as both a very weak acid and a very weak base, producing one hydronium ion (H_3O^+) for every one hydroxide ion (OH^-). Water is displaying amphiprotic properties.

The concentration of hydronium 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:

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 25°C$$

Acidic and basic solutions

In solutions of acidic substances, H_3O^+ ions are formed by reaction of the acid with water, as well as from self-ionisation of water. So the concentration of H_3O^+ ions will be greater than $10^{-7}\,mol\,L^{-1}$ at 25°C. Because 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 concentration of H_3O^+ in aqueous solutions

The expression for K_w can be used to determine the concentrations of hydronium and hydroxide ions in solution, because we know that the value of K_w in solutions at 25°C is 1.00×10^{-14}.

Worked example 4.3.1

CALCULATING CONCENTRATION OF HYDRONIUM AND HYDROXIDE IONS IN AN AQUEOUS SOLUTION

For a 0.10 mol L^{-1} HCl solution at 25°C, calculate $[H_3O^+]$ and $[OH^-]$.

Thinking	Working
Find the concentration of hydronium (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} 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.	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[OH^-] = \frac{1.00 \times 10^{-14}}{[H_3O^+]}$ 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}

Worked example 4.3.1: Try yourself

CALCULATING CONCENTRATION OF HYDRONIUM AND HYDROXIDE IONS IN AN AQUEOUS SOLUTION

For a 5.6×10^{-6} mol L^{-1} HNO_3 solution at 25°C, calculate $[H_3O^+]$ and $[OH^-]$.

pH: A CONVENIENT WAY TO MEASURE ACIDITY

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:

$$[H_3O^+] = 10^{-pH}$$

The pH scale eliminates the need to write cumbersome powers of 10 when you 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 4.3.2 A pH meter is used to measure the acidity of a solution.

Figure 4.3.2 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.
- Acidic solutions have a pH less than 7.
- Basic solutions have a pH greater than 7.

On the pH scale, the most acidic solutions have pH values slightly less than 0 and the most basic solutions have values of about 14. The pH values of some common substances are provided in Table 4.3.1.

TABLE 4.3.1 pH values of some common substances at 25°C

Solution	pH	$[H_3O^+]$ (mol L^{-1})	$[OH^-]$ (mol L^{-1})	$[H_3O^+] \times [OH^-]$
1.0 mol L^{-1} HCl	0.0	1.00	1.00×10^{-14}	1.00×10^{-14}
Lemon juice	3.0	1.00×10^{-3}	1.00×10^{-11}	1.00×10^{-14}
Vinegar	4.0	1.00×10^{-4}	1.00×10^{-10}	1.00×10^{-14}
Tomatoes	5.0	1.00×10^{-5}	1.00×10^{-9}	1.00×10^{-14}
Rain water	6.0	1.00×10^{-6}	1.00×10^{-8}	1.00×10^{-14}
Pure water	7.0	1.00×10^{-7}	1.00×10^{-7}	1.00×10^{-14}
Seawater	8.0	1.00×10^{-8}	1.00×10^{-6}	1.00×10^{-14}
Soap	9.0	1.00×10^{-9}	1.00×10^{-5}	1.00×10^{-14}
Oven cleaner	13.0	1.00×10^{-13}	1.00×10^{-1}	1.00×10^{-14}
1.0 mol L^{-1} NaOH	14.0	1.00×10^{-14}	1.00	1.00×10^{-14}

The acidities of solutions 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.

A solution with pH 2 has 10 times the concentration of hydronium ions as one of pH 3. The solution of pH 2 also has one-tenth the concentration of hydroxide ions as the one of pH 3.

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pH of toothpaste

The pH in your mouth varies, but a healthy pH is above 7. When you eat food containing sugar, it gets consumed by bacteria, which produce acids that lower the pH and cause tooth decay. The following reaction shows what happens when tooth enamel reacts with acid:

$$Ca_5(PO_4)_3OH(s) + H_3O^+(aq) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + 2H_2O(l)$$

Saliva is naturally alkaline and neutralises some acid, but excess acid remains unaffected and lowers the pH below 7. Tooth demineralisation can begin at a pH of 6.5 in the root and 5.5 at the enamel.

The average pH of regular toothpastes is 8, which neutralises any acids remaining at the time of use. The active ingredients in regular toothpaste are abrasives such as silica, and fluoride, which is basic and raises the pH in the mouth.

In contrast, whitening toothpastes (Figure 4.3.3) usually contain peroxide bleaching agents in the form of hydrogen peroxide or carbamide peroxide. These compounds are acidic and lower the pH in the mouth. The average pH of whitening products is around 6.8 (slightly acidic) but can be as low as 3.7 (highly acidic), depending on the peroxide concentration in the toothpaste.

FIGURE 4.3.3 Whitening toothpaste contains peroxide.

Scanning electron microscope studies have shown that a concentration as low as 10% peroxide in the toothpaste causes surface dissolution of tooth enamel, exposing a porous surface beneath to further decay. Concentrations of up to 35% are found in some whitening toothpastes.

Indicators

One of the characteristic properties of acids and bases is their ability to change the colour of certain plant extracts. These extracts are called indicators. **Indicators** are used to estimate the pH range of a solution. You will learn more about indicators in Chapter 6.

Calculations involving pH

pH can be calculated from the formula $pH = -\log_{10}[H_3O^+]$. Your scientific calculator has a logarithm function that will simplify pH calculations.

Worked example 4.3.2

CALCULATING pH OF AN AQUEOUS SOLUTION FROM $[H_3O^+]$

What is the pH of a solution in which $[H_3O^+]$ is $0.14\,mol\,L^{-1}$? Express your answer to two decimal places.

Thinking	Working
Write down $[H_3O^+]$ 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.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(0.14)$ (use your calculator) $= 0.85$

Worked example 4.3.2: Try yourself

CALCULATING pH OF AN AQUEOUS SOLUTION FROM $[H_3O^+]$

What is the pH of a solution in which $[H_3O^+]$ is $6.0 \times 10^{-9}\,mol\,L^{-1}$? Express your answer to two significant figures.

Worked example 4.3.3

CALCULATING pH IN A SOLUTION OF A BASE

What is the pH of a $0.005\,mol\,L^{-1}$ solution of $Ba(OH)_2$ at 25°C?

Thinking	Working
Write down 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 $[OH^-]$	$[OH^-] = 2 \times [Ba(OH)_2]$ $= 2 \times 0.005\,mol\,L^{-1}$ $= 0.01\,mol\,L^{-1}$
Determine $[H_3O^+]$ in the diluted solution by substituting $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.00 \times 10^{-14}}{0.01}$ $= 1 \times 10^{-12}\,mol\,L^{-1}$
Substitute the value of $[H_3O^+]$ into: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine the answer.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(1 \times 10^{-12})$ (use your calculator) $= 12.0$

Worked example 4.3.3: Try yourself

CALCULATING pH IN A SOLUTION OF A BASE

What is the pH of a 0.01 mol L^{-1} solution of $Ba(OH)_2$ at 25°C?

Worked example 4.3.4

CALCULATING pH IN A SOLUTION WHEN SOLUTE CONCENTRATION IS NOT GIVEN

What is the pH of a solution at 25°C that contains 1.0 g NaOH in 100 mL of solution?

Thinking	Working
Determine the number of moles of NaOH.	$n(\text{NaOH}) = \frac{m}{M}$ $n(\text{NaOH}) = \frac{1.0}{40.0}$ $= 0.025$ mol
Write the equation for dissociation of NaOH.	$\text{NaOH(aq)} \rightarrow \text{Na}^+\text{(aq)} + \text{OH}^-\text{(aq)}$ NaOH is completely dissociated in water.
Determine the number of moles of OH^- based on the dissociation equation.	$n(\text{OH}^-) = n(\text{NaOH})$ $= 0.025$ mol
Use the formula for determining concentration given number of moles and volume: $c = \frac{n}{V}$	$n = 0.025$ mol $V = 0.100$ L $c = \frac{n}{V} = \frac{0.025}{0.100} = 0.25$ mol L^{-1}
Determine $[H_3O^+]$ in the diluted solution by substituting $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.00 \times 10^{-14}}{0.25}$ $= 4.0 \times 10^{-14}$ 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.	$\text{pH} = -\log_{10}[H_3O^+]$ $= -\log_{10}(4.0 \times 10^{-14})$ (use your calculator) $= 13.4$

Worked example 4.3.4: Try yourself

CALCULATING pH IN A SOLUTION WHEN SOLUTE CONCENTRATION IS NOT GIVEN

What is the pH of a solution at 25°C that contains 0.50 g KOH in 500 mL of solution?

Worked example 4.3.5

CALCULATING $[H_3O^+]$ IN A SOLUTION OF A GIVEN pH

Calculate $[H_3O^+]$ in a solution of pH 5.0 at 25°C.	
Thinking	**Working**
Decide which form of the relationship between pH and $[H_3O^+]$ should be used: $pH = -\log_{10}[H_3O^+]$ or $[H_3O^+] = 10^{-pH}$	As you have the pH and are calculating $[H_3O^+]$, use: $[H_3O^+] = 10^{-pH}$
Substitute the value of pH into the relationship expression and use a calculator to determine the answer.	$[H_3O^+] = 10^{-pH}$ $= 10^{-5.0}$ $= 1.0 \times 10^{-5}\,mol\,L^{-1}$ (or $0.000010\,mol\,L^{-1}$)

Worked example 4.3.5: Try yourself

CALCULATING $[H_3O^+]$ IN A SOLUTION OF A GIVEN pH

Calculate $[H_3O^+]$ in a solution of pH 10.4 at 25°C.

Worked example 4.3.6

CALCULATING pH OF A SOLUTION AFTER PARTIAL NEUTRALISATION

50.0 mL of $0.200\,mol\,L^{-1}$ NaOH is added to 100.0 mL of $0.150\,mol\,L^{-1}$ HCl. Calculate the pH of the final solution.	
Thinking	**Working**
Identify the type of reaction and write an equation for the reaction.	acid + base → salt + water $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
Identify the values for the concentrations and volumes of the reactants.	HCl $c = 0.150\,mol\,L^{-1}$ $V = 100.0\,mL$ NaOH $c = 0.200\,mol\,L^{-1}$ $V = 50.0\,mL$
Calculate the number of moles of H^+ and OH^-.	H^+ $n = c \times V$ $= 0.150 \times 0.100$ $= 0.0150$ mol OH^- $n = c \times V$ $= 0.200 \times 0.050$ $= 0.0100$ mol
Identify the relationship between the number of moles of H^+ and OH^-. (This will always be 1:1.)	1 mol of H^+ reacts with 1 mol of OH^-
Identify which of H^+ and OH^- is in excess.	HCl is in excess.
Calculate the number of moles of reactant in excess.	Number of moles of H^+ in excess $= 0.015 - 0.010\,mol$ $= 0.0050\,mol$
Calculate the concentration of the excess H^+ (H_3O^+). The volume of the final solution will equal the sum of the volumes of the solutions mixed together.	$c = \frac{n}{V}$ $= \frac{0.0050}{0.150}$ $= 0.333$ $[H_3O^+] = 0.033\,mol\,L^{-1}$
Calculate pH using: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine pH.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10} 0.033$ $= 1.48$

Worked example 4.3.6: Try yourself

CALCULATING THE pH OF A SOLUTION AFTER PARTIAL NEUTRALISATION

43.0 mL of 0.200 mol L^{-1} nitric acid is added to 15.0 mL of 0.300 mol L^{-1} barium hydroxide (at 25°C). Calculate the pH of the final solution.

Effect of temperature on pH

Earlier, the ionisation constant of water was defined as:

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 25°C$$

You can use this relationship to calculate either $[H_3O^+]$ or $[OH^-]$ at 25°C in different solutions.

If the temperature is not 25°C, then the value of K_w will be different. Experiments have shown that the value of K_w increases as the temperature increases, as shown in Table 4.3.2. This is because the self-ionisation of water is an endothermic equilibrium reaction:

$$\Delta H + H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad \Delta H = +56 \text{ kJ mol}^{-1}$$

The pH of pure water is only 7.00 at 25°C. At other temperatures, even though the pH is not equal to 7.00, pure water can still be described as neutral because the concentrations of H_3O^+ and OH^- ions are equal.

TABLE 4.3.2 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

4.3 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:
  $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ at 25°C
- The concentration of $[H_3O^+]$ can be 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.

KEY QUESTIONS

1 Calculate $[OH^-]$ at 25°C in an aqueous solution with $[H_3O^+] = 0.001\ mol\ L^{-1}$.

2 What is $[OH^-]$ in a solution at 25°C with $[H_3O^+] = 5.70 \times 10^{-19}\ mol\ L^{-1}$?

3 Calculate $[H_3O^+]$ at 25°C in an aqueous solution in which $[OH^-] = 1.0 \times 10^{-5}\ mol\ L^{-1}$.

4 What is the pH of a solution in which $[H_3O^+] = 0.01\ mol\ L^{-1}$?

5 Calculate the pH of a $0.001\ mol\ L^{-1}$ solution of nitric acid (HNO_3).

6 The pH of water in a lake is 6.0. Calculate $[H_3O^+]$ in the lake.

7 Determine the pH of a 200.0 mL solution that contains 0.365 g of dissolved HCl.

8 Determine the pH of the final solution when 100.0 mL of a solution HCl with a pH of 2 is mixed with 200.0 mL of a solution NaOH with a pH of 11.

4.4 Dilution of acids and bases

Although acids are frequently purchased as concentrated solutions, they often need to be diluted. For example, a bricklayer uses a 10% solution of hydrochloric acid to remove mortar splashes from bricks used to build a house. The brick-cleaning solution is prepared by diluting concentrated hydrochloric acid by a factor of ten.

In this section, you will learn how to calculate the concentration and pH of acids and bases once they have been diluted.

CONCENTRATION OF ACIDS AND BASES

The concentration of acids and bases is usually expressed in units of mol L^{-1}. This is also referred to as **molar concentration**.

The molar concentration of a solution, in mol L^{-1}, is given by the expression:

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

where c is the molar concentration (mol L^{-1}), n is the amount of solute (mol) and V is the volume of the solution (L).

The most convenient way of preparing a solution of a dilute acid is by mixing concentrated acid with water, as shown in Figure 4.4.1. This is known as a **dilution**.

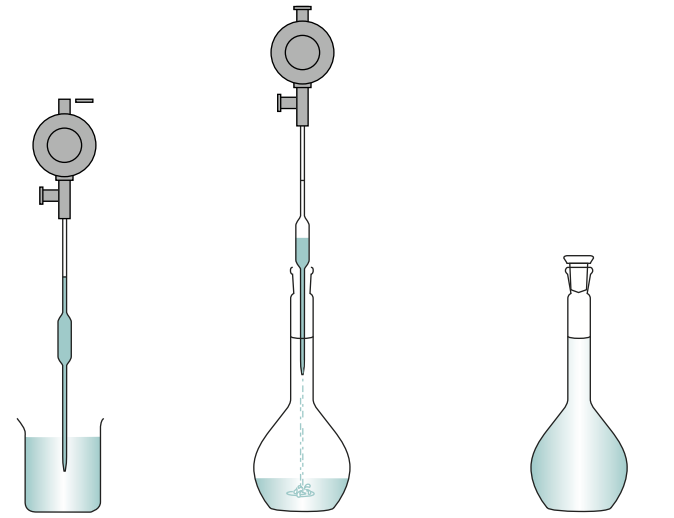

FIGURE 4.4.1 Preparing a 1.00 mol L^{-1} HCl solution by diluting a 10.0 mol L^{-1} solution. Heat is released when a concentrated acid is added to water, so the volumetric flask is partly filled with water before the acid is added. (Extra safety precautions would be required for diluting concentrated sulfuric acid.)

The amount of solute (in moles) in a solution does not change when a solution is diluted. As the number of moles is given by the following relationship:

$$n = cV$$

if we change the volume, the number of moles will stay the same, or mathematically:

$$c_1V_1 = n \text{ and } c_2V_2 = n$$

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. (So as the volume of the solution increases, the concentration decreases.)

This can be simplified to give the relationship:

$$c_1V_1 = c_2V_2$$

which can be rearranged to:

$$c_2 = \frac{c_1 V_1}{V_2}$$

to calculate the new concentration of the diluted solution.

To calculate the concentration of a dilute acid, you need to know the:

- volume of the concentrated solution (V_1)
- concentration (molarity) of the concentrated solution (c_1)
- total volume of water added (V_2 = initial volume + volume of water added).

The molar concentrations of some concentrated acids are shown in Table 4.4.1.

TABLE 4.4.1 Molar concentrations of some concentrated acids

Concentrated acid (% by mass)	Formula	Concentration (mol L^{-1})
Ethanoic acid (99.5%)	CH_3COOH	17
Hydrochloric acid (36%)	HCl	12
Nitric acid (70%)	HNO_3	16
Phosphoric acid (85%)	H_3PO_4	15
Sulfuric acid (98%)	H_2SO_4	18

In the laboratory, you can prepare solutions of a base of a required concentration by:

- diluting a more concentrated solution
- dissolving a weighed amount of the base in a measured volume of water, as shown in Figure 4.4.2.

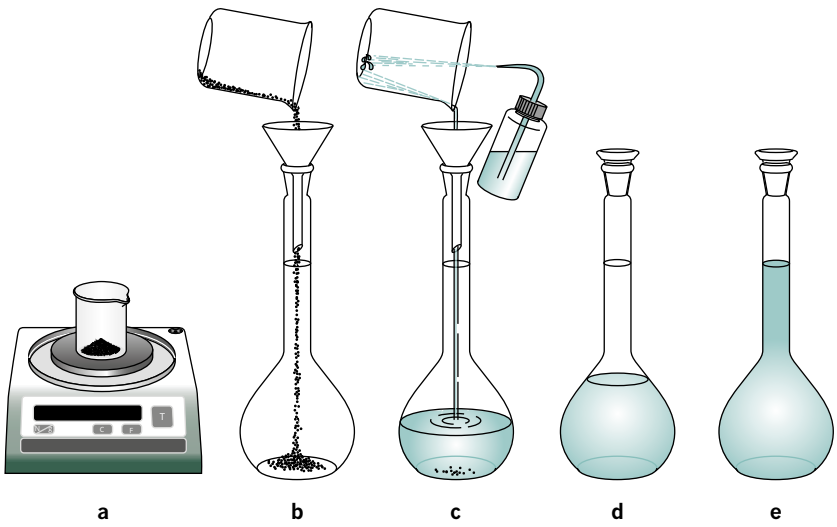

FIGURE 4.4.2 Preparing a solution by dissolving a weighed amount of base in a measured volume of water.
(a) Accurately weigh out a mass of the base.
(b) Transfer the base to a volumetric flask.
(c) Ensure complete transfer of the base by washing with water.
(d) Dissolve the base in water.
(e) Add water to make the solution up to the calibration mark and shake thoroughly.

Worked example 4.4.1

CALCULATING MOLAR CONCENTRATION AFTER DILUTION

Calculate the molar concentration of hydrochloric acid when 10.0 mL of water is added to 5.0 mL of 1.2 mol L^{-1} HCl.

Thinking	Working
The number of moles of solute does not change during a dilution. So, $c_1V_1 = c_2V_2$, where c is the concentration in mol L^{-1} and V is the volume of the solution. (Each of the volume units must be the same, litres or millilitres.)	$c_1V_1 = c_2V_2$
Identify given values for concentrations and volumes before and after dilution. Identify the unknown.	10.0 mL was added to 5.0 mL, the final volume is 15.0 mL. $c_1 = 1.2\ \text{mol L}^{-1}$ $V_1 = 5.0\ \text{mL}$ $V_2 = 15.0\ \text{mL}$ You are required to calculate c_2, the concentration after dilution.
Transpose the equation and substitute the known values into the equation to find the required value.	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= 1.2 \times \frac{5.0}{15.0}$ $= 0.40\ \text{mol L}^{-1}$

Worked example 4.4.1: Try yourself

CALCULATING MOLAR CONCENTRATION AFTER DILUTION

Calculate the molar concentration of nitric acid when 80.0 mL of water is added to 20.0 mL of 5.00 mol L^{-1} HNO_3.

Worked example 4.4.2

CALCULATING THE VOLUME OF WATER TO BE ADDED IN A DILUTION

How much water must be added to 30.0 mL of 2.50 mol L^{-1} HCl to dilute the solution to 1.00 mol L^{-1}?

Thinking	Working
The number of moles of solute does not change during a dilution. So, $c_1V_1 = c_2V_2$, where c is the concentration in mol L^{-1} and V is the volume of the solution. (Each of the volume units must be the same, although not necessarily litres.)	$c_1V_1 = c_2V_2$
Identify given values for concentrations and volumes before and after dilution. Identify the unknown.	$c_1 = 2.50\ \text{mol L}^{-1}$ $V_1 = 30.0\ \text{mL}$ $c_2 = 1.00\ \text{mol L}^{-1}$ You are required to calculate V_2, the volume of the diluted solution.

Transpose the equation and substitute the known values into the equation to find the required value.	$V_2 = \frac{c_1 \times V_1}{c_2}$ $= \frac{2.50 \times 30.0}{1.00}$ $= 75.0\,\text{mL}$
Calculate the volume of water to be added.	Volume of dilute solution = 75.0 mL Initial volume of acid = 30.0 mL So 75.0 – 30.0 = 45.0 mL of water must be added.

Worked example 4.4.2: Try yourself

CALCULATING THE VOLUME OF WATER TO BE ADDED IN A DILUTION

How much water must be added to 15.0 mL of 10.0 mol L^{-1} NaOH to dilute the solution to 2.00 mol L^{-1}?

EFFECT ON pH OF DILUTION OF STRONG ACIDS AND BASES

Calculation of pH of an acid after dilution

Consider a 0.10 mol L^{-1} solution of hydrochloric acid. HCl is a strong acid, so the concentration of H_3O^+ ions in this solution is 0.10 mol L^{-1}. Since $pH = -\log_{10}[H_3O^+]$, the pH of this solution is 1.0.

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 pH to 3.0. However, when acids are repeatedly diluted, the pH cannot increase above 7.

Similarly, the progressive dilution of a 0.10 mL NaOH solution will cause the pH to decrease until it reaches very close to 7.

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 4.4.3

CALCULATING pH OF A DILUTED ACID

5.0 mL of 0.010 mol L^{-1} HNO_3 is diluted to 100.0 mL. What is the pH of the diluted solution?	
Thinking	**Working**
Identify given values for concentrations and volumes before and after dilution.	$c_1 = 0.010\,\text{mol L}^{-1}$ $V_1 = 5.0\,\text{mL}$ $V_2 = 100.0\,\text{mL}$ $c_2 = ?$
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: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine pH.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(0.00050)$ $= 3.30$

Worked example 4.4.3: Try yourself

CALCULATING pH OF A DILUTED ACID

10.0 mL of 0.10 mol L^{-1} HCl is diluted to 30.0 mL. Calculate the pH of the diluted solution.

CHEMFILE

Transporting sulfuric acid

Transportation of sulfuric acid can be very dangerous because the acid is extremely corrosive. Rather than transport it as diluted acid, which would seem safer, it is transported in the concentrated form and diluted at its destination. Concentrated sulfuric acid is 98% pure acid and is almost completely molecular (Figure 4.4.3). It is not ionised and so does not react with iron or steel in the way that it would in the dilute (aqueous) form.

$$2H^+(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + H_2(g)$$

Therefore, sulfuric acid can be stored in steel containers and transported in tankers. It is preferable to transport the acid in the concentrated form in this way because steel is stronger than glass or plastic and therefore safer. This also means that, when storing or transporting the acid, care must be taken to avoid contamination with water. The concentrated acid is then diluted at its destination.

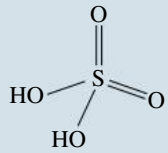

FIGURE 4.4.3 The structure of molecular H_2SO_4

When diluting a concentrated solution of sulfuric acid, the acid is always added to water, not the water to the acid. When molecular sulfuric acid reacts with water, it hydrolyses in two stages. The first hydrolysis reaction is in equilibrium, but the value of *K* is very high, so that protonation of water is strongly favoured. The hydrolysis reaction is also highly exothermic. These two factors mean that large quantities of heat are produced during the dilution process:

$$H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$$
$$HSO_4^-(aq) + H_2O(aq) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$$

If you add water to the acid, you form an extremely concentrated solution of hydrolysed acid initially and enough heat can be released that the solution may boil violently. Addition of a small quantity of the concentrated acid to water ensures the acid is the limiting reagent and the small quantity of heat released is dissipated through the solution.

This is a good general rule to apply to any dilution procedure.

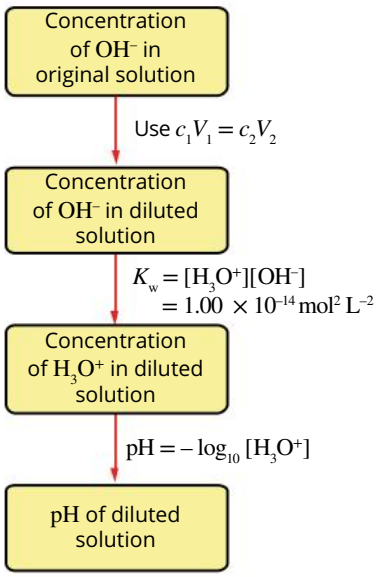

FIGURE 4.4.4 Calculating the pH of a diluted solution of a base

Calculation of pH of a base after dilution

The following steps and flow chart shown in Figure 4.4.4 show the sequence used to calculate the pH of a base after it has been diluted. Remember that pH is a measure of the hydronium ion concentration.

1 Calculate $[OH^-]$ in the diluted solution.
2 Calculate $[H_3O^+]$, using the expression for the ionic product of water:
$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$
3 Calculate the pH of the solution, using $pH = -\log_{10}[H_3O^+]$ (Figure 4.4.4).

Worked example 4.4.4

CALCULATING pH OF A DILUTED BASE

10.0 mL of 0.10 mol L^{-1} NaOH is diluted to 100.0 mL. Calculate the pH of the diluted solution.

Thinking	Working
Identify given values for concentrations and volumes before and after dilution.	$c_1 = 0.10\,\text{mol L}^{-1}$ $V_1 = 10.0\,\text{mL}$ $V_2 = 100.0\,\text{mL}$ $c_2 = ?$
Calculate c_2, which is $[OH^-]$ after dilution, by transposing the formula: $c_1V_1 = c_2V_2$	$c_2 = \frac{c_1 \times V_1}{V_2}$ $= \frac{0.10 \times 10.0}{100.0}$ $= 0.01\,\text{mol L}^{-1}$
Determine $[H_3O^+]$ in the diluted solution by substituting $[OH^-]$ into the ionic product of water: $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$	$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$ $[H_3O^+] = \frac{K_w}{[OH^-]}$ $= \frac{1.00 \times 10^{-14}}{0.01}$ $= 1 \times 10^{-12}\,\text{mol L}^{-1}$
Calculate pH using: $pH = -\log_{10}[H_3O^+]$ Use the logarithm function on your calculator to determine pH.	$pH = -\log_{10}[H_3O^+]$ $= -\log_{10}(1 \times 10^{-12})$ $= 12.0$

Worked example 4.4.4: Try yourself

CALCULATING pH OF A DILUTED BASE

15.0 mL of 0.02 mol L^{-1} KOH is diluted to 60.0 mL. Calculate the pH of the diluted solution.

4.4 Review

SUMMARY

- Amounts of acid or base in solution do not change during a dilution. The volume of the solution increases and 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 volume and concentration, and c_2 and V_2 are the final volume and concentration 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 hydronium 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 hydronium ions in the diluted base.

KEY QUESTIONS

1 1.0 L of water is added to 3.0 L of 0.10 mol L^{-1} HCl. What is the concentration of the diluted acid?

2 Calculate the volume of water that must be added to 10 mL of a 2.0 mol L^{-1} sulfuric acid solution to dilute it to 0.50 mol L^{-1}.

3 What volume of water must be added to dilute 20.0 mL of 0.600 mol L^{-1} HCl to 0.100 mol L^{-1}?

4 Describe the effect on the pH of a strong monoprotic acid solution of pH 0.1 when it is diluted by a factor of 10.

5 Calculate the pH of the solution at 25°C that is formed by the dilution of a 20.0 mL solution of 0.100 mol L^{-1} NaOH to 50.0 mL.

6 For each of the solutions **a–e** (all at 25°C), calculate the:

i concentration of H_3O^+ ions
ii concentration of OH^- ions
iii pH.

a 0.001 mol L^{-1} HNO_3(aq)
b 0.03 mol L^{-1} HCl(aq)
c 0.010 mol L^{-1} NaOH(aq)
d $1.0 \times 10^{-4.5}$ mol L^{-1} HCl(aq)
e 0.005 mol L^{-1} $Ba(OH)_2$(aq)

4.5 pH of salt solutions

In section 4.2, you were introduced to the concept that some ions act as Brønsted–Lowry acids and bases in hydrolysis reactions. For example, the ammonium ion can donate a proton to water and act as a Brønsted–Lowry acid:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

The ethanoate ion can accept a proton from water and act as a Brønsted–Lowry base:

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

In this section, you will learn how to predict the acidity of the salt solutions that are formed during neutralisation reactions.

SALTS

A **salt** is an ionic compound that contains a positive ion (a **cation**) other than a hydrogen ion (H^+) or a negative ion (an **anion**) other than the oxide ion (O^{2-}) or the hydroxide ion (OH^-). Sodium fluoride, calcium carbonate, iron(III) sulfate and ammonium nitrate are examples of salts.

Salts are formed in neutralisation reactions by the combination of an acid with a base. A salt formed in this type of reaction can be thought of as a compound whose positive ions are derived from the base and negative ions from the acid.

For the salt potassium chloride, the potassium ions may have come from the base potassium hydroxide and the chloride ions from hydrochloric acid:

$$KOH(aq) + HCl(aq) \rightarrow KCl(aq) + H_2O(l)$$

Ammonium carbonate ($(NH_4)_2CO_3$) is the salt produced when carbonic acid (H_2CO_3) reacts with ammonia, a base:

$$H_2CO_3(aq) + 2NH_3(aq) \rightarrow (NH_4)_2CO_3(aq)$$

A dissociation reaction takes place when a salt dissolves in water. The cations or anions produced may then react with water to produce either H_3O^+ ions or OH^- ions. This reaction of an ion with water is an example of a hydrolysis reaction. For example, the salt ammonium ethanoate dissociates in aqueous solution and reacts with water in the following way:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$
$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

Sodium carbonate dissociates in water according to the following equation:

$$Na_2CO_3(s) \rightarrow 2Na^+(aq) + CO_3^{2-}(aq)$$

In a solution of sodium carbonate, the carbonate ion undergoes hydrolysis to produce the hydrogencarbonate ion and a hydroxide ion:

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

In this reaction the carbonate ion acts as a Brønsted–Lowry base, accepting a hydrogen ion from water to form the hydrogencarbonate ion as the conjugate acid. The formation of hydroxide ions in the reaction explains why a solution of sodium carbonate is basic. (The Na^+ ions in the solution do not undergo hydrolysis.)

SALT SOLUTIONS FROM NEUTRALISATION REACTIONS

Salts are formed by a reaction between an acid and a base. For example, sodium chloride is formed by the reaction between hydrochloric acid and sodium hydroxide:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

A solution of NaCl is neutral, i.e. its pH is 7. However, some salts, such as ammonium chloride, form acidic solutions when dissolved in water. Other salts, such as sodium ethanoate, produce basic solutions. The pH of the solution produced during a neutralisation reaction depends on the strength of the acid and base being reacted.

Salts of a strong acid and a strong base

Sodium nitrate is the salt of the strong acid, HNO_3, and the strong base, NaOH:

$$HNO_3(aq) + NaOH(aq) \rightarrow NaNO_3(aq) + H_2O(l)$$

Sodium ions do not hydrolyse in water. Nitrate ions, the conjugate base of the strong acid, HNO_3, are very weak bases and do not react with water. Sodium nitrate solution therefore has a pH of 7.

A salt produced in the reaction between a strong acid and a strong base is a **neutral salt**.

The anion and cation of a neutral salt do not react with water by accepting or donating a proton.

Salts of a strong acid and a weak base

Solutions of salts of a strong acid and a weak base are acidic because the conjugate acid of the weak base hydrolyses to form hydronium ions.

Ammonium chloride (NH_4Cl) is the salt of a strong acid (HCl) and a weak base (NH_3):

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

An acidic solution is formed when ammonium chloride is dissolved in water. The ammonium ion (NH_4^+), which is the conjugate acid of the weak base ammonia (NH_3) undergoes a hydrolysis reaction:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

The NH_4^+ ion acts as a Brønsted–Lowry acid and donates a proton to water to form the hydronium ion. The ammonium ion is a weak acid and the ionisation reaction with water does not go to completion. The Cl^- ion shows no acid–base properties because it does not hydrolyse in water.

A salt produced in the reaction between a strong acid and a weak base is an **acidic salt**.

The anion or cation of an acidic salt reacts with water by donating a proton.

Salts of a weak acid and a strong base

Solutions of salts of a weak acid and a strong base are basic because the anions hydrolyse to form hydroxide ions. Sodium ethanoate (CH_3COONa) is the salt of the weak acid ethanoic acid (CH_3COOH) and the strong base sodium hydroxide (NaOH):

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

Sodium ethanoate dissociates in water to form Na^+ ions and CH_3COO^- ions. The Na^+ ions do not hydrolyse and show no acid–base properties. The CH_3COO^- ion is a Brønsted–Lowry base and accepts a proton from a water molecule to produce a hydroxide ion:

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

Consequently the solution is basic.

A salt produced in the reaction between a weak acid and a strong base is a **basic salt**.

The anion or cation of a basic salt reacts with water by accepting a proton.

Salts of a weak acid and a weak base

A solution of a salt formed from the reaction of a weak acid and a weak base involves two competing hydrolysis reactions.

- The conjugate base of the weak acid reacts with water to form hydroxide ions.
- The conjugate acid of the weak base reacts with water to form hydronium ions.

The pH of a solution of a salt of a weak acid and a weak base will depend upon the extent to which each of these competing reactions occurs.

For example, ammonium hypochlorite (NH_4ClO) is a salt of the weak base ammonia (NH_3) and the weak acid hypochlorous acid (HClO):

$$NH_3(aq) + HClO(aq) \rightleftharpoons NH_4^+(aq) + ClO^-(aq)$$

Two hydrolysis reactions take place when ammonium hypochlorite is dissolved in water:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \qquad K_a = 5.6 \times 10^{-10}$$
$$ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq) \qquad K_b = 3.3 \times 10^{-8}$$

An indication of the extent to which each of these reactions occurs is provided by the value of the equilibrium constants, K, for these reactions. The hydrolysis of ClO^- occurs to a greater extent than the hydrolysis of NH_4^+. Therefore, a solution of NH_4ClO is basic because more OH^- ions are produced than H_3O^+ ions.

Therefore, the acidity of salts produced by the reaction of a weak acid and weak base depends on the degree of hydrolysis of the anion and cation in the salt produced.

The acid–base properties of the salts formed by reactions of acids and bases is summarised in Table 4.5.1.

TABLE 4.5.1 Acid–base properties of salts derived from neutralisation reactions

	Strong acid	Weak acid
Strong base	Neutral salts	Basic salts
Weak base	Acidic salts	Depends on extent of hydrolysis of each ion

As can be seen from the information above, it is the ions in the salt that enable the pH of the solution of the salt to be predicted. The acid–base properties of some common ions are summarised in Table 4.5.2.

TABLE 4.5.2 Acid–base properties of common ions

Neutral (derived from strong acids/bases)	Acidic (derived from weak bases)	Basic (derived from weak acids)
Cl^- Br^- NO_3^-	NH_4^+ HSO_4^- $H_2PO_4^-$	CO_3^{2-} HCO_3^- SO_4^{2-} HPO_4^{2-} PO_4^{3-} F^-

CHEMFILE

Urinary alkalinisers

Urinary alkalinisers form part of a range of treatments for urinary tract infections and kidney stones. Urinary alkalinisers are salts that form solutions of weak bases when dissolved in water. Taken orally, they are rapidly absorbed into the bloodstream, raising the pH of the blood. They also raise the pH of urine, providing relief for the sufferer. The active ingredients are usually potassium hydrogencarbonate ($KHCO_3$) and potassium citrate ($K_3C_6H_5O_7$)

The anions of these salts act as Brønsted–Lowry bases, accepting protons from water, and producing a basic (alkaline) solution:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$
$$C_6H_5O_7^{3-}(aq) + 3H_2O(l) \rightleftharpoons C_6H_8O_7(aq) + 3OH^-(aq)$$

Worked example 4.5.1

DETERMINING THE ACIDITY OF A SALT PRODUCED IN A NEUTRALISATION REACTION

Determine the acidity of the salt produced by the reaction of sodium hydroxide and phosphoric acid.	
Thinking	**Working**
Write the equation for the neutralisation reaction.	$3NaOH(aq) + H_3PO_4(aq) \rightarrow Na_3PO_4(aq) + 3H_2O(l)$
Identify the anion and cation in the salt.	Na^+ and PO_4^{3-}
Determine whether the ions will react with water in a hydrolysis reaction. (Are the ions neutral, acidic or basic?)	Na^+ cannot accept a proton from water (Na^+ is a neutral ion) $PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq)$ (PO_4^{3-} is a basic ion)
If an ion accepts a proton from water, it is basic. If an ion donates a proton to water, it is acidic.	The salt is basic.

Worked example: Try yourself 4.5.1

DETERMINING THE ACIDITY OF A SALT PRODUCED IN A NEUTRALISATION REACTION

Determine the acidity of the salt produced by the reaction of calcium hydroxide ($Ca(OH)_2$) and oxalic acid ($H_2C_2O_4$).

Hydrolysis of salts of polyprotic acids

Aqueous solutions of the salts of polyprotic acids can be neutral, acidic or basic.

Sodium carbonate (Na_2CO_3) and sodium hydrogencarbonate ($NaHCO_3$) are both salts of carbonic acid (H_2CO_3). Solutions of sodium hydrogencarbonate and sodium carbonate are basic. The carbonate ion undergoes hydrolysis that produces a basic solution. Figure 4.5.1 shows the reaction of the carbonate ion with water:

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

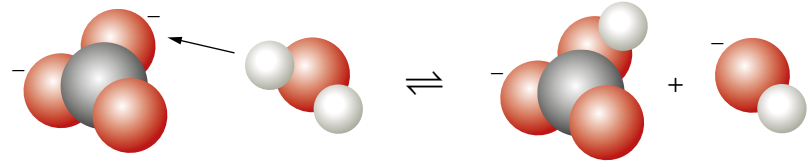

FIGURE 4.5.1 The reaction of the carbonate ion with water

The hydrogencarbonate ion is amphiprotic and undergoes hydrolysis reactions that produce OH^- and H_3O^+:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

The first reaction occurs to a greater extent than the second reaction, so the sodium hydrogencarbonate solution is basic.

Sodium hydrogensulfate ($NaHSO_4$) is a salt of sulfuric acid and forms an acidic solution in water because the following reaction dominates:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$$

Sodium phosphate (Na_3PO_4) sodium hydrogenphosphate (Na_2HPO_4) and sodium dihydrogenphosphate (NaH_2PO_4) are all salts of phosphoric acid.

Sodium dihydrogenphosphate dissolves in water forming an acidic solution:

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

Solutions of sodium dihydrogenphosphate and sodium phosphate in water are basic:

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$$
$$PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq)$$

CHEMISTRY IN ACTION

Tartaric acid

Tartaric acid is a diprotic acid that occurs naturally in many plants, but is most commonly associated with grapes. Tartaric acid and its partially neutralised salt, potassium hydrogentartrate, are responsible for the sour taste in wine. Figure 4.5.2 shows the structures of tartaric acid and potassium hydrogentartrate.

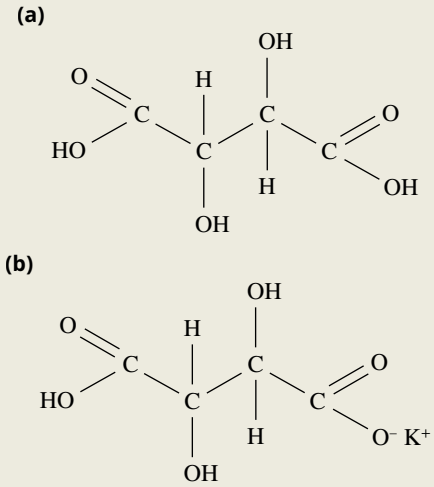

FIGURE 4.5.2 Structures of (a) tartaric acid and (b) potassium hydrogentartrate

Potassium hydrogentartrate, otherwise known as potassium bitartrate or 'cream of tartar,' crystallises naturally from wine as it ferments and is widely used in cooking. It stabilises egg whites and syrups, and is used in bread-making for its leavening effect.

The hydrogentartrate ion is amphiprotic and may act as both a Brønsted–Lowry acid and Brønsted–Lowry base.

Equation 1 $HOOCC_2H_4O_2COO^-(aq) + H_2O(l) \rightleftharpoons {}^-OOCC_2H_4O_2COO^-(aq) + H_3O^+(aq)$

Equation 2 $HOOCC_2H_4O_2COO^-(aq) + H_2O(l) \rightleftharpoons HOOCC_2H_4O_2COOH(aq) + OH^-(aq)$

K_a for equation 1 > K_b for equation 2. Therefore, a solution of hydrogentartrate is acidic.

Cream of tartar (Figure 4.5.3) can be mixed with other acidic liquids, such as lemon juice or white vinegar, to make a paste that is an excellent cleaning agent for metals such as brass, aluminium or copper. As these metals tarnish, they react with oxygen in the air to produce metal oxides. The combined mixtures of vinegar or lemon juice and cream of tartar are all acidic, so do not react together when the paste is prepared. When the mixture is used to clean the metal, the metal oxides on the surface react with the acids in the paste according to the equation:

metal oxide + acid → salt + water

FIGURE 4.5.3 Cream of tartar is a crystalline solid.

This mixture is sometimes mistakenly made with vinegar and sodium hydrogencarbonate (baking soda). The hydrogencarbonate ion (HCO_3^-) is also amphiprotic and can act as a Brønsted–Lowry acid and base.

Equation 1 $HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$

Equation 2 $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

In this case, K_b for equation 2 is greater than K_a for equation 1 and the hydrogencarbonate solution is basic. The baking soda and vinegar react to neutralise one another, creating carbon dioxide and sodium ethanoate solution.

$CH_3COOH(aq) + NaHCO_3(aq) \rightarrow NaCH_3COO(aq) + H_2O(l) + CO_2(g)$

The ethanoate ion in solution can only act as a proton acceptor (Brønsted–Lowry base), and so it is ineffective at cleaning tarnished metals.

4.5 Review

SUMMARY

- Salts are ionic compounds that, if soluble, completely dissociate in aqueous solution.
- Salts are produced in neutralisation reactions. The anions are derived from the acid and cations from the base.
- Some anions and cations of salts can act as Brønsted–Lowry acids and bases.
- The conjugate base of a weak acid reacts with water to form hydroxide ions.
- The conjugate acid of a weak base reacts with water to form hydronium ions.
- Salts produced by the reaction of a strong acid and strong base are neutral salts.
- Salts produced by the reaction of a strong acid and weak base are acidic salts.
- Salts produced by the reaction of a weak acid and strong base are basic salts.
- The acidity of salts produced by the reaction of a weak acid and weak base varies and depends on the degree of hydrolysis of the anion and cation in the salt produced.

KEY QUESTIONS

1 Complete the following table of neutralisation reactions.

Reactants	Name of salt formed	Formulae of ions present in the salt solution
Hydrochloric acid+magnesium hydroxide		
Sulfurous acid + zinc hydroxide		
	Potassium phosphate	
		$Ca^{2+}(aq) + CH_3COO^-(aq)$
	Ammonium nitrate	
		$Na^+(aq) + H_2PO_4^-(aq)$

2 Write equations for the hydrolysis of the following ions.

a S^{2-}
b ClO_2^-
c PH_4^+
d F^-

3 Classify the following salts as acidic, basic or neutral. Write relevant hydrolysis reactions to support your choice.

a KNO_3
b NH_4NO_3
c $Ca(HCOO)_2$
d $MgBr_2$

Chapter review

04

KEY TERMS

acid
acid–base reaction
acidic proton
acidic salt
acidic solution
acidity
acidity constant
alkali
amphiprotic
anion
base
basic salt
basic solution
Brønsted–Lowry theory
cation
concentrated solution
concentration
conjugate acid
conjugate acid–base pair
conjugate base
dilution
diprotic acid
dissociate
hydrolysis reaction
hydronium ion
hydroxide ion
indicator
ionic product of water
ionisation
ionisation constant of water
ionise
molar concentration
monoprotic acid
neutral salt
pH scale
polyprotic acid
salt
self-ionisation
solute
solution
strong acid
strong base
super acid
triprotic acid
weak acid
weak base

Introducing acids and bases

1 The NH_4^+ ion acts as a weak acid. Which of the following species is likely to be most abundant in $1\,mol\,L^{-1}$ NH_4Cl solution?
- **A** NH_4^+
- **B** Cl^-
- **C** NH_3
- **D** H_3O^+

2 In which of the following equations is the first-listed substance acting as a base?
- **A** $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$
- **B** $Cr_2O_7^{2-}(aq) + 2OH^-(aq) \rightarrow 2CrO_4^{2-}(aq) + H_2O(l)$
- **C** $2Na(s) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g)$
- **D** $CH_3NH_2(aq) + CH_3COOH(l) \rightarrow CH_3NH_3^+(aq) + CH_3COO^-(aq)$

3 Identify the reactant that acts as an acid in each of the following reactions.
- **a** $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
- **b** $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
- **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** $CO_3^{2-}(aq) + CH_3COOH(aq) \rightarrow HCO_3^-(aq) + CH_3COO^-(aq)$

4 Write 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.

5 Write 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.

6 Using suitable examples, distinguish between a:
- **a** diprotic and an amphiprotic substance
- **b** strong acid and a concentrated acid.

7 Draw a structural formula of the monoprotic ethanoic acid molecule. Identify which proton is donated in an acid–base reaction.

8 Identify which one or more of the following reactions are Brønsted–Lowry acid–base reactions.
- **a** $HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$
- **b** $2HNO_3(aq) + Mg(s) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$
- **c** $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
- **d** $CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$

Strengths of acids and bases

9 The dihydrogenphosphate ion is amphiprotic. The equilibrium constants for the $H_2PO_4^-$ ion acting as an acid and as a base are provided below.

$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$
$K_a = 6.3 \times 10^{-8}$
$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3PO_4(aq) + OH^-(aq)$
$K_b = 1.6 \times 10^{-7}$

Which one of the following can correctly be inferred from the data provided?
- **A** $H_2PO_4^-$ readily loses two protons to water.
- **B** $H_2PO_4^-$ will form an acidic solution in water.
- **C** $H_2PO_4^-$ will accept and donate a proton to an equal extent in water.
- **D** $H_2PO_4^-$ more readily accepts a proton than donates a proton in water.

10 The following table lists the pH of 0.00001 mol L^{-1} solutions of four acids.

Acid solution	pH
I	4.0
II	3.5
III	5.0
IV	3.0

The acid that cannot be monoprotic and weak is:

A I
B II
C III
D IV

11 Write an equation to show that perchloric acid ($HClO_4$) acts as a strong acid in water.

12 Write an equation to show that hypochlorous acid ($HClO_3$) acts as a weak acid in water.

13 Write an equation to show that ammonia (NH_3) acts as a weak base in water.

14 Write a balanced ionic equation showing the HPO_4^{2-} ion acting as a weak base in water.

Acidity of solutions

15 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 5.7×10^{-9} mol L^{-1}
d 3.4×10^{-12} mol L^{-1}
e 6.5×10^{-2} mol L^{-1}
f 2.23×10^{-13} mol L^{-1}

16 What is the concentration of hydronium and hydroxide ions in solutions, at 25°C, with the following pH values?

a 1
b 3
c 7
d 11.7

17 Human blood has a pH of 7.4. Is blood acidic, basic or neutral?

18 The pH of a cola drink is 3 and of black coffee is 5. How many more times acidic is the cola than black coffee?

19 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

20 The pH of tomato juice is 5.3 at 25°C. What is the concentration of hydroxide ions in tomato juice?

Dilution of acids and bases

21 A solution of hydrochloric acid has a pH of 2.

a What is the molar concentration of hydrogen ions in the solution?
b What amount of hydrogen ions, in mol, would be present in 500 mL of this solution?

22 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.

23 The molarity of concentrated sulfuric acid is 18.0 mol L^{-1}. What volume of concentrated sulfuric acid is required to prepare 1.00 L solution of 2.00 mol L^{-1} H_2SO_4?

24 When a 10.0 mL solution of hydrochloric acid is diluted, the pH changes from 2.00 to 4.00. What volume of water is added to the acid solution?

25 40.0 mL of 0.10 mol L^{-1} HNO_3 is diluted to 500.0 mL. Will the pH increase or decrease?

pH of salt solutions

26 Three of the following solutions have a pH very close to 7. One has a pH of close to 4. Which is the solution with pH 4?

A ammonium ethanoate (NH_4CH_3COO)
B ammonium chloride (NH_4Cl)
C ammonium phosphate ($(NH_4)_3PO_4$)
D sodium bromide (NaBr)

27 **a** The following ionic salts were all dissolved separately in equal volumes of water at 25°C. The approximate pH of the solutions formed was measured and recorded as being either neutral (7), acidic (5) or basic (9). Complete the following table.

Salt dissolved	Approximate pH (5, 7 or 9)
Potassium nitrate	
Ammonium chloride	
Sodium phosphate	
Potassium hydrogensulfate	

b Another ionic salt, phosphonium ethanoate (PH_4CH_3COO), was dissolved in water and found to have a pH of below 7. Use your knowledge of acid–base chemistry to account for this observation. Use equations to support your answer.

Connecting the main ideas

28 A laboratory assistant forgot to label 0.1 mol L^{-1} solutions of sodium hydroxide (NaOH), hydrochloric acid (HCl), glucose ($C_6H_{12}O_6$), ammonia (NH_3) and ethanoic acid (CH_3COOH). In order to identify them, temporary labels A–E were placed on the bottles and the electrical conductivity and pH of each solution was measured. The results are shown in the table below. Identify each solution and briefly explain your reasoning.

Solution	Electrical conductivity	pH
A	Poor	11
B	Zero	7
C	Good	13
D	Good	1
E	Poor	3

29 **a** Write concise definitions for:
- **i** Brønsted–Lowry acid
- **ii** strong base
- **iii** molar concentration
- **iv** conjugate acid.

b Explain, with the aid of equations, why HCO_3^- is classified as amphiprotic.

30 Construct a concept map that demonstrates your understanding of the links between the following terms: acid, base, proton, hydrogen ion, hydronium ion, conjugate.

31 Like water, liquid ammonia is able to react with itself and self-ionise, according to the following equation:
$NH_3(l) + NH_3(l) \rightleftharpoons NH_4^+(am) + NH_2^-(am)$
where 'am' means 'dissolved in ammonia'.

a Rewrite the reaction and link the conjugate acid–base pairs, clearly identifying the acids and bases. The value of the equilibrium constant (at 25°C) for this reaction is about 1.0×10^{-30}.

b It is found that, as the temperature of the ammonia increased, the value of K and electrical conductivity also increased. Is the ionisation of ammonia endothermic or exothermic?

CHAPTER

05 Buffers

Buffers are important in environmental and living systems. They have many uses. In medicines, buffers are used to maintain the stability and effectiveness of the medicine. In food, they preserve flavour and colour. Buffers are used during the fermentation of wine and in stages of textile dyeing. Buffers have a role in the maintenance and proper functioning of delicate chemical processes that can only occur within a narrow pH range. For example, there are buffer systems that ensure the pH of your blood is tightly maintained between pH 7.35 and pH 7.45.

In this chapter, you will study what a buffer is, how buffers are made and how they work. You will also examine the application of buffers as dynamic equilibrium systems and predict how they respond to pH changes according to Le Châtelier's principle.

Science understanding

- buffer solutions are conjugate in nature and resist changes in pH when small amounts of strong acid or base are added to the solution; buffering capacity can be explained qualitatively; Le Châtelier's principle can be applied to predict how buffers respond to the addition of hydrogen ions and hydroxide ions
- the characteristics of a system in dynamic equilibrium can be described and explained in terms of reaction rates and macroscopic properties

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5.1 Introducing buffers

FIGURE 5.1.1 A pH meter is calibrated by measuring a series of reference standards, known as pH buffers, that have known and accurate pH values.

You might have come across buffers around your house, particularly if you have a swimming pool, spa or aquarium. You might also have used buffer solutions in your chemistry lessons to calibrate a pH meter (Figure 5.1.1). pH is probably the most commonly measured quantity in laboratories because pH affects many chemical and biochemical reactions. Buffers are used where it is important to maintain a solution at a known pH.

In this section, buffer solutions will be defined and you will be introduced to the preparation of buffer solutions.

BUFFER SOLUTIONS

Buffer solutions are able to resist a change in pH when small amounts of acid or base are added. This is important for processes that require stable and narrow pH ranges.

A buffer consists of a weak **conjugate acid–base pair**. This means that a buffer could be made of a:

- weak acid and its conjugate base
- weak base and its conjugate acid.

A **weak acid** donates hydrogen ions (protons) to a base to a limited extent. The acid's **conjugate base** contains one less hydrogen ion (proton) than the acid.

A **weak base** accepts hydrogen ions (protons) from acids to a limited extent. The base's **conjugate acid** contains one more hydrogen ion (proton) than the base.

The conjugate acid–base pair chosen for preparing a buffer helps determine the pH of the buffer.

Buffer solutions can resist a change in pH when small amounts of acid or base are added.

Buffers can be made from a weak acid and one of its salts. For example, a mixture of ethanoic (acetic) acid and sodium ethanoate (acetate) solution produces the CH_3COOH/CH_3COO^- buffer. If the solution contains equal molar concentrations of ethanoic acid and sodium ethanoate salt solution, it would produce a buffer solution of pH 4.76.

It does not matter what the concentrations for the ethanoic acid and sodium ethanoate solutions are—as long as they are the same, the pH will always be 4.76. To change the pH of this buffer solution, you need to change the ratio of acid to salt.

The equilibrium system that acts as a buffer in this situation is:

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

When making the buffer solution, the aim is to produce a solution that contains a high enough concentration of ethanoic acid molecules and ethanoate ions to enable the system to shift in either direction.

The ethanoic acid/sodium ethanoate buffer is prepared by dissolving approximately equal molar amounts of ethanoic acid (CH_3COOH) and sodium ethanoate (CH_3COONa) in water.

The sodium ethanoate dissociates completely in water, producing ethanoate ions and sodium ions:

$$CH_3COONa(s) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

At the same time, only a small proportion of ethanoic acid molecules will ionise, producing ethanoate (CH_3COO^-) and hydronium (H_3O^+) ions. The vast majority of the ethanoic acid molecules remain as molecules.

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

The resulting solution is an equilibrium mixture of CH_3COOH molecules, CH_3COO^- ions and H_3O^+ ions. Sodium ions are spectator ions and are not involved in the equilibrium:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq) \qquad K_a = 1.7\times10^{-5}$$

Therefore, the buffer solution contains a significant amount of both the weak acid, CH_3COOH, and its conjugate base, CH_3COO^-. This equilibrium system can resist changes in pH when a small amount of an acid or base is added.

Buffers can be made from a weak base and one of its salts. For example, a mixture of ammonia solution and ammonium chloride solution produces the NH_3/NH_4^+ buffer. If equal molar concentrations of weak base and its salt are mixed, the buffer solution will have pH 9.25.

An NH_3/NH_4^+ buffer can be prepared by dissolving approximately equal molar amounts of ammonia solution, and an ammonium salt, such as ammonium chloride (NH_4Cl) in water.

The ammonium chloride dissociates completely in water, producing ammonium ions and chloride ions:

$$NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

At the same time, only a small proportion of ammonia molecules will ionise, producing ammonium ions (NH_4^+) and hydroxide ions (OH^-):

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

The resulting solution is an equilibrium mixture of NH_3 molecules, OH^- ions and NH_4^+ ions. Chloride ions are spectator ions and are not involved in the equilibrium. The equation for the equilibrium system is:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_a = 5.6\times10^{-10}$$

The buffer solution contains a significant amount of both the weak base, NH_3, and its conjugate acid, NH_4^+. This equilibrium system can resist changes in pH when a small amount of an acid or base is added.

5.1 Review

SUMMARY

- Buffer solutions resist changes in pH when small amounts of acid or base are added.
- A buffer consists of a conjugate acid–base pair (with a weak base or weak acid).
- Buffer solutions that are acidic are usually made by mixing approximately equal molar concentrations a weak acid and one of its salts.
- Buffer solutions that are alkaline are usually made by mixing approximately equal molar concentrations a weak base and one of its salts.

KEY QUESTIONS

1 Which one of the following substances could be used to maintain the pH range of water in an aquarium?

A a solution of a weak acid
B a solution of a strong acid
C a solution of a strong acid and its conjugate base
D a solution of a weak acid and its conjugate base

2 Write the equation for the equilibrium that exists in the ammonia/ammonium chloride buffer.

3 Write the equation for the equilibrium that exists in the hydrofluoric acid/fluoride buffer.

4 Write the equation for the equilibrium that exists in the hydrogencarbonate/carbonate buffer.

5 Classify the three buffer solutions identified in questions 2, 3 and 4 as either acidic or alkaline buffers (assume the components are present in roughly equimolar concentrations).

5.2 How buffers work

When 0.01 mol of hydrochloric acid is added to 1.0 L of water, the pH falls from 7.0 to 2.0, a drop of five pH units (Figure 5.2.1). The hydronium ion concentration in the solution has increased 100 000 times!

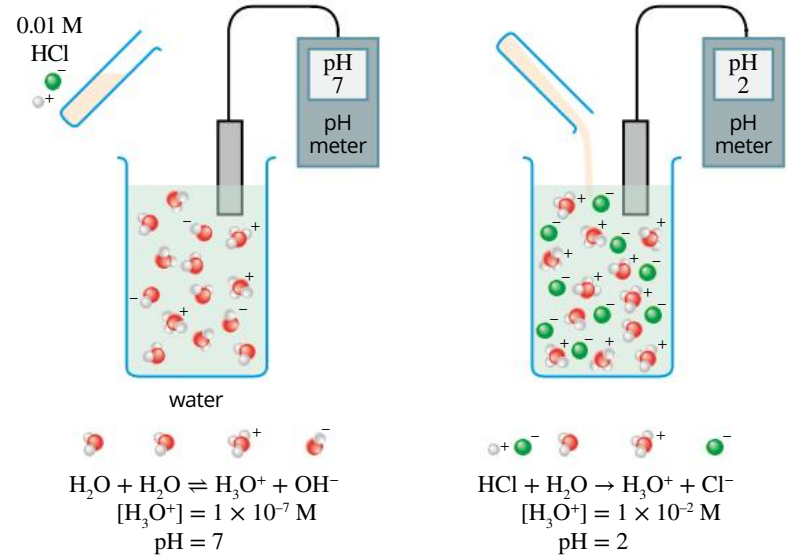


FIGURE 5.2.1 A significant change in pH occurs when a small amount of hydrochloric acid is added to 1.0 L of water.

When the same amount of hydrochloric acid is added to a particular buffer solution initially at pH 7, the pH might only drop to 6.9, a decrease of only 0.1 pH unit.

In this section, you will investigate how buffers work to maintain a stable pH range.

ADDING AN ACID TO A BUFFER

If a small amount of a strong acid, such as HCl, is added to an ethanoic acid/ethanoate buffer (CH_3COOH/CH_3COO^-), the pH will decrease to a small extent, but not as much as if the buffer were not present. For example, if you add HCl to a buffer solution, the extra H_3O^+ ions disturb the existing equilibrium of the buffer solution. **Le Châtelier's principle** tells you that the system will respond to oppose the change and restore equilibrium. Therefore, some of the additional H_3O^+ will react with CH_3COO^- ions present in the buffer. This produces more CH_3COOH molecules, decreasing the concentration of H_3O^+ ions in solution.

The equilibrium in a buffer system is represented in Figure 5.2.2. Note that when acid is added, the conjugate base (A^-) combines with any H_3O^+ that is added to maintain a stable pH.

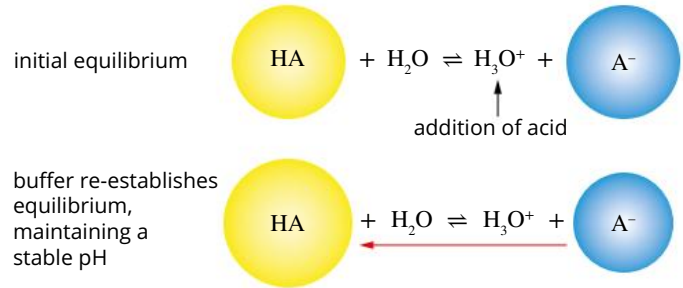


FIGURE 5.2.2 A constant pH is maintained by the equilibrium between a weak acid, HA, and its conjugate base, A^-, when acid is added because $A^-(aq)$ combines with the added H_3O^+.

ADDING A BASE TO A BUFFER

When a strong base is added to the CH_3COOH/CH_3COO^- buffer, the OH^- ions from the base react with CH_3COOH molecules in the buffer. This generates more CH_3COO^- ions and consumes most of the extra OH^- ions:

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

The overall effect of adding a small amount of an acid or a base to a buffer solution on the final concentration of H_3O^+ or OH^- in the solution is small. Therefore, the overall change in pH is also very small.

The effect of adding an acid or a base to a buffer system made from a weak acid with the general formula, HA, is shown in Figure 5.2.3.

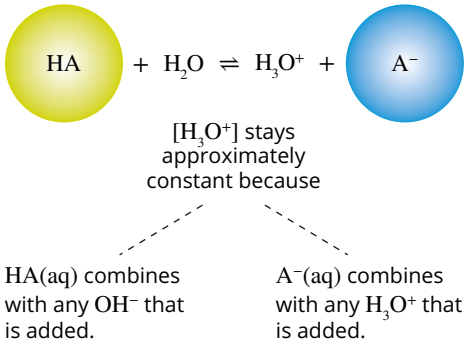


FIGURE 5.2.3 A constant pH is maintained by the equilibrium between a weak acid, HA, and its conjugate base, A^-.

BUFFER CAPACITY

Buffer solutions have a working pH range and capacity that determine how much acid or base can be neutralised before the pH changes, and by how much the pH will change. It is the concentrations of the buffer, weak acid (HA) and its conjugate base (A^-) that influence how effective the buffer will be in resisting changes in pH. A buffer is most effective when more HA molecules and A^- are available to react with and neutralise the effect of the addition of a strong acid or base, so that the pH of the system only changes a small amount.

> The more A^- and HA molecules available, the less of an effect adding a strong acid or base will have on the pH of a system.

If HCl is added to an ethanoic acid/ethanoate buffer, the H_3O^+ ions from the HCl will react with CH_3COO^- ions to form CH_3COOH. As more HCl is added, a new stage is reached where most of the CH_3COO^- ions have reacted. At this point, the buffer system is no longer effective. Additional H_3O^+ ions can no longer be removed by reaction with CH_3COO^- ions. From this point onwards, there will be a sharp decrease in pH as more HCl is added. Figure 5.2.4 (page 128) shows how the pH of a 1.0 L buffer solution (0.1 M CH_3COOH and 0.1 M CH_3COO^-) changes as HCl is added. A buffer can only resist changes in pH if some of each of its conjugate acid and base pair is present. If they are consumed, for example by the addition of a large amount of strong acid or base, the solution is no longer a buffer.

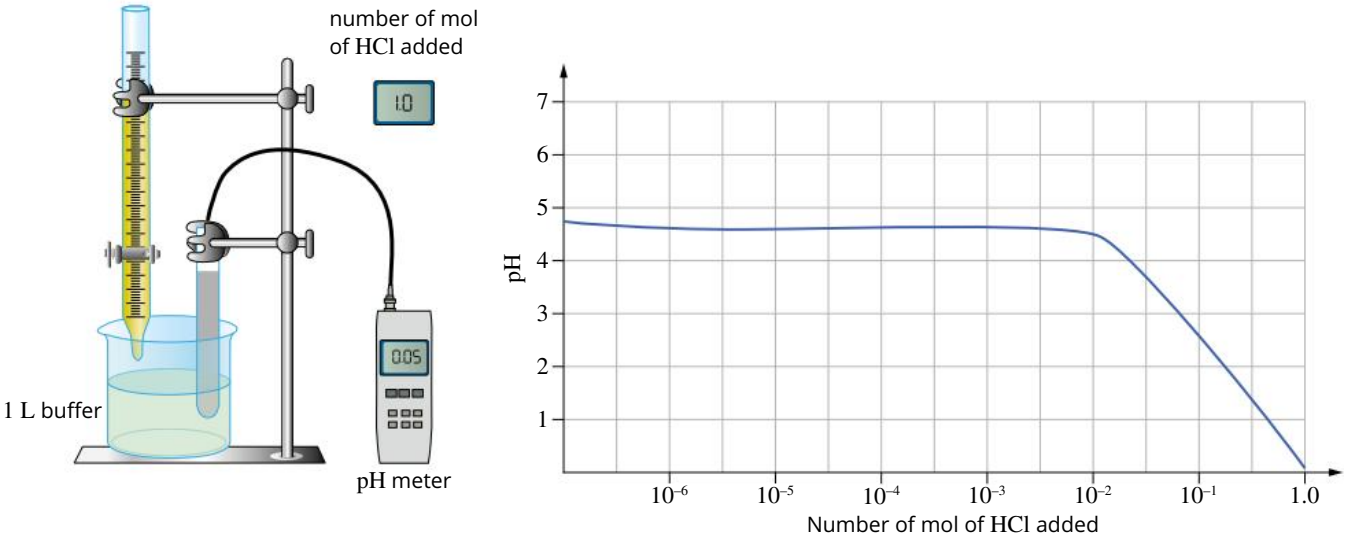
Buffer capacity is a measure of the effectiveness of a buffer solution at resisting a change in pH when either a strong acid or a strong base is added.

Buffer capacity is greatest when:

- there is a high concentration of the weak acid and its conjugate base
- the concentrations of the acid and its conjugate base are equal.

In the ethanoic acid/ethanoate buffer, a solution that has a high concentration of ethanoic acid can react with a greater amount of base. Similarly, a buffer that has a high concentration of ethanoate ions can react with a greater amount of added acid, H_3O^+. In general, for a buffer solution to be effective at maintaining pH, the ratio of the concentrations of the weak acid and its conjugate base should be within the range of 10:1 and 1:10.

Buffer capacity is a measure of the effectiveness of a buffer solution to resist a change in pH when either a strong acid or strong base is added.



Number of mol of HCl added	0	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1.0
pH	4.74	4.7	4.7	4.7	4.7	4.6	2.7	0.05

FIGURE 5.2.4 The pH change of a 1.0 L buffer solution (0.1 mol L^{-1} CH_3COOH and 0.1 mol L^{-1} CH_3COO^-) when HCl is added

5.2 Review

SUMMARY

- When a buffer is present, the pH of a solution will change when a strong acid or base is added, but only to a small degree.
- Le Châtelier's principle can be used to predict the change in equilibrium of a buffer solution when an acid or a base is added.
- When acid is added to a buffer solution, the conjugate base combines with any H_3O^+ that is added to maintain a stable pH.
- When base is added to a buffer solution, the weak acid combines with any OH^- that is added to maintain a stable pH.
- Buffer capacity is a measure of the effectiveness of a buffer solution to resist a change in pH when either a strong acid or a strong base is added.
- Buffer capacity is greatest when:
  - there is a high concentration of the weak acid and its conjugate base
  - the concentrations of the acid and its conjugate base are equal.

KEY QUESTIONS

1 A small amount of sodium hydroxide solution is added to the ammonia/ammonium chloride buffer. Which one of the following statements is true?

A The OH^- ions react with NH_4^+ ions and the pH decreases significantly.

B The OH^- ions react with NH_3 molecules and the pH decreases significantly.

C The OH^- ions react with NH_4^+ ions and the pH remains almost constant.

D The OH^- ions react with NH_3 molecules and the pH remains almost constant.

2 The chemical equation that describes the CH_3COOH/CH_3COO^- buffer system is:

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

Complete the following paragraph, choosing from the words and species listed:

right, left, small, large, H_3O^+, CH_3COOH, CH_3COO^-, OH^-, H_2O

The addition of a small amount of HCl to the ethanoic acid buffer system will disturb the equilibrium. As equilibrium is re-established, the added H_3O^+ reacts with _____. The position of the equilibrium in the equation given above shifts to the _____. Because the buffer contains a relatively large amount of CH_3COO^-, most of the added _____ is consumed and there is a _____ change in the concentration of H_3O^+.

When a small amount of base is added to the buffer system the OH^- reacts with _____. The excess OH^- is consumed without any large change in the concentration of _____.

3 The compositions of four solutions, each containing 100 mL of a mixture of lactic acid (a weak acid) and sodium lactate (a weak base), are given below. Identify the solution with the greatest buffer capacity and explain your choice.

A 0.1 mol L^{-1} lactic acid and 0.1 mol L^{-1} sodium lactate

B 0.1 mol L^{-1} lactic acid and 0.01 mol L^{-1} sodium lactate

C 0.5 mol L^{-1} lactic acid and 0.5 mol L^{-1} sodium lactate

D 0.05 mol L^{-1} lactic acid and 0.25 mol L^{-1} sodium lactate

5.3 Applications of buffers

Buffers are used in a variety of fields, including analytical chemistry, biochemical systems, agriculture and industry.

In analytical chemistry, buffers have applications in both qualitative and quantitative analysis. They are used to control the concentration of ions such as phosphate, oxalate, borate and fluoride, which can interfere with reactions. Section 5.1 noted the importance of the accurate measurement of pH and that buffer solutions of known pH values (usually pH 4, 7 and 10) are used to standardise pH meters.

This section investigates some specific buffers and their applications in biochemical systems, agriculture and the food and paper industries.

BIOCHEMICAL SYSTEMS

Biological fluids have characteristic pH values. Cell fluids, both inside and outside of all cells, have water as the solvent. Like all aqueous solutions, cell fluids contain the dissociation products of H_2O: hydrogen ions (H^+) and hydroxide ions (OH^-). Therefore, pH plays a significant role in biochemical reactions. A small change of just 0.2 pH units can cause death, while certain enzymes are only activated at specific pH values.

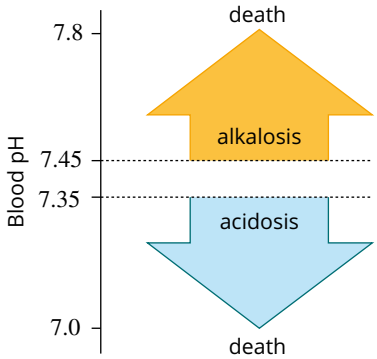


FIGURE 5.3.1 Physiological consequences of changes in blood pH

Many reactions that occur in the human body involve acid–base reactions. Buffers provide a means of controlling the amount of H_3O^+ or OH^- ions present in cells and tissues and are vital. Without a buffer, the pH of body fluids could fluctuate from extremely basic to extremely acidic, making it impossible for biological systems, including those that involve enzymes, to function.

For example, blood is maintained within a narrow pH range of 7.35–7.45. Diseases such as pneumonia, emphysema and diabetes can cause pH to drop to potentially lethal levels, a condition called **acidosis**. On the other hand, hyperventilation, caused by rapid breathing, increases pH and causes **alkalosis**. Figure 5.3.1 shows a graphical representation of the effect of blood pH on the human body.

The presence of buffers maintains pH values within narrow limits in the body. Control of pH in the blood is achieved by different buffers. One important buffer is made up of carbonic acid (H_2CO_3) and the hydrogencarbonate ion (HCO_3^-):

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

How the carbonic acid buffer in blood works

Respiration in the cells produces carbon dioxide. The carbon dioxide dissolves and decreases blood pH according to the reaction:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

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

The buffers in the blood act to reduce the effect of additional acid (H_3O^+). According to Le Châtelier's principle, the system responds to oppose the change and restore equilibrium as some of the additional H_3O^+ produced by the carbon dixide will react with CH_3COO^- ions present in the buffer. This produces more CH_3COOH molecules, decreasing the overall concentration of H_3O^+ ions in solution. You can refer to the general equation showing the equilibrium in a buffer system in Figure 5.2.3 (page 127).

Phosphate buffer system

In the internal fluid of all cells another important buffer system is at work, the **phosphate buffer** system. This buffer system consists of dihydrogenphosphate ions ($H_2PO_4^-$) as a weak acid and hydrogenphosphate ions (HPO_4^{2-}) as the conjugate base of the weak acid. These two ions are in equilibrium with each other:

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

If additional hydrogen ions enter the cellular fluid, they are consumed in the reverse reaction. The HPO_4^{2-} reacts with the extra hydrogen ions and the equilibrium shifts to the left. If additional hydroxide ions enter the cellular fluid, they react with $H_2PO_4^-$, producing more H_3O^+ and HPO_4^{2-}. This shifts the equilibrium to the right to stabilise the pH. If the phosphate buffer in cell fluid were absent, sharp changes in pH of cell fluids would occur, causing cell death or different proteins and cell organelles to malfunction.

AGRICULTURE

The pH of the soil is very important. Soil pH affects all soil chemistry and nutrient reactions. It is usually the first consideration when testing and evaluating a soil and when maximising crop yield and choosing a fertiliser.

Most plants perform best in slightly acid soils at pH 6.0–7.0. Some plants, such as strawberries (Figure 5.3.2), blueberries and citrus, grow better in more acid soils (pH 4.0–6.5). Other plants, such as plums, sage and sunflowers, tolerate a slightly alkaline soil (pH 7.0–7.5). Small changes in a soil pH can have large effects on nutrient availability and plant growth. Soils are naturally buffered by the presence of carbonates, bicarbonates and phosphates salts, as well as organic acids.

FIGURE 5.3.2 Strawberry plants grow best in more acidic soils at pH 4.0–6.5.

Soil acidification, a decrease in soil pH, is a natural process that occurs very slowly as soil is weathered. Unfortunately, this process is accelerated by agricultural practices such as the use of nitrogen fertilisers. The chemical and biological properties of soil change as it becomes more acidic. One chemical change is an increase in the solubility of aluminum (Al) and manganese (Mn), which can be toxic to plants.

When you measure the soil pH, you are measuring the concentration of hydrogen ions in the soil solution only. But hydrogen ions in soil are present both in the soil solution and adsorbed onto the soil surfaces. To counteract an increase in soil acidity, lime (calcium oxide) or limestone (calcium carbonate) can be added to the soil. By adding lime, hydrogen ions in the soil solution are neutralised. Hydrogen ions from the soil surfaces are then released into the soil solution. This buffering effect happens to maintain equilibrium and resist the change in pH. Well-buffered soils are slower to acidify. But once they are acidic, it takes more lime to increase pH. The Department of Agriculture and Food Western Australia (DAFWA) has identified that more than 40% of the agricultural land in south-west Western Australia consists of poorly buffered sandy soil types.

THE FOOD INDUSTRY

Buffers in food

The colour, flavor, texture and nutritional value of many foods can be altered by food additives. Some food additives help preserve the food. Food additives are classified by codes called **E numbers**. E numbers between E330 and E340 represent a group of antioxidants that can also act as buffers (Figure 5.3.3). Citric acid (E330) is added to control pH.

By keeping the acidity of a food at the appropriate level, flavour and appearance can be maintained. A stable pH is also critical to the preservation of many processed foods. Food additives that act as buffers usually consist of metal salts with a weak acid found naturally within the food to be preserved. For example, sodium citrate could be added to a food containing citric acid to create a buffer solution. Calcium and potassium citrate could also be used.

Citrate additives are widely used antioxidants and buffers, with a range of applications. All citrate additives can reduce the chemical reaction that causes the discoloration of fruit and are often added to fruit products. Citrate additives include:

- E331, sodium citrate, a buffer mainly used in jams and jellies
- E332, potassium citrate, an antioxidant and buffer often found in cakes, biscuits and cheese
- E333, calcium citrate, an important buffer in carbonated drinks.

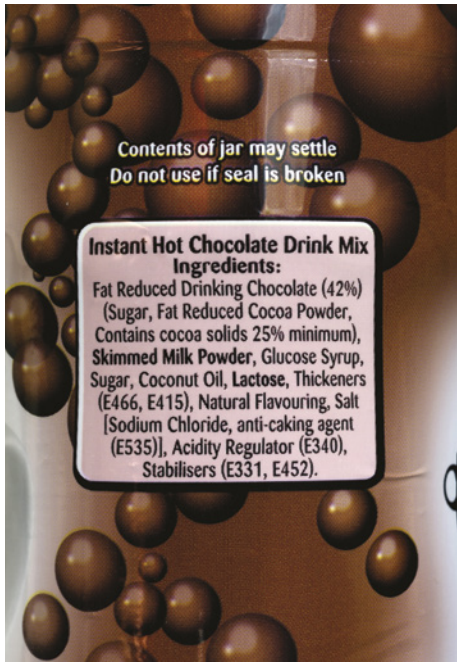


FIGURE 5.3.3 Food additive E340 (monopotassium phosphate) is an antioxidant that can also act as a buffer.

Potassium tartrate (E336) is obtained from grapes during the wine-making process. In addition to its buffering action, potassium tartrate helps bread to rise consistently.

Monopotassium phosphate (potassium dihydrogenphosphate) (E340), principally used as an antioxidant, also has buffering capabilities. It is used in products such as custard, milk powder and jelly mixes, and may be added to cooked meat. Monopotassium phosphate is an important ingredient in many sports drinks, acting as a buffer and providing the potassium electrolyte.

The presence of buffers maintains pH values within a narrow range in many foods. For example, control of pH in some jams can be achieved with citric acid. The formula for citric acid is shown in Figure 5.3.4.

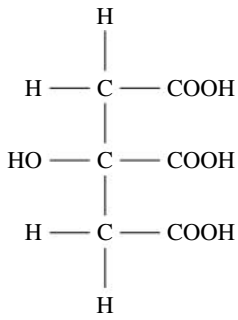


FIGURE 5.3.4 The structural formula of citric acid has three carboxylic acid groups (COOH) and can also be written as $H_6C_8O_7$. This shows that citric acid is triprotic, capable of releasing three hydrogen ions per molecule of citric acid.

The citric acid buffer can be represented by the chemical equation:

$$H_6C_8O_7(aq) + H_2O(l) \rightleftharpoons H_5C_8O_7^-(aq) + H_3O^+(aq)$$

The citric acid buffer in a food such as jam acts to reduce the effect of additional acid (H_3O^+). According to Le Châtelier's principle, the system responds to oppose the change and restore equilibrium. In this case, the H_3O^+ produced by the fermentation of sugar in the jam will react with $H_5C_8O_7^-$ ions present in the buffer. This produces more citric acid molecules ($H_6C_8O_7$) and decreases the concentration of H_3O^+ ions, keeping the pH stable. Refer to the general equation in Figure 5.2.3 (page 127) to see how the equilibrium in a buffer system works.

THE PAPER INDUSTRY

Nearly all industries use buffers in one process or the other. Major industries that employ the use of buffers include the paper, dye, ink, paint and drug industries.

Carbon dioxide is widely used as a buffer in the paper industry to adjust and stabilise pH. To buffer the papermaking system, to decrease calcium levels, and to increase dewatering, which is needed to help with pulp brightness and in the production of acid-free paper. Enzymes are often introduced into the paper-bleaching process (Figure 5.3.5) to achieve a higher level of pulp brightness while using fewer bleaching chemicals. These enzymes are most effective when used in a narrow, neutral pH range.

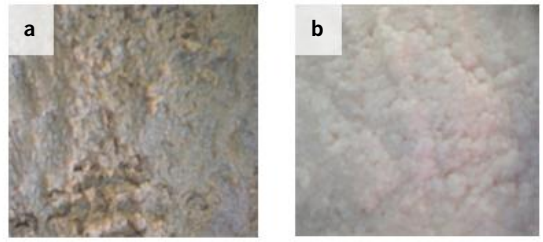


FIGURE 5.3.5 (a) Unbleached paper pulp. (b) Bleached paper pulp. The paper-bleaching process often uses enzymes to achieve a higher level of pulp brightness and to use fewer bleaching chemicals.

The production of acid-free paper is often buffered with the carbonic acid/hydrogencarbonate buffer to prevent the formation of additional acids that can occur during various stages of production:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

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

5.3 Review

SUMMARY

- Biological fluids have characteristic pH values.
- Biological buffer systems include the carbonic acid buffer system and the phosphate buffer system.
- Hydrogen ions in soil can be buffered by limestone (calcium carbonate).
- E numbers are used to classify food additives, with E330–E340 representing additives that can act as buffers.
- Carbon dioxide is widely used in the paper industry as a buffer.
- Le Châtelier's principle can be used to describe the response of a buffer system to external changes.

KEY QUESTIONS

1 List the buffers described in this section.

2 The carbonic acid buffer involving the weak acid/weak conjugate base pair H_2CO_3/HCO_3^- helps control the pH in the blood and in the manufacture of paper.

a Write the equation for the equilibrium that exists in the H_2CO_3/HCO_3^- buffer.

b Describe how the buffer works to stabilise the pH when acid is added.

3 The phosphate buffer system is described by the chemical equation: $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$

Will the concentration of $H_2PO_4^-$ increase or decrease if the system is subjected to a more alkaline environment?

4 Food additives that act as buffers usually consist of metal salts with a weak acid found naturally within the food to be preserved. Write the equation for the sodium citrate buffer ($H_5C_8O_7^-/H_6C_8O_7$).

Chapter review

05

KEY TERMS

acidosis
alkalosis
buffer capacity
buffer solution
conjugate acid
conjugate acid–base pair
conjugate base
E number
Le Châtelier's principle
phosphate buffer
weak acid
weak base

Introducing buffers

1 Define a buffer solution.

2 A buffer consists of a weak conjugate acid–base pair. Define a conjugate acid–base pair.

3 Give two examples of buffer solutions.

4 Which of the two pairs of substances could be used to make a buffer system? Explain.
A: NaOH and H_2O
B: CH_3COONa and CH_3COOH

5 The phosphate buffer system ($H_2PO_4^-/HPO_4^{2-}$) is described by the chemical equation:
$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$
Identify the weak conjugate acid—base pair in the phosphate buffer system.

How buffers work

6 The phosphate buffer system is described by the chemical equation:
$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$
To predict the effect of adding H_3O^+ to the $H_2PO_4^-/HPO_4^{2-}$ buffer system, complete the paragraph by filling in the blanks, using the words and species listed:
right, left, small, large, H_3O^+, $H_2PO_4^-$, HPO_4^{2-}, OH^-, H_2O
The addition of a small amount of HCl to the phosphate buffer system will disturb the equilibrium. As equilibrium is re-established, the added H_3O^+ reacts with _____. The position of the equilibrium in the equation given above shifts to the _____. Since the buffer contains a relatively large amount of HPO_4^{2-}, most of the added _____ is consumed and there is a _____ change in the concentration of H_3O^+.
When a small amount of base is added to the buffer system the OH^- reacts with _____. The excess OH^- is consumed without any large change in the concentration of _____.

7 Define buffer capacity.

8 Which one of the following statements is true?
A If a buffer is present, the pH of a solution will not change at all when a strong acid or base is added.
B When base is added to a buffer solution, the weak acid combines with any OH^- that is added to lower the pH of the buffer solution.
C Buffer capacity is greatest when there is a low concentration of the weak acid and its conjugate base.
D Buffer capacity is greatest when the concentrations of the acid and its conjugate base are equal.

Applications of buffers

9 Name two buffers:
a essential in maintaining blood and cell pH.
b used in the paper and food industry.

10 What are E numbers and which E numbers identify buffers used in the food industry?

11 Blood is buffered by the carbonic acid buffer, H_2CO_3/HCO_3^-. Write the equation for the buffer equilibrium. If the pH of blood increases, what happens to the concentrations of H_2CO_3, HCO_3^- and H^+?

Connecting the main ideas

12 Dihydrogenphosphate ($H_2PO_4^-$) and hydrogenphosphate (HPO_4^-) are important ions in intracellular fluids. They act as a buffer in the fluid inside cells. Using equations and Le Châtelier's principle, describe how these ions act to maintain a pH balance.

13 The concentration of carbonic acid (H_2CO_3) in blood is 1/20th of the concentration of the hydrogen carbonate ion (HCO_3^-), yet this blood buffer can buffer the pH of blood against bases as well as acids. Explain.

14 Distance running and other strenuous muscle activity can cause a build-up of lactic acid in the blood. You may have experienced the effect of lactic acid accumulation as a wobbly feeling in your leg muscles. How would the build-up of lactic acid in the blood affect blood pH? Using Le Châtelier's principle, describe how the buffers in blood work to regulate this pH change.

15 Cardiac arrest occurs when the heart fails to effectively pump and circulate blood around the body. Cell reactions still continue.
a Explain the effect of cardiac arrest on blood pH.
b Doctors often inject sodium hydrogencarbonate solution ($NaHCO_3$) into the heart muscle. Explain how this injection counteracts the pH effect.

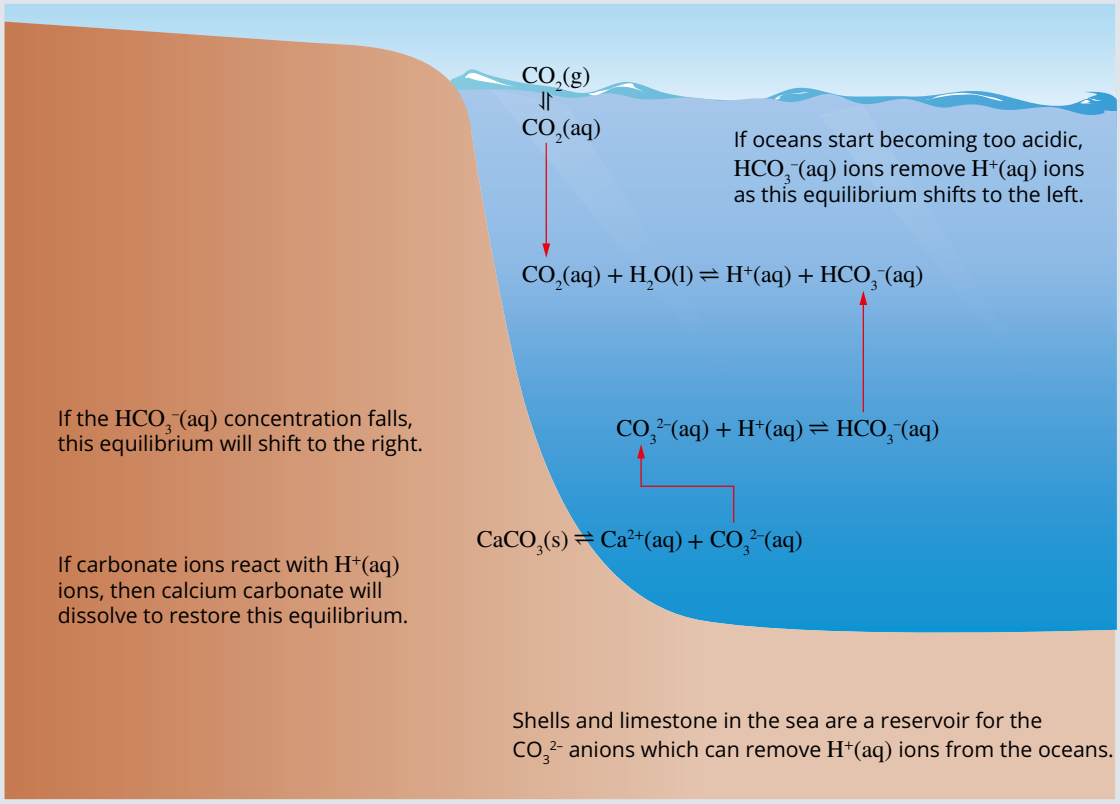
16 Citric acid, E330, is a food additive that acts as a buffer and helps to preserve food.

- **a** Write an equilibrium equation for the citric acid buffer. (Hint: citric acid can be written as $C_6H_8O_7$)
- **b** Identify the conjugate base of citric acid.
- **c** Describe how this buffer behaves to stabilise pH when acid is added.

17 Lakes with lake beds and surrounding rock and soil rich in limestone ($CaCO_3$) have a capacity to be able to buffer themselves against appreciable changes in pH. Using equations, explain how the water in these lakes behaves as a buffer to neutralise the effects of acid rain. For this question assume the acid rain is mainly a dilute solution of sulfurous acid, H_2SO_3.

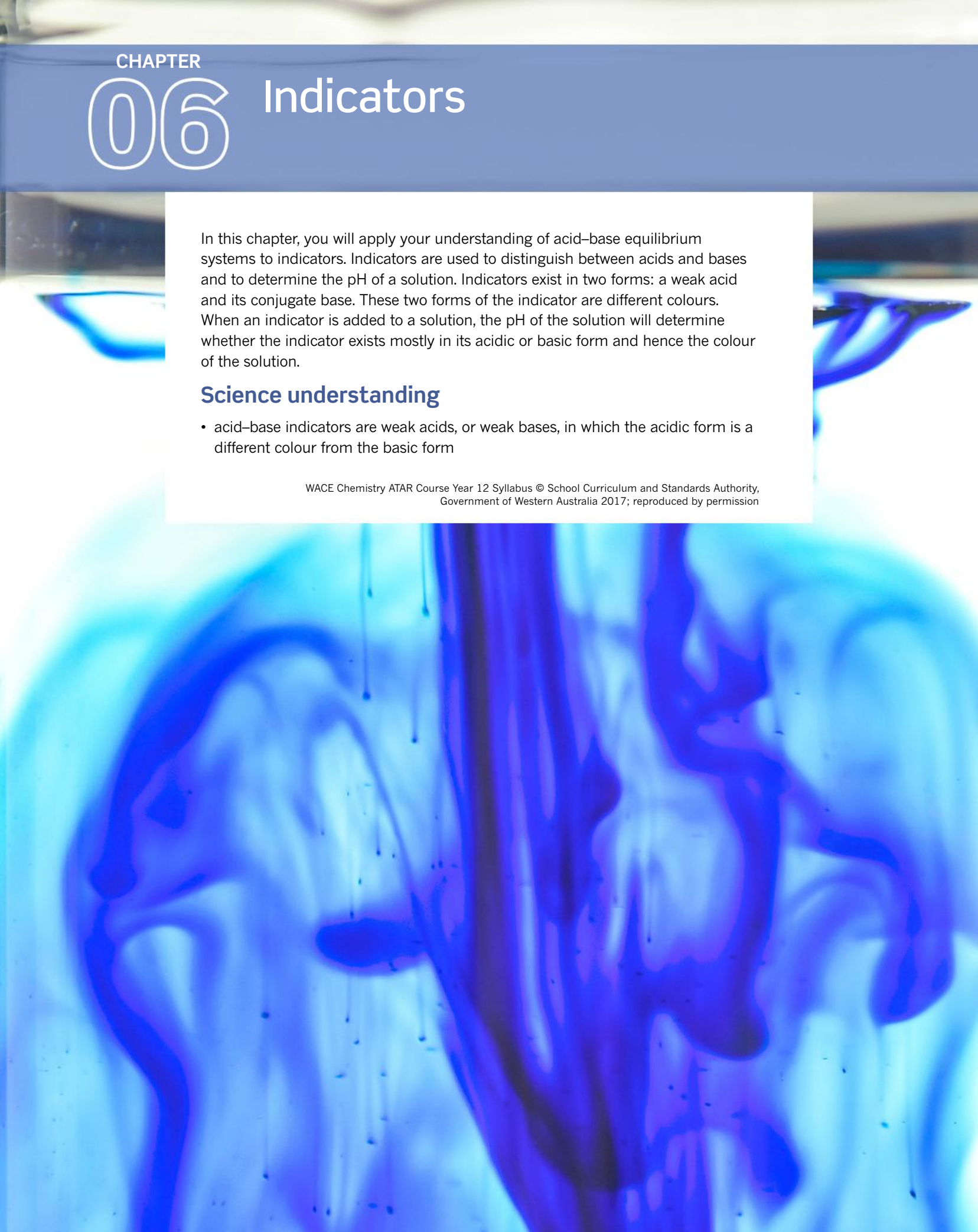
18 The following diagram shows how HCO_3^- ions act as a buffer to prevent oceans from becoming too acidic or alkaline.

- **a** If sea water is slightly alkaline, would you expect the concentration of dissolved CO_2 to be higher or lower than in pure water? Explain.
- **b** Describe and explain the impact of increasing atmospheric carbon dioxide concentration on coral reefs.



CHAPTER

06 Indicators



In this chapter, you will apply your understanding of acid–base equilibrium systems to indicators. Indicators are used to distinguish between acids and bases and to determine the pH of a solution. Indicators exist in two forms: a weak acid and its conjugate base. These two forms of the indicator are different colours. When an indicator is added to a solution, the pH of the solution will determine whether the indicator exists mostly in its acidic or basic form and hence the colour of the solution.

Science understanding

- acid–base indicators are weak acids, or weak bases, in which the acidic form is a different colour from the basic form

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6.1 Characteristics of 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 colour 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 6.1.1. Today, most indicators used in laboratories and industry, such as bromothymol blue, methyl orange and phenolphthalein, are synthetic.

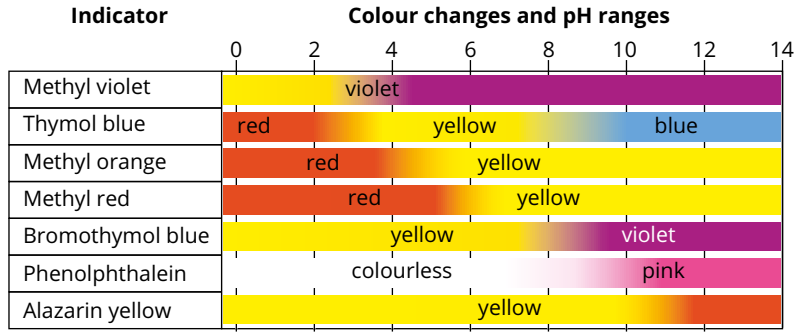


FIGURE 6.1.1 Common indicators and their pH ranges

Indicators are weak acids or weak bases. The conjugate acid form of the indicator is one colour and the conjugate base form is another. Indicators that undergo a single colour change are used for many analyses.

Figure 6.1.2 shows the variation in colour that can be achieved when red cabbage is used as an indicator. The colour of juice extracted from the leaves of red cabbage depends on the pH of the solution.

FIGURE 6.1.2 The colour of extract from red cabbage in solutions (from left, anticlockwise) of pH 1, pH 3, pH 5, pH 8 and pH 10

PROPERTIES OF INDICATORS

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 acidic 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 depends on the pH.

The acidic form of an indicator (HIn) and the conjugate base form (In^-) are different colours. The colour of the acidic or basic form is visible at low indicator concentrations. Changing the pH of an indicator solution changes the relative concentrations of the acidic and basic forms, and hence the overall colour of the solution can change.

The characteristics of some common laboratory indicators and how their colour changes with pH will be discussed in the following section.

Remember from Chapter 4 that according to the Brønsted–Lowry definition of acids and bases, acids and their conjugate base differ by the presence of a proton (H^+).

CHEMFILE

Plant colour and pH

Irish chemist Robert Boyle (1627–91) is credited with conducting the first systematic investigation into the colour of plant extracts in acidic and basic solutions. As part of his investigations, he soaked paper in litmus extract. Litmus is a dye obtained from lichens. In the presence of acids, litmus turns red (Figure 6.1.3), and in the presence of bases, it turns blue.

Boyle used the dried litmus paper to identify substances as either acids or bases. Litmus paper is still used for this purpose today.

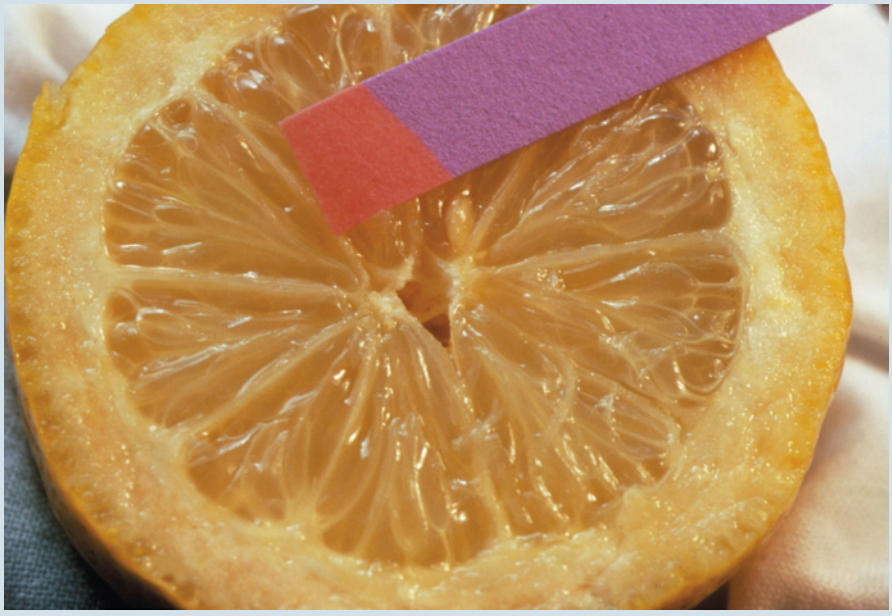


FIGURE 6.1.3 Blue litmus turns red in the presence of citric acid, a component of lemon juice.

6.1 Review

SUMMARY

- Indicators are large organic molecules that change colour in solution at different pH values.
- Indicators are either weak acids or weak bases.
- In solution, the acidic form of an indicator is in equilibrium with its conjugate base.
- Depending on the pH of the solution, the position of the equilibrium between the acidic and basic forms of an indicator changes.
- The colour of the acidic form of an indicator is different from the colour of its conjugate base.

KEY QUESTIONS

1 A substance has the following properties. Which one or more of these properties would make this compound unsuitable for use as an indicator?

A The compound is a weak acid.

B The compound turns dark blue in acidic solutions but is colourless in basic solutions.

C The compound colours are only visible at high concentrations of the compound.

2 Referring to Figure 6.1.1 on page 138, at what pH range would you expect:

a methyl violet to appear yellow?

b phenolphthalein to appear pink?

c methyl red to change colour from red to yellow?

6.2 Common indicators

Indicators are used to provide information about the pH (and therefore acidity and properties) of a chemical. As seen in Figure 6.1.1 on page 138, a number of indicators are commonly used in laboratories. Each indicator has a unique pH range in which they change colour. Indicators are different colours in acidic solutions and basic solutions. Commonly used indicators, their colours and the pH ranges in which they change colour, will be discussed in this section.

UNIVERSAL INDICATOR

Universal indicator (Figure 6.2.1) 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. If a more accurate measurement of pH is needed, you can use a pH meter instead of universal indicator.

FIGURE 6.2.1 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 0 to 14 from left to right. The 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, 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 6.2.2. Bromothymol blue changes colour between pH 6.0 and pH 7.6.

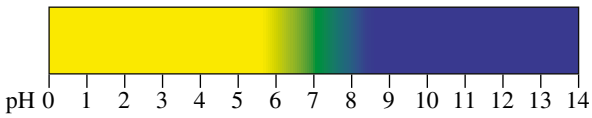


FIGURE 6.2.2 Bromothymol blue is yellow in acidic solutions and blue in basic solutions.

The equilibrium principles studied in Chapter 2 apply to indicators. You can use Le Châtelier's principle to predict the colour of an indicator, such as bromothymol blue, in acidic and basic solutions.

Bromothymol blue is a complex organic compound. The equation for the ionisation of bromothymol blue in water is shown here. For the sake of simplicity, the acidic form of bromothymol blue can be represented as HBB and the basic 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 cause the indicator equilibrium system to shift to the left to oppose the increase in the concentration of the H_3O^+ ions.

$$HBB(aq) + H_2O(l) \rightleftharpoons BB^-(aq) + H_3O^+(aq)$$

$\Leftarrow$

The concentration of HBB molecules becomes 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 system shifts to the right to oppose the increase in the concentration of the OH^- ions.

$$HBB(aq) + H_2O(l) \rightleftharpoons BB^-(aq) + H_3O^+(aq)$$

$\Rightarrow$

This (forward) reaction can also be written as shown below with the OH^- ions reacting with the HBB:

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

The concentration of BB^- ions becomes much greater than the concentration of HBB molecules and the solution is blue in colour (Figure 6.2.3).

FIGURE 6.2.3 Bromothymol blue is yellow in acidic solutions (left), blue in basic solutions (right) and green in neutral solutions (centre).

At pH 7, the concentrations of HBB molecules and 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. The transition point is the midpoint of the indicator colour change.

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. The addition of a strong base to a solution reduces the concentration of H_3O^+ ions. For indicator solutions, this causes a shift in the position of the equilibrium between its acid and conjugate base forms, forming more of the base form of the indicator.

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 is orange. A colour chart for methyl orange indicator is shown in Figure 6.2.4.

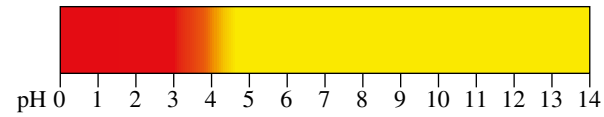
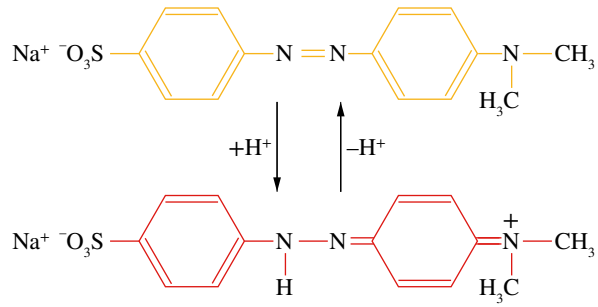


FIGURE 6.2.4 Methyl orange is red in acidic solutions and yellow in basic solutions. The indicator changes colour over the pH range 3.1 to 4.4.

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 6.2.5.

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

FIGURE 6.2.5 The structure of methyl orange is dependent upon the pH of the solution. The red form of methyl orange has a different structure from the yellow form.

PHENOLPHTHALEIN

Phenolphthalein is a synthetic indicator used in the analysis of weak acids. It has also been used as the active ingredient in some laxatives. In acidic solutions, phenolphthalein is colourless, whereas in basic solutions it has a pink colour. Phenolphthalein changes colour over the pH range 8.3–10.0.

A colour chart for phenolphthalein indicator is shown in Figure 6.2.6.

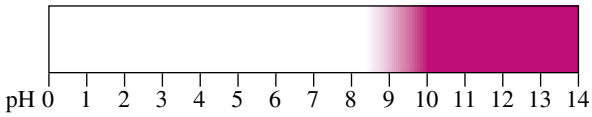


FIGURE 6.2.6 Phenolphthalein is colourless in solutions when the pH is below 8.3 and pink when the pH is greater than 10. The indicator changes colour over the pH range 8.3 to 10.0.

CHEMISTRY IN ACTION

Phenolphthalein and the carbonation of concrete

Phenolphthalein is used to determine the extent of carbonation in concrete—the reaction of concrete with atmospheric carbon dioxide.

As concrete sets, atmospheric carbon dioxide reacts with water, forming carbonic acid:

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

The carbonic acid reacts with lime ($Ca(OH)_2$) in the concrete to form calcium carbonate. Calcium carbonate binds to the silicates in the sand, increasing the strength of the concrete:

$$H_2CO_3(aq) + Ca^{2+}(aq) + 2OH^-(aq) \rightarrow CaCO_3(s) + 2H_2O(l)$$

Hydroxide ions are consumed in this reaction, lowering the pH. Steel rods used to reinforce concrete begin to corrode when the pH is below 8. Corrosion of these rods weakens the concrete structure.

The extent of carbonation is determined by spraying a concrete section with phenolphthalein. As shown in Figure 6.2.7, the area unaffected by carbonation, which has a high pH, shows up as pink. The indicator will remain colourless in the carbonated area because the pH is below 8.3.

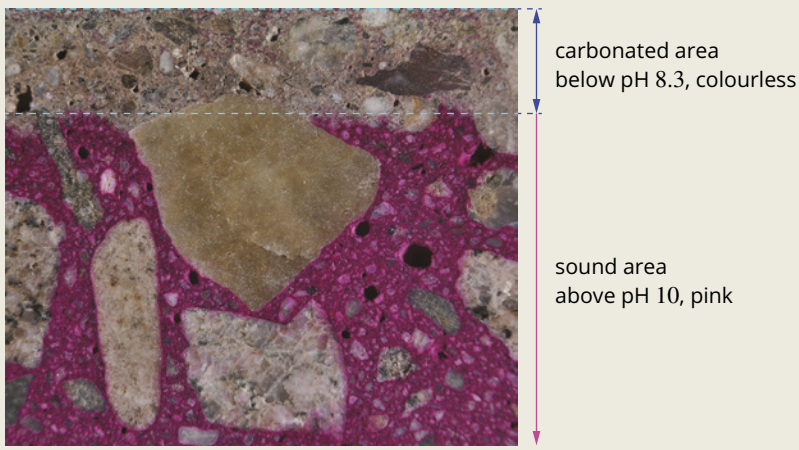


FIGURE 6.2.7 Phenolphthalein is used to indicate the extent of carbonation in concrete. The clear section has been affected by carbonation while the pink section is unaffected.

6.2 Review

SUMMARY

- An equilibrium exists between the acidic and basic forms of an indicator. The equilibrium can be represented by the equation:
  $$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$
- The colour change of an indicator can be explained by the equilibrium shifts that occur when H_3O^+ ions or OH^- ions are added.
- Under acidic conditions, the equilibrium is shifted to the left, resulting in a higher [HIn]. As a result, the solution has the colour of the acidic form of the indicator.
- Under basic conditions, the equilibrium is shifted to the right, producing more In^- ions. As a result, the solution has the colour of the basic form of the indicator.
- Indicators are different colours when in the acidic form compared to when in a basic form.
- A variety of indicators is available and each changes colour over a unique pH range. Table 6.2.1 provides a summary of the indicators discussed in this chapter.

TABLE 6.2.1 Colour of indicators in acid and basic forms

Indicator	Colour in acidic form	Colour in basic form
Universal indicator	Universal indicator is a mixture of several indicators and changes through a range of colours, from red through yellow (in acidic solutions), green (neutral solutions) and blue to violet (in alkaline solutions).	
Bromothymol blue	Yellow	Blue
Methyl orange	Red	Yellow
Phenolphthalein	Colourless	Pink

KEY QUESTIONS

1 Four beakers contain solutions of lemon juice, ammonia solution, sugar and sodium hydroxide. Some phenolphthalein is added to each beaker. In which beakers does the phenolphthalein change colour?

2 Methyl red is red in acidic solutions and yellow in basic solutions. It changes colour between pH 4.4 and pH 6.7. The acidic form of the indicator can be represented as HIn and the basic form of the indicator can be represented as In^-.

a Complete the equation below by filling in the gaps.

$$____ + H_2O(l) \rightleftharpoons ____ + H_3O^+(aq)$$

b A few drops of methyl red are added to a solution that has a pH of 3. What would you expect to happen to the indicator?

3 A solution is yellow with both bromothymol blue and methyl orange. 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 4.4 and 6.0
C between 3.1 and 7.6
D between 4.4 and 7.6

4 Four beakers each contain a solution with a pH of 9. What is the colour of each solution after the addition of:

a universal indicator?
b bromothymol blue?
c methyl orange?

6.3 pH range of an indicator

As you have seen earlier in this chapter, indicators do not necessarily change colour at pH 7. 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 8.3–10.0. 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 6.1.1 on page 138.

Table 6.3.1 summarises common indicators and their pH ranges.

TABLE 6.3.1 Common indicators and their pH ranges

Indicator	Colour in acidic solution	Colour in basic solution	pH range
Methyl violet	Yellow	Violet	0.0–1.6
Methyl orange	Red	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.4–6.2
Bromothymol blue	Yellow	Blue	6.0–7.6
Phenolphthalein	Colourless	Pink	8.3–10.0
Alizarin yellow	Yellow	Red	10.0–12.0

USING INDICATORS

The reactions of acids were 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 point during a neutralisation reaction when the amount of acid and base are in the stoichiometric ratio represented by the reaction equation.

A neutralisation reaction occurs when an acid reacts with a base to form a salt and water.

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 amounts (in mol) of HCl and NaOH are equal 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 solutions of unknown concentrations. A **titration** is a form of analysis in which a base of known concentration and volume is reacted with an acid of unknown concentration. The volume needed to neutralise the base can be used to determine the concentration of the acid by stoichiometric calculations. The concentration of a base can also be determined by titration with an acid of known concentration and volume.

In titrations, accurate glassware such as burettes, volumetric flasks and pipettes are used to measure the volumes so you can accurately determine the amount (in moles) and concentration of solutions involved in the reaction. Volumetric analysis will be discussed in more detail in Chapter 7.

The **end point** of the indicator is the point in a titration when the indicator changes colour. It is vital that an indicator is chosen that changes colour sharply in the region of the equivalence point. At this point, the colour of the indicator will be intermediate between its colour in acidic solution and its colour in alkaline solution.

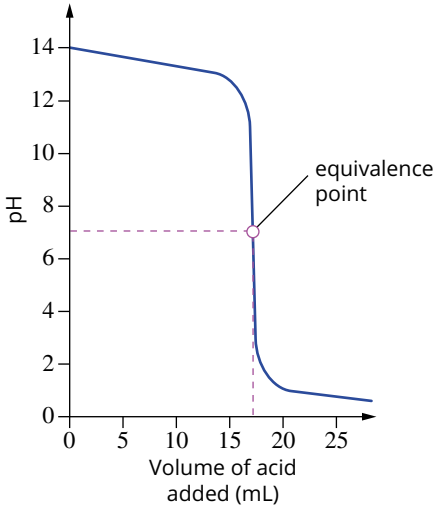


FIGURE 6.3.1 Titration curve for a strong acid being added to a strong base

When a strong acid such as HCl is titrated against a strong base such as NaOH, the change in pH can be graphed to produce 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 6.3.1.

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 in this pH range (for example, bromothymol blue pH range 6.0–7.6), one drop will cause a colour change. This is referred to as a sharp end point. Therefore, it is important to know the pH range of an indicator to ensure a sharp end point. Other indicators, including phenolphthalein (pH range 8.3–10.0), could also be used for this titration because they would also produce a sharp end point.

EXTENSION

Determining 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^- represents 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.

Figure 6.3.2 shows the colour of phenol red at different pH values. Phenol red has a K_a of 10^{-8}. Therefore, the concentration of hydronium 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 and pH 9.

FIGURE 6.3.2 Phenol red indicator at pH 5, pH 8 and pH 11.

6.3 Review

SUMMARY

- 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 during the titration at which the indictor changes colour.
- Indicators used in titrations should be chosen so that they give a sharp end point.
- The end point in an acid–base titration must be at or close to the equivalence point.

KEY QUESTIONS

1 Explain the difference between the end point and equivalence point of a titration.

2 The acidic form of alizarin yellow is yellow, whereas its basic form is red. At pH 11, the concentrations of the acidic form and its conjugate base are equal. Which one of the following statements about alizarin yellow is correct?

A Alizarin yellow changes colour at exactly 11.

B A solution of alizarin yellow at pH 11 is neutral.

C The indicator can be used to distinguish between a solution of pH 9 and a solution of pH 13.

3 Congo red is an acid–base indicator. The acid colour of the indicator is blue and the base colour is red. The acidic 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 Complete the balanced equation that represents the ionisation of Congo red in aqueous solution.

$HCgr(aq) + H_2O(l) \rightleftharpoons$ _____ + _____

b What will the colour of the solution be:

i at pH 4?

ii in a neutral solution?

iii at pH 2?

iv at pH 12?

Chapter review

06

KEY TERMS

bromothymol blue
end point
equivalence point
indicator
indicator range
methyl orange
pH curve
phenolphthalein
titration
titration curve
transition point
universal indicator
volumetric analysis

Characteristics of indicators

1 Write the general equation for the equilibrium that exists between the acidic form of an indicator and its conjugate base.

2 Which of the following statements about acid–base indicators is not true?

- **A** Indicators are coloured compounds that change colour as the pH of a solution changes.
- **B** Indicators can act as weak acids.
- **C** All indicators are derived from plant extracts.
- **D** Indicator colours are visible at low concentrations of the indicator.

Common indicators

3 Refer to Figure 6.1.1 on page 138 to determine what colour the following indicators will produce in pure water.

- **a** methyl orange
- **b** phenolphthalein
- **c** bromothymol blue

4 State whether the following indicators are natural or synthetic in origin. If natural, what have they been extracted from?

- **a** methyl orange
- **b** litmus
- **c** bromothymol blue

5 Why does universal indicator appear coloured across a range of pH values?

6 Bromothymol blue is added to a solution of pH 5.

- **a** What colour would the solution be?
- **b** What does this indicate about the position of the equilibrium of the indicator reaction?

pH range of an indicator

7 At what pH would phenolphthalein provide a sharp end point during a titration and what colour would you expect to see at the end point of the titration?

8 Define ‘end point’ and 'equivalence point'.

Connecting the main ideas

9 Why is it important to select an indicator with an end point close to the equivalence point for the reaction?

10 Use Le Châtelier’s principle to describe why indicators are different colours in acidic and basic solutions.

CHAPTER

07 Volumetric analysis

There are two main types of chemical analysis—qualitative and quantitative. In qualitative analysis, chemists identify the substances that are present. For example, they might determine what type of acid, what metal or whether a salt is a chloride or a bromide. Quantitative analysis determines how much of a substance is present. Quantitative analysis can use physical methods or chemical methods for determining quantities of chemicals. Volumetric analysis is an example of chemical quantitative analysis. It involves using a chemical reaction, and the equation for that reaction, to calculate the unknown amount of one chemical, in this case, an acid or a base, from the known quantity of the acid or base that it is reacting with.

There are many situations in which a chemist may want to determine 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 begins by introducing a few examples of where knowing the amount or concentration of an acid or a base is important. It then describes a method used for the analysis of acids and bases in water. This is volumetric analysis, often called titration, and involves chemical reactions between accurately measured quantities of substances in aqueous solution. During this chapter, you will be using chemistry calculation skills that you have learnt earlier in the course, as well as knowledge of acids and bases, and indicators as encountered in Chapters 4 and 6.

Volumetric analysis requires the measuring of accurate volumes using specialised pieces of glassware. This chapter also includes the equipment and techniques of volumetric analysis, as well as the specific calculation skills involved. It concludes by considering the issues of accuracy of measurements and sources of error in volumetric analysis.

Science understanding

- acid–base indicators are weak acids, or weak bases, in which the acidic form is a different colour from the basic form
- volumetric analysis methods involving acid–base reactions rely on the identification of an equivalence point by measuring the associated change in pH, using appropriate acid–base indicators or pH meters, to reveal an observable end point
- data obtained from acid–base titrations can be used to calculate the masses of substances and concentrations and volumes of solutions involved

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7.1 Acids and bases in water

Pure water has a pH of 7 at 25°C, which is described as neutral. A substance that dissolves in water to give a pH of less than 7 is described as acidic, while a substance that gives a pH greater than 7 is described as basic. pH is a measure of the acidity of an acidic or basic solution and the pH of a solution is linked to the concentration of the hydrogen ions in the solution.

Volumetric analysis is a technique that can be used in a range of situations to calculate accurate quantities of acid or base in a sample of a substance. This data can then be used to compare different substances (for example, the acid contents of different wines or car batteries) or measure changes in the acidity of solutions over time (for example, monitoring the acidity of rain water or run-off from polluted industrial or mine sites).

Common acids include hydrochloric acid, produced naturally in the stomach to help with digestion, and citric acid, naturally found in citrus fruits. Another common acid is sulfuric acid, an important industrial acid. It is used in many different industries, for example, to treat steel, to make fertiliser and in car batteries.

The following situations are examples of where it may be important to determine the concentration and/or the amount of acid or base present.

NATURAL ACIDITY OF RAIN AND RIVER WATER

You might expect rainwater, oceans and mountain streams to have a neutral pH. However, unpolluted rainwater has a pH between 5.5 and 6, and rainwater falling near large cities and industrial areas can be even more acidic.

Water in even the most pristine, unpolluted rivers and lakes has a pH in the range 6.5–8.5. Domestic, agricultural and industrial wastes discharged into rivers can further affect the pH.

pH of rainwater

The natural acidity of rainwater is due to the presence of carbon dioxide in the atmosphere. Carbon dioxide dissolves in rain, forming a very dilute solution of carbonic acid (H_2CO_3):

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

Carbonic acid is a weak acid and only donates a proton to a limited extent to form hydrogencarbonate ions (HCO_3^-) and hydronium ions (H_3O^+) in solution. You will recall that the properties of acid solutions are due to the presence of hydronium ions. This process is represented by the following equation:

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

Small amounts of oxides of nitrogen, NO and NO_2, are formed during lightning strikes. Sulfur dioxide (SO_2) is emitted by volcanic eruptions. The acidic oxides NO_2 and SO_2 in the atmosphere only make a minor contribution to the natural acidity of rainwater.

ACID RAIN

Since the Industrial Revolution, human activity has produced more acidic gases than the amount produced by natural processes. This has resulted in an increase in the acidity (decrease in pH) of rain falling near or downwind from industrial areas, as shown in Figure 7.1.1. This is known as **acid rain**.

The pH of unpolluted rainwater is between 5.5 and 6, but the pH of rainwater in industrial areas may be close to 4 and has even been measured to be as low as 2.4.

Sulfur dioxide gas is the main cause of acid rain. It is produced by the burning of sulfur-containing fossil fuels:

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

Sulfur dioxide is also produced in power stations and from the smelting of ores such as copper sulfide.

FIGURE 7.1.1 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.

The sulfur dioxide is converted to sulfuric acid in a series of reactions that occur in the atmosphere:

$$SO_2(g) \rightarrow SO_3(g) \rightarrow H_2SO_4 \text{ (in rain)}$$

Sulfuric acid is a strong, diprotic acid:

$$H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$$

The internal combustion engine is responsible for the emission of large amounts of nitrogen(II) oxide (NO) and nitrogen(IV) oxide (NO_2). Nitrogen(IV) oxide dissolves in water, forming acid rain. This acid rain is a mixture of nitrous acid (HNO_2) and nitric acid (HNO_3):

$$2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$$

The acid rain created by power stations and smelters is particularly severe in parts of the United States, eastern Canada, Europe and Asia. Some industries, such as those involved in the smelting of ores containing metal sulfides, have produced localised acid rain in Australia. Stricter government regulations and international treaties aimed at reducing the emissions of sulfur dioxide and nitrogen oxides have been adopted. Regulations have decreased the concentration of these gases over recent years.

The acidity of rainwater can be measured by using an indicator such as universal indicator or by using a pH probe, which is more accurate. However, quantitative analysis techniques, such as volumetric analysis, can be used to calculate more accurate data relating to the concentration of hydrogen (or hydronium) ions, and therefore the acidity of the water.

ACIDS IN WINE

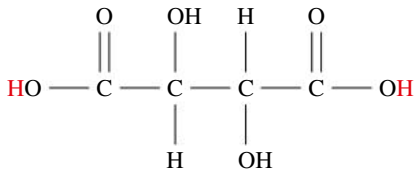
Grapes and several plants contain the naturally occurring acid tartaric acid (Figure 7.1.2). There are several acids present in wine, many of which form during the fermentation process. Two of the main acids present in wine occur naturally in the grape (fixed acids). Tartaric acid is the primary and strongest acid, giving wine its crisp, tart flavour. Malic acid is the other main acid. Both of these acids are weak dicarboxylic acids. Their structures are shown in Figure 7.1.3. Citric acid is also present in significant amounts and gives wine its fruity taste.

FIGURE 7.1.2 Malic acid is a common acid found in fruit, but tartaric acid is mainly found in grapes.

It is important that the wine has the correct level of acid, as too much will cause it to taste tart and sour, while too little will leave the wine tasting flat. The acidity of wine is referred to as total acidity (TA) and is expressed in grams per litre or as a percentage. TA will vary depending on the wine. Sweet wines, for example, tend to have a higher TA or 7.0–8.5 g L^{-1}, while dry wines have a TA of 6.0–7.5 g L^{-1}. To determine the total acidity of wine an acid-base titration can be performed.

Total acidity is also referred to as titratable acidity, as the acidity of wine is determined by titration.

a



b

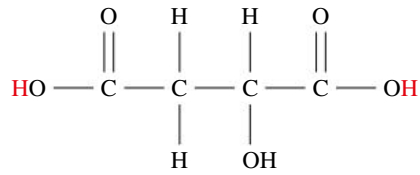


FIGURE 7.1.3 The structural formula of the dicarboxylic acids (a) tartaric acid and (b) malic acid. They have two carboxyl groups and therefore two protons that can ionise (shown in red).

CHEMFILE

The winemaking process

The winemaking process will vary depending on whether the wine is red, white or sparkling, and then there are also fortified wines such as port and sherry to consider. Below is a general outline of the winemaking process.

1 The ripe grapes are picked and crushed in a press.
2 The crushed grapes and juice are drained from the stems and seeds. At this stage the juice is referred to as the must. The skin is left with the must for red wine. For white wines, the skin is separated and only the pulp is used. Red wines are fermented with their skins to give colour and tannins to the wine.
3 The must is added to a vat, barrel or tank along with yeast to ferment for two to four weeks. To ensure the process is proceeding correctly, the fermenting must is checked regularly for acceptable pH levels. This can be done using volumetric analysis.
4 The wine is stored in oak barrels or stainless steel tanks for ageing, which can take from a few months to several years.
5 The wine is racked (by siphoning or pouring) to remove it from the lees (impurities, including the yeast, insoluble salts and remnants of grapes). Some winemakers leave the wine in contact with the lees to allow more flavour to develop.
6 The wine is bottled. Further ageing may occur in the bottle (Figure 7.1.4).
7 Sample testing of the wine, including using volumetric analysis, continues during this storage period.

FIGURE 7.1.4 The bottling of wine is an automated process in many wineries. After bottling, further ageing may occur, particularly for red wine.

7.1 Review

SUMMARY

- Natural and artificial processes affect the acidity of rainwater and waterways.
- Rainwater is naturally acidic due to the presence of dissolved carbon dioxide.
- Waste gases, such as sulfur dioxide and nitrogen oxides that are produced by industry, can cause acid rain.
- Unpolluted water in rivers and lakes has a natural pH between 6.5 and 8.5.
- Dissolved carbon dioxide tends to make river water acidic.
- There are many acids present in wine, including the two naturally occurring, dicarboxylic acids, tartaric acid and malic acid.
- Total acidity is a measure of all the acid content of wine and is determined by titration.

KEY QUESTIONS

1 What type of compounds tend to react with rainwater to lower its pH?
2 What is the source of nitrogen oxides and what effect do they have on the pH of rainwater?
3 Write a balanced equation for the reaction between sulfuric acid in acid rain and the limestone found in many statues and buildings.
4 Draw the structural formula of ethanoic (acetic) acid and tartaric acid. Circle the carboxylic acid functional groups in each and highlight the ionisable protons. Explain why ethanoic acid is a monoprotic acid and tartaric acid is called a diprotic acid.

7.2 Calculations involving acids and bases

In this section, you will revise how to calculate how much product is produced and how much reactant is required in these reactions.

For example, it is very useful to be able to determine 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 carry out calculations involving acids and bases.

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 earlier chapters that the:

- coefficients in a balanced chemical equation give the ratio in which substances react
- amount of solid, in moles, 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}
- amount of solute, in moles, in a solution is given by $n = cV$
- where c is the concentration in mol L^{-1} and V is the volume in litres.

The following worked examples show the four main steps in solving calculation problems involving solutions of acids and bases.

1. Write a balanced equation for the reaction.
2. Identify the substance that is the 'known'. This is the substance for which there is enough information (normally the volume and concentration) to calculate the number of moles and calculate the amount, in mol, of this known substance.
3. Use the mole ratio from the equation to calculate the amount, in mol, of the 'unknown' substance.
4. Calculate the volume or concentration from the number of moles.

The steps in a stoichiometric calculation can be summarised as shown in the flow chart in Figure 7.2.1.

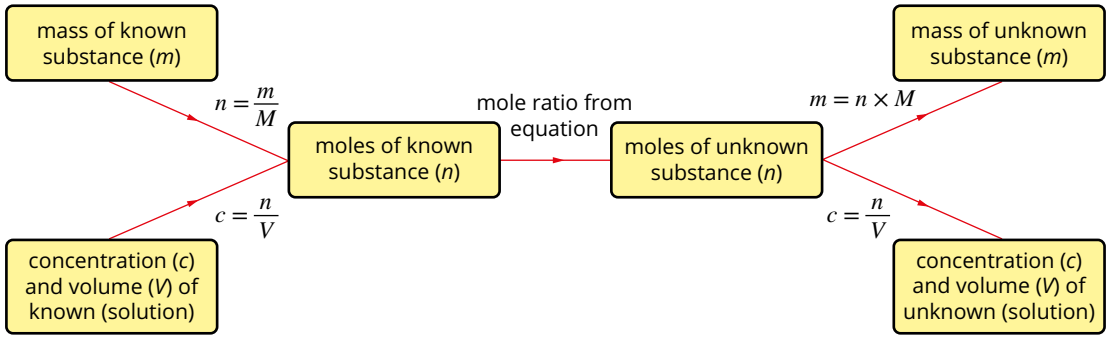


FIGURE 7.2.1 Flow chart for mass and solution calculations

Worked example 7.2.1

A SOLUTION VOLUME–VOLUME CALCULATION

What volume of 0.100 mol L^{-1} sulfuric acid reacts completely with 17.8 mL of 0.150 mol L^{-1} potassium hydroxide?

Thinking	Working
Write a balanced full equation for the reaction.	$2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$
Identify the 'known', and calculate the amount, in mol, of the substances with known volume and concentration.	The known is potassium hydroxide (the volume and concentration of potassium hydroxide solution are given). 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 amount, in mol, 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 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 So 13.4 mL of 0.100 mol L^{-1} H_2SO_4 will react completely with 17.8 mL of 0.150 mol L^{-1} KOH solution.

Worked example: Try yourself 7.2.1

A SOLUTION VOLUME–VOLUME CALCULATION

What volume of 0.500 mol L^{-1} hydrochloric acid (HCl) 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.

Worked example 7.2.2

A SOLUTION VOLUME–CONCENTRATION CALCULATION

15.5 mL of dilute hydrochloric acid reacts completely with 20.8 mL of 0.0100 mol L^{-1} calcium hydroxide. Calculate the concentration of the hydrochloric acid.

Thinking	Working
Write a balanced full equation for the reaction.	$Ca(OH)_2(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$
Identify the 'known', and calculate the amount, in mol, of the substance with known volume and concentration.	The known is calcium hydroxide (the volume and concentration of calcium hydroxide solution are given). Use $n = cV$ (remember that volume must be expressed in litres). $n(Ca(OH)_2) = cV$ $= 0.0100 \times 0.0208$ $= 0.000208$ mol
Use the mole ratio from the equation to calculate the amount, in mol, of the required substance.	The balanced equation shows that 2 mol of hydrochloric acid reacts with 1 mol of calcium hydroxide. $\frac{n(HCl)}{n(Ca(OH)_2)} = \frac{2}{1}$ $n(HCl) = \frac{2}{1} \times n(Ca(OH)_2)$ $= \frac{2}{1} \times 0.000208$ $= 0.000416$ mol
Calculate the concentration required.	The concentration of HCl is found by using $c = \frac{n}{V}$ $c(HCl) = \frac{n}{V}$ $= \frac{0.000416}{0.0155}$ $= 0.0268$ mol L^{-1}

Worked example: Try yourself 7.2.2

A SOLUTION VOLUME–CONCENTRATION CALCULATION

20.5 mL of 0.200 mol L^{-1} hydrochloric acid reacts completely with 18.8 mL of sodium hydroxide solution. Calculate the concentration of the sodium hydroxide.

7.2 Review

SUMMARY

- 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. Write a balanced equation for the reaction.
  2. Calculate the amount, in mol, of the known substance.
  3. Use the mole ratio of reactants and products in the balanced chemical equation to calculate the amount, in mol, of the unknown substance.
  4. Convert the amount, in mol, of the required substance to the quantity required in the question.
- The most common unit of concentration is moles per litre ($mol\,L^{-1}$). Volumes should be converted to litres before being used in these calculations.

KEY QUESTIONS

1 A $0.100\,mol\,L^{-1}$ H_2SO_4 solution is neutralised with 10.0 mL of a solution of 0.300 M KOH.
- **a** Write a balanced equation for this reaction.
- **b** What volume of sulfuric acid was neutralised?

2 15.0 mL of a nitric acid solution is required to react completely with 10.0 mL of a $0.100\,mol\,L^{-1}$ $Ca(OH)_2$ solution.
- **a** Write a balanced equation for this reaction.
- **b** What is the concentration of the nitric acid solution?

3 18.26 mL of dilute nitric acid reacts completely with 20.00 mL of $0.09927\,mol\,L^{-1}$ potassium hydroxide solution.
- **a** Write a balanced chemical equation for the reaction between nitric acid and potassium hydroxide.
- **b** Calculate the amount, in mol, of potassium hydroxide consumed in this reaction.
- **c** What amount, in mol, of nitric acid reacted with the potassium hydroxide in this reaction?
- **d** Calculate the concentration of the nitric acid.

7.3 Standard solutions

FIGURE 7.3.1 Apparatus and materials needed to prepare a standard solution. The measured mass of solid will be dissolved in water in a volumetric flask to make an accurate volume of solution.

Volumetric analysis can be used to accurately determine the concentration of solutions of acids and bases. This involves reacting the solution of unknown concentration with a solution of accurately known concentration (a **standard solution**). This section focuses on the preparation of standard solutions. Some of the equipment used to prepare a standard solution is shown in Figure 7.3.1.

PRIMARY STANDARDS

Pure substances are widely used in the laboratory to prepare solutions of accurately known concentrations.

Substances that are so pure that the amount of substance, in moles, can be calculated accurately from their mass are called **primary standards**.

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.

Examples of primary standards are the base anhydrous sodium carbonate (Na_2CO_3) and the acid hydrated oxalic acid ($H_2C_2O_4 \cdot 2H_2O$). (The term **anhydrous** indicates there is no water present in the compound.)

PREPARING STANDARD SOLUTIONS

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 7.3.2.

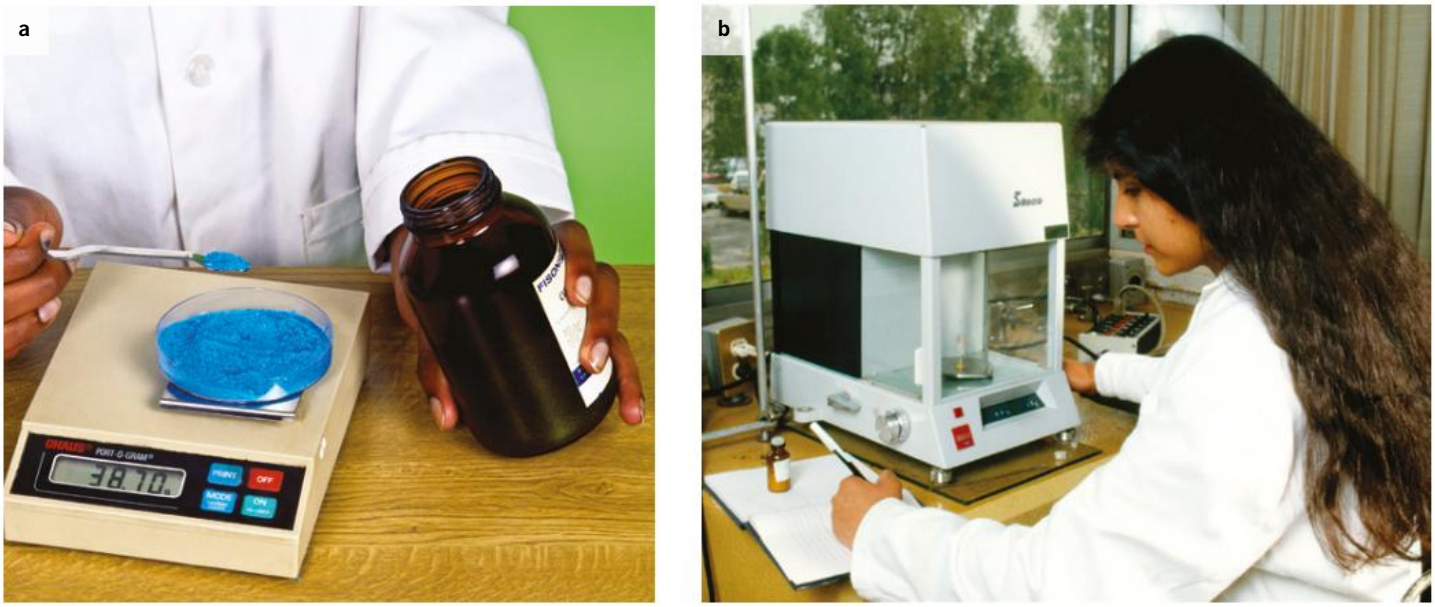


FIGURE 7.3.2 (a) A top-loading balance and (b) an analytical balance can be used to accurately weigh substances used in chemical analysis.

A **volumetric flask** or standard flask (Figure 7.3.3) is used to prepare a solution that has an accurately known volume. Volumetric flasks of 50.00 mL, 100.00 mL and 250.0 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 (Figure 7.3.4). Your eye should be level with the line to avoid **parallax errors**.

FIGURE 7.3.3 Volumetric flasks of various sizes are used to prepare standard solutions.

FIGURE 7.3.4 This close-up view of the neck of a volumetric flask shows the bottom of the meniscus level with the graduation line.

To prepare a standard solution from a primary standard, you need to dissolve an accurately known amount of the substance in distilled water to produce a solution of known volume. The steps in this process are shown in Figure 7.3.5.

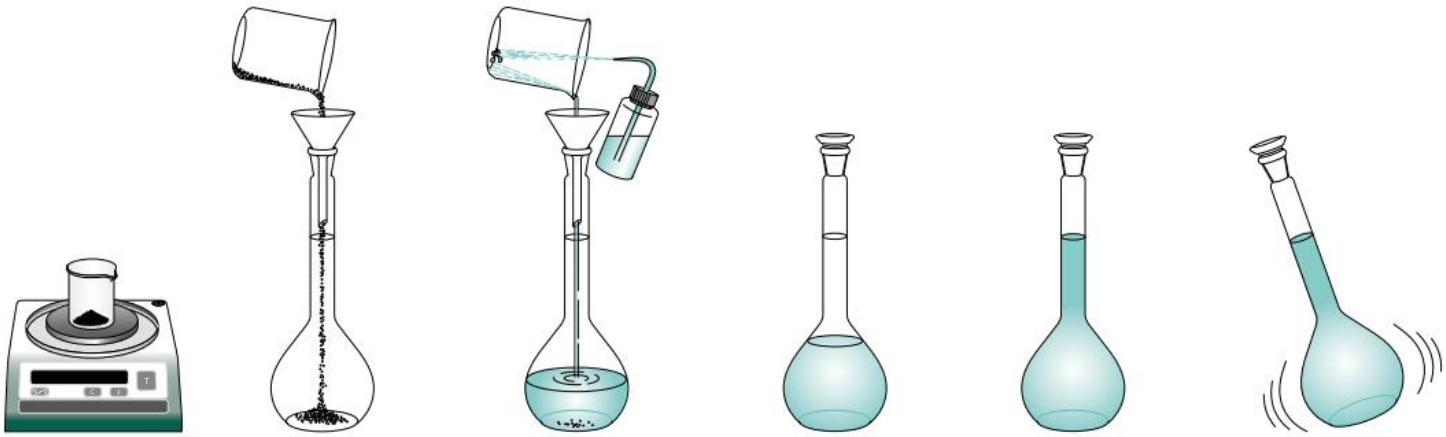


FIGURE 7.3.5 Preparing a standard solution from a primary standard

The molar concentration of the standard solution is then found by using these formulas:

$$\text{amount in mol, } n = \frac{\text{mass of solute (in g)}}{\text{molar mass (in g mol}^{-1}\text{)}} = \frac{m}{M}$$

$$\text{concentration, } c = \frac{\text{amount of solute (in mol)}}{\text{volume of solution (in L)}} = \frac{n}{V} = \frac{m}{M \times V}$$

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
- many hydrated salts, such as hydrated 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 (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). This is done by titration, which is discussed in the next section.

Concentration of standard solutions

Figure 7.3.6 summarises the steps involved in calculating the concentration of a standard solution from the accurately measured mass of a primary standard.

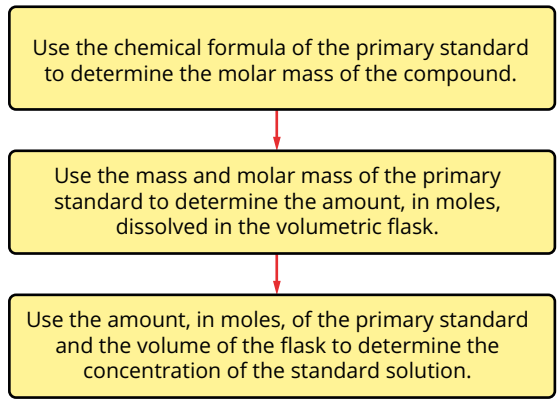


FIGURE 7.3.6 A summary of the steps used in the calculation of the concentration of a standard solution prepared from a primary standard

Worked example 7.3.1

CALCULATING THE CONCENTRATION OF A STANDARD SOLUTION PREPARED FROM A PRIMARY STANDARD

The primary standard sodium carbonate is used to standardise solutions of acids. Calculate the concentration of a standard solution prepared from 5.05 g of sodium carbonate (Na_2CO_3) dissolved in a 500 mL volumetric flask.

Thinking	Working
Use the chemical formula to determine the molar mass (M) of the compound.	The molar mass (M) of Na_2CO_3 is $(22.99 \times 2) + 12.01 + (16.00 \times 3) = 105.99\ g\ mol^{-1}$
Use the mass (m) and molar mass (M) of the compound and the formula $n = \frac{m}{M}$ to determine the amount, in mol.	$n = \frac{5.05}{105.99}$ $= 0.04765\ mol$
Use the amount, in mol, to determine the concentration of the solution using the formula $c = \frac{n}{V}$.	$c = \frac{0.04765}{0.500}$ $= 0.0953\ mol\ L^{-1}$

Worked example: Try yourself 7.3.1

CALCULATING THE CONCENTRATION OF A STANDARD SOLUTION PREPARED FROM A PRIMARY STANDARD

Calculate the concentration of a standard solution prepared from 17.0 g of oxalic acid dihydrate ($H_2C_2O_4.2H_2O$) dissolved in a 250.0 mL volumetric flask.

7.3 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.
- 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.

KEY QUESTIONS

1 Describe the steps required for the correct preparation of a standard solution.

2 Potassium hydrogen phthalate ($KH(C_8H_4O_4)$) is used as a primary standard for the analysis of bases. 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 $204.2\ g\ mol^{-1}$.

3 Calculate the mass of anhydrous sodium carbonate (Na_2CO_3) required to prepare 250.0 mL of a $0.500\ mol\ L^{-1}$ standard solution.

7.4 Volumetric analysis

The pain caused by indigestion occurs when your stomach produces excessive quantities of acidic gastric juices. The protein-digesting enzyme pepsin in gastric secretions works best at pH 3. This pH is due to hydrochloric acid contained in the gastric juice. Commercial antacids (Figure 7.4.1) contain bases such as magnesium hydroxide, sodium hydrogencarbonate and aluminium hydroxide to neutralise the acid secretions and relieve the discomfort.

FIGURE 7.4.1 The suitability of antacids can be assessed by acid–base reactions.

To compare the effectiveness of antacids, you could design experiments to find out what volume of hydrochloric acid reacts with each brand. This would allow you to determine which antacid is best at neutralising the acidic secretions.

There are many situations when you may want to find the amount of a substance in solution. For example, you might want to determine the composition of antacid tablets, the chemicals present in industrial waste, or the acidity of polluted rainwater.

This section describes a method used for the analysis of acids or bases in a solution. The method is called volumetric analysis and involves chemical reactions between substances in aqueous solution.

You will also learn how specialised glassware is used during volumetric analysis.

ACID–BASE TITRATIONS

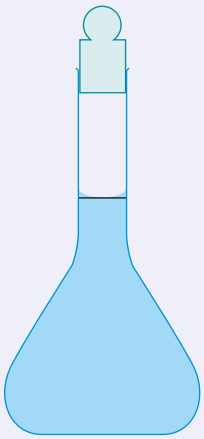
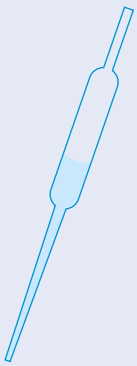
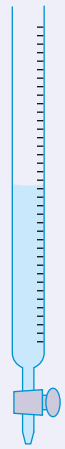
Volumetric equipment

Often the concentrations of acids and bases used in industry are unknown. The laboratory equipment shown in Table 7.4.1 is used to make precise measurements of mass and volume. These instruments, combined with calculations similar to those in section 7.2 of this chapter, 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. This is called the **equivalence point**.

TABLE 7.4.1 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 mol of HCl has been added for each 1 mol of Na_2CO_3. This whole process is called a **titration**.

The reaction is complete when the equivalence point is reached. The concentration of the standard sodium carbonate solution is known, and volume of sodium carbonate is now known (measured from the burette), as is the volume of the aliquot of hydrochloric acid used. The concentration of the acid can then 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. 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.

Figure 7.4.2 shows how the equipment listed would be used to complete the titration for the reaction of Na_2CO_3 and HCl.

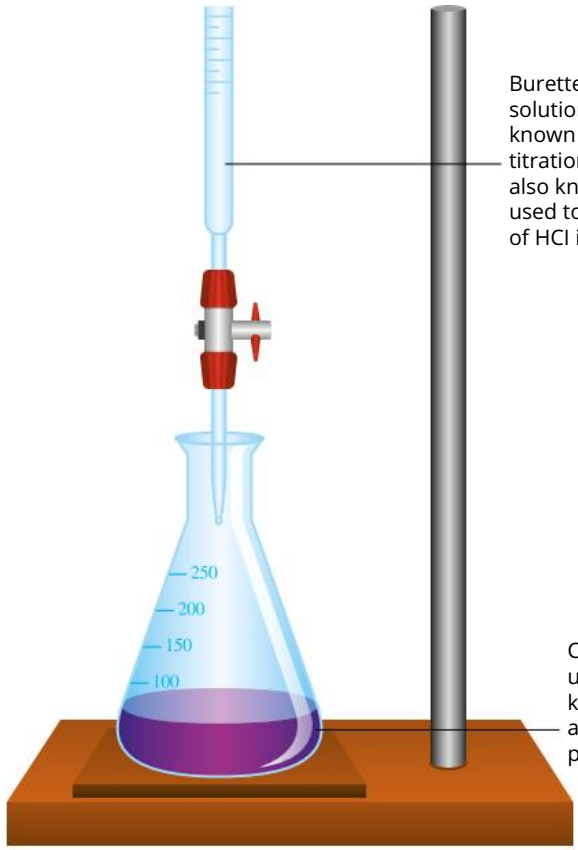


FIGURE 7.4.2 The equipment used in the titration of Na_2CO_3 (in the burette) to determine the concentration of HCl (in the conical flask)

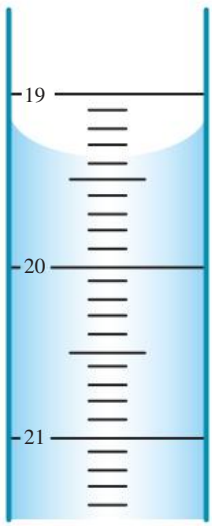


FIGURE 7.4.3 The burette is read from the bottom of the meniscus and the volume is estimated to the second decimal place. The volume measurement in this case is 19.38 mL.

Using a burette

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 the nearest 0.02 mL, as shown in Figure 7.4.3.

To minimise errors, the titration is repeated several times and the **average titre** is found. Usually three **concordant titres** are used to find this average. Concordant titres are within 0.20 mL from highest to lowest of each other.

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 a couple of drops over or under the accurate titre.

Consider the titration data represented in Table 7.4.2.

TABLE 7.4.2 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, which gives an idea of the approximate end point. Titres 2, 4 and 5 are the concordant titres: they are within 0.20 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. The mean (average) titre is:

$$\frac{19.82 + 19.78 + 19.86}{3} = 19.82\,\text{mL}$$

INDICATORS

You will recall from Chapter 6 that one of the characteristic properties of acids and bases is their ability to change the colour of certain chemicals called indicators.

The colours of indicators are usually intense and highly visible, even at low concentrations. As Figure 7.4.4 and Table 7.4.3 show, different indicators change colour over different pH ranges.

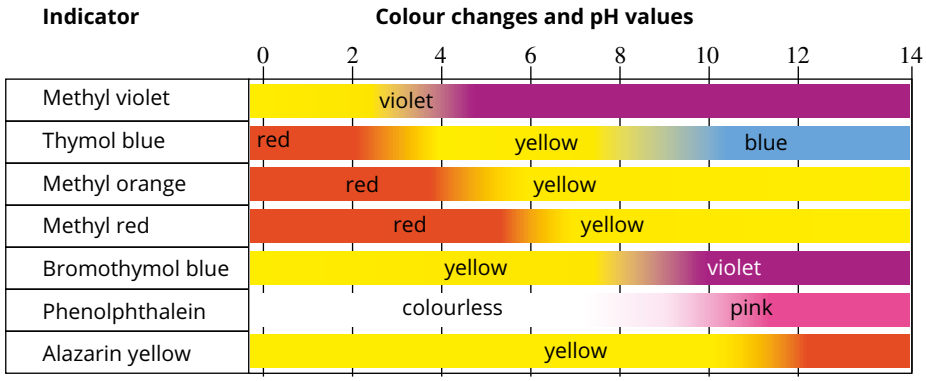


FIGURE 7.4.4 The colours of common indicators at different pH values

TABLE 7.4.3 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	3.2–4.4
Bromothymol blue	Yellow	Blue-violet	6.0–7.6
Phenolphthalein	Colourless	Pink	8.2–10.0

Characteristics of indicators

- Indicators are large organic molecules whose colour changes in response to changes in the pH of the solution in which they are dissolved.
- 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 depends 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.

To better understand the characteristics of indicators in titrations, review the section on the common laboratory indicators in Chapter 6 (page 141).

As an example of an indicator, bromothymol blue is one that is widely used. The indicator is yellow in acidic solutions and blue-violet in basic solutions. The simplified equation for the ionisation of bromothymol blue in water is:

$$HBB(aq) + H_2O(l) \rightleftharpoons BB^-(aq) + H_3O^+(aq)$$

yellow blue-violet

The indicator colour we see depends on the relative concentrations of HBB and BB^-.

pH change during a titration

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 7.4.5.

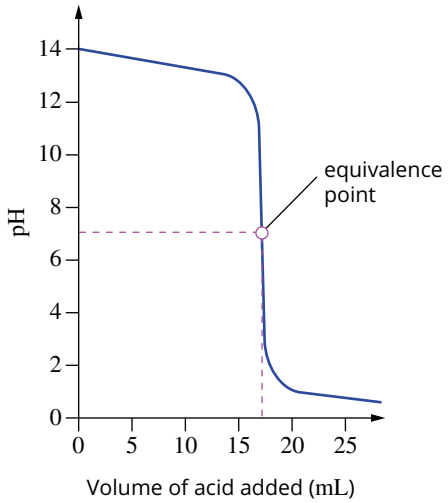


FIGURE 7.4.5 Titration curve for a strong acid being added to a strong base

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 (pH 6.0–7.6), 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 8.3–10.0), could be used for this titration because they would also produce a sharp end point for this reaction.

Figure 7.4.6 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.

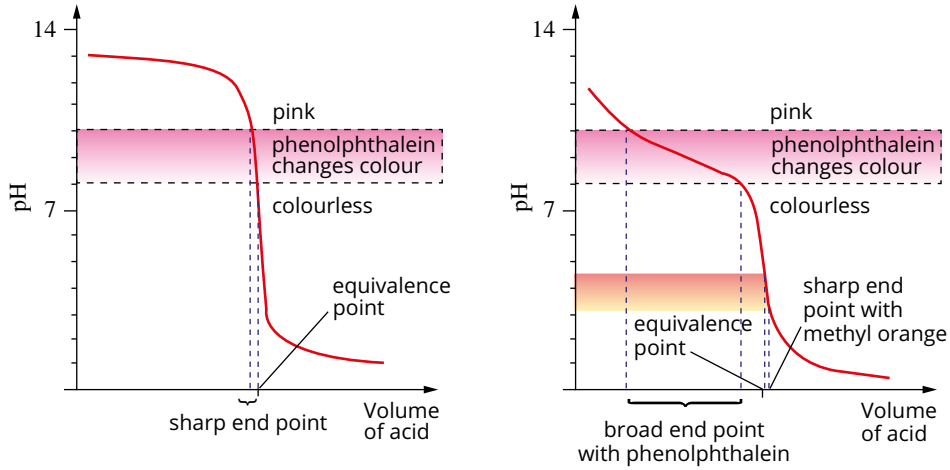


FIGURE 7.4.6 Titration curves showing the pH during a titration of (a) a strong base with a strong acid, and (b) a weak base with a strong acid. Phenolphthalein, which changes colour between pH 8.3 and 10.0, gives a sharp end point in (a) but a broad end point in (b). Methyl orange, which changes colour between pH 3.2 and 4.4, would be a more suitable indicator for the second titration.

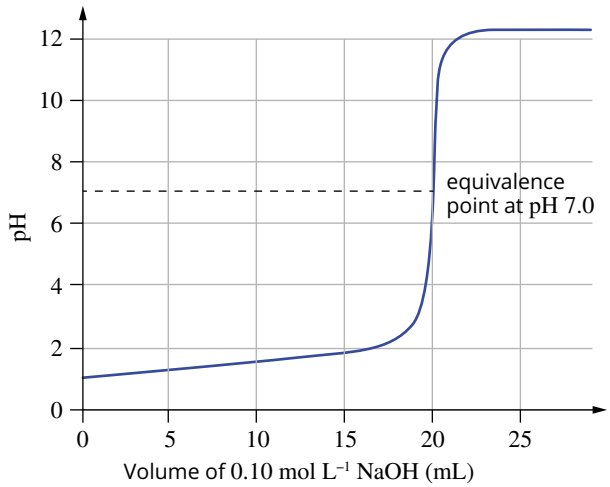
7.4 Review

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.

KEY QUESTIONS

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



The titration is repeated using 0.20 mol L^{-1} sodium hydroxide solution. Which one of the following statements about the second titration is correct?

A The equivalence point occurs when 10 mL of NaOH is added and the pH is then 7.

B The equivalence point occurs when 10 mL of NaOH is added and the pH is then greater than 7.

C The equivalence point occurs when 40 mL of NaOH is added and the pH is then 7.

D The equivalence point occurs when 40 mL of NaOH is added and the pH is then greater than 7.

2 Five test-tubes each contain the same solution, which has a pH of 5. A different indicator is added to the solution in each test-tube, as shown in the table below. Use the indicator colour chart in Figure 7.4.4 on page 165 to find the colour of each solution after the indicator is added.

Indicator	Colour after adding indicator
Alizarin yellow	
Bromothymol blue	
Methyl red	
Methyl orange	
Phenolphthalein	

3 The following titres were obtained when a solution of sulfuric acid 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 sulfuric acid that would be used in volumetric calculations.

7.5 Calculations in volumetric analysis

Using volumetric analysis, chemists are able to determine the amount, in mol, of an unknown substance in solution by reacting it with a known standard solution.

This section shows you how to use data from a titration to calculate the concentration of the acid or base being analysed. You will also be introduced to ideas of accuracy and precision in experimental work.

TITRATIONS

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 7.5.1.

TABLE 7.5.1 Sample data obtained from a volumetric analysis

Volume of aliquot of HCl (mL)	25.00
Concentration of standard NaOH solution (mol L^{-1})	1.00
Titre volumes of NaOH (mL)	25.05, 22.10, 22.00, 22.05

The concentration of hydrochloric acid is calculated by following a number of steps. These steps are summarised in the flow chart shown in Figure 7.5.1.

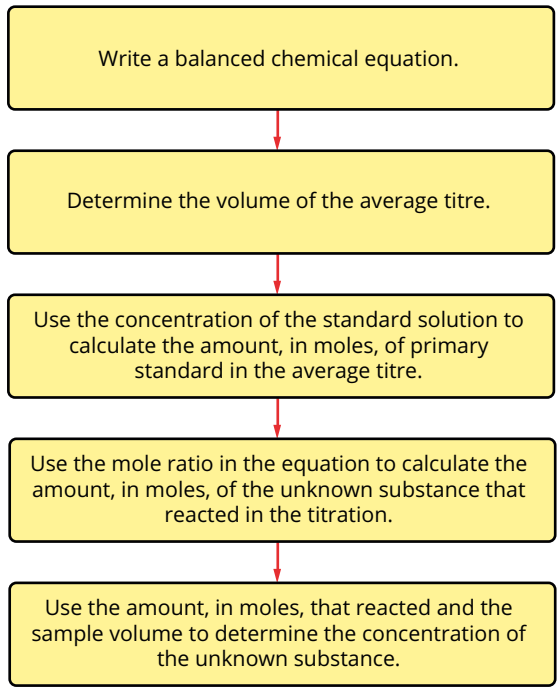


FIGURE 7.5.1 This flow chart summarises the steps in calculating the concentration of an unknown substance using the data from a titration in which the standard solution was in the burette.

Worked example 7.5.1

SIMPLE TITRATIONS

The concentration of hydrochloric acid was determined by titration with a standard solution of sodium hydroxide.

A 25.00 mL aliquot of HCl was titrated with a 1.00 mol L^{-1} solution of sodium hydroxide. Titres of 25.05 mL, 22.10 mL, 22.05 mL and 22.00 mL were required to reach the end point.

What is the concentration of the hydrochloric acid solution?

Thinking	Working
Write 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 because it is not concordant (i.e. it is not within a range of 0.20 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 amount, in mol, of the standard ('known') solution that was required to reach the end point. Remember the volume must be expressed in litres.	$n(NaOH) = cV$ $= 1.00 \times 0.02205$ $= 0.02205\ \text{mol}$
Use the mole ratio in the equation to calculate the amount, in mol, of the unknown substance that would have reacted with the given amount, in mol, 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 three 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}

Worked example: Try yourself 7.5.1

SIMPLE TITRATION

The concentration of a solution of barium hydroxide ($Ba(OH)_2$) was determined by titration with a standard solution of hydrochloric acid.

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 and 17.21 mL of HCl were required to reach the end point.

What is 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 7.5.2.

TABLE 7.5.2 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 later in the calculations.

The steps required to calculate the concentration of undiluted concrete cleaner are summarised in the flow chart shown in Figure 7.5.2.

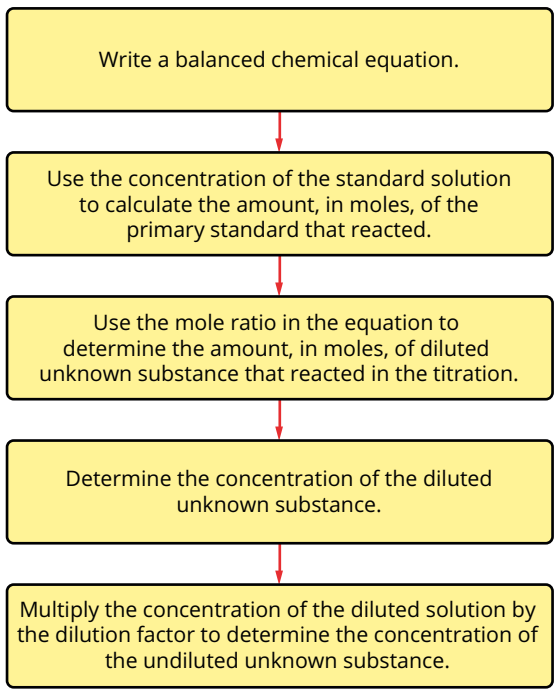


FIGURE 7.5.2 This flow chart shows the steps used in the calculation of the concentration of an unknown substance that has been diluted for use in a titration.

Worked example 7.5.2

TITRATION THAT INVOLVES DILUTION

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 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 red when 19.84 mL of the cleaner was added.

Calculate the concentration of hydrochloric acid in the concrete cleaner.

Thinking	Working
Write 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 amount, in mol, of the known substance that reacted in the titration. Remember that volume must be expressed in litres.	$n(Na_2CO_3) = cV$ $= 0.4480 \times 0.02000$ $= 0.008960\ \text{mol}$
Use the mole ratio in the equation to calculate the amount, in mol, of the diluted unknown solution that reacted in the titration.	$\frac{n(HCl)}{n(Na_2CO_3)} = \frac{2}{1}$ $n(HCl) = \frac{2}{1} \times n(Na_2CO_3)$ $= \frac{2}{1} \times 0.008960$ $= 0.01792\ \text{mol}$
Calculate the concentration of diluted unknown solution reacting in the titration.	$V(\text{diluted HCl}) = 0.01984\ \text{L}$ $c(HCl) = \frac{n}{V}$ $= \frac{0.01792}{0.01984}$ $= 0.9032\ \text{mol}\ L^{-1}$
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 $c(HCl) \times 10.00$ $= 0.9032 \times 10.00$ $= 9.032\ \text{mol}\ L^{-1}$

Worked example: Try yourself 7.5.2

TITRATION THAT INVOLVES DILUTION

A commercial concrete cleaner contains hydrochloric acid. 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.

Back titrations

Some acids or bases do not lend themselves to a 'normal' titration. This is often because they have limited solubility in water, so it is not possible to dissolve them to make a completely homogeneous solution. Examples of this are measuring the amount of an insoluble hydroxide in an indigestion tablet, the amount of carbonate in sea shells or the amount of ammonia in the cleaner 'cloudy ammonia', which is a colloid containing ammonia and soap.

A method called **back titration** can be used to determine the amount of acid or base in this situation. The concentration of the acid or base is determined by reacting it with a known amount of excess reagent, usually a standard solution of a strong acid or base.

Some of the added acid or base reacts with the sample being analysed. The remaining excess reagent is titrated with a standard solution of a strong acid or base. Once the amount of excess reactant is determined by the titration, this can be compared to the initial total amount of the acid or base added in excess to calculate, by subtraction, the amount of the acid or base that actually reacted with the sample being analysed.

This process can be illustrated using the following example.

Back titration is used to determine the concentration of ammonium ions (NH_4^+) in lawn feed. The analysis involves two different chemical reactions.

- A measured mass of a lawn feed sample is mixed and heated with a known excess amount of sodium hydroxide (NaOH). All of the ammonium ions in the lawn feed react, leaving some of the strong base unreacted:

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

- The unreacted NaOH is then titrated with a standard solution of a strong acid, hydrochloric acid (HCl):

$$NaOH(aq) + HCl(aq) \rightarrow NaOH(aq) + H_2O(l)$$

The flow chart in Figure 7.5.3 shows the steps followed to calculate the amount, and therefore the concentration of NH_4^+ that was present in the sample of lawn feed.

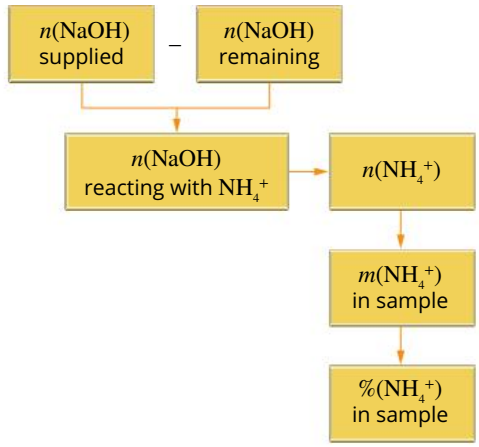


FIGURE 7.5.3 Steps in the calculation of the ammonium content in lawn fertiliser using a back titration

A similar procedure can be used to determine the concentration of a weak base by adding an excess of a strong acid.

Worked example 7.5.3

BACK TITRATION

A student was asked to determine the concentration of ammonia in cloudy ammonia solution used for cleaning. First she pipetted 20.00 mL of the cloudy ammonia solution into a 250.0 mL conical flask.

She then added 50.00 mL of 0.100 mol L^{-1} HCl(aq) to the conical flask to react with the ammonia in solution. The resultant mixture of excess, unreacted HCl was then titrated with 0.050 mol L^{-1} Na_2CO_3(aq). A volume of 20.50 mL of Na_2CO_3(aq) was required.

Calculate the concentration of the ammonia in the cloudy ammonia solution.

Step 1: From the titration results determine the amount of HCl in excess. This is the HCl that is left over after all the ammonia is used up in the first step.

Thinking	Working
Write the equation for the titration.	$2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$
Calculate the moles, n, of Na_2CO_3(aq) that reacted in the titration: moles = concentration (mol L^{-1}) × volume (L)	$n(Na_2CO_3) = c \times V$ $c(Na_2CO_3) = 0.050$ mol L^{-1} $V(Na_2CO_3) = 20.50$ mL = 0.02050 L $n(Na_2CO_3) = 0.050 \times 0.02050 = 0.001025$ mol
Use the balanced chemical reaction for the titration to determine the moles of excess HCl that reacted in the titration.	From the balanced chemical equation, 1 mole Na_2CO_3 reacts with 2 moles of HCl So, 0.001025 mol Na_2CO_3 reacted with 2×0.001025 mol HCl $n(HCl)_{excess} = 0.001025$ mol = 0.002050 mol
Step 2: Determine the amount of ammonia in the cloudy ammonia solution	
Calculate the total moles of HCl originally added to the diluted cloudy ammonia solution: moles = concentration (mol L^{-1}) × volume (L)	$n(HCl) = c \times V$ $c(HCl) = 0.100$ mol L^{-1} $V(HCl) = 50.00$ mL = 0.05000 L $n(HCl)_{total\ added} = 0.100 \times 0.05000 = 0.00500$ mol
Calculate the moles of HCl that reacted with the ammonia in the diluted cloudy ammonia solution by taking away the amount in excess from the total amount.	$n(HCl)_{titrated} + n(HCl)_{reacted\ with\ ammonia} = n(HCl)_{total\ added}$ $n(HCl)_{total\ added} = 0.00500$ mol $n(HCl)_{titrated} = 0.002050$ mol (calculated in Step 1) $n(HCl)_{reacted\ with\ ammonia} = n(HCl)_{total\ added} - n(HCl)_{titrated}$ $n(HCl)_{reacted\ with\ ammonia} = 0.00500 - 0.002050 = 0.00295$ mol
Write the balanced chemical equation for the reaction between ammonia in the cloudy ammonia solution and the HCl(aq).	$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$
From the balanced chemical equation, calculate the number of moles of NH_3 that reacted with HCl.	From the equation, 1 mol HCl reacts with 1 mol NH_3 $n(NH_3) = (1/1) \times n(HCl)$ $= 0.00295$ mol
Calculate the ammonia concentration in the cloudy ammonia solution. concentration (mol L^{-1}) = $\frac{n}{V}$ = moles/volume (L)	$c(NH_3) = \frac{n}{V}$ $n(NH_3) = 0.00295$ mol (moles of NH_3 that reacted with HCl) $V(NH_3) = 20.00$ mL = 0.02000 L (volume of ammonia solution that reacted with HCl) $c(NH_3) = \frac{0.00295}{0.02000} = 0.1475$ mol L^{-1}
State the concentration of ammonia in the cloudy ammonia solution to the correct number of significant figures.	$c(NH_3)$ in the cloudy ammonia = 0.147 mol L^{-1}

Worked example: Try yourself 7.5.3

BACK TITRATION

A student was given a 0.122 g sample of chalk and asked to determine the mass, in grams, of calcium carbonate in the chalk.

The student made the following notes:

- The chalk sample was placed in a 250 mL conical flask.
- Using a 50.00 mL pipette, 50.00 mL of standardised 0.198 mol L^{-1} HCl solution was added to the flask.
- The excess HCl left in the 250 mL conical flask was then titrated using 0.250 mol L^{-1} NaOH solution.
- The experiment was repeated three times and volumes of NaOH added: Trial 1: 32.15 mL, Trial 2: 32.05 mL, Trial 3: 32.10 mL
- The average volume of NaOH titrated was 32.10 mL

Using the student's results, calculate the mass of calcium carbonate, in grams, present in the chalk sample.

UNCERTAINTIES

In this course you are required to estimate the degree of **uncertainty** in experiments such as titration experiments. The accuracy with which the volumes of the aliquot and titre are measured in volumetric analysis depends on the calibration of the pieces of equipment used. 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: ±0.02 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: ±0.3 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 7.5.4 compares accuracy and precision.

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.

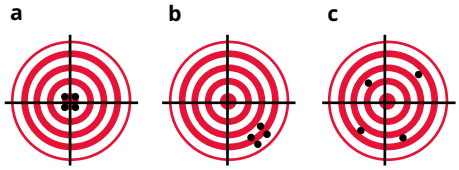


FIGURE 7.5.4 The holes in the targets illustrate the difference between accuracy and precision. Target (a) shows good accuracy and good precision. Target (b) illustrates poor accuracy but good precision, and target (c) shows both poor accuracy and poor precision. Analytical chemists aim to produce results that are both precise and accurate.

TYPES OF 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
- some of a substance or solution being left in the original container, such as a beaker, when being transferred to a new container
- an unsuitable indicator being used
- the mass of the primary standard being inflated because it has not been dried properly and contains some water
- a person reading the scale on a burette with a constant parallax error.

Whatever the cause, the resulting error is in the same direction for every measurement and the average will be either always higher than or always lower than the true value.

Systematic errors are eliminated or minimised through calibration of apparatus and the careful design of a procedure. If you cannot eliminate the error, then you should try 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 using a pipette to measure a volume
- 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.

Mistakes

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 7.5.3.

TABLE 7.5.3 Rinsing glassware for volumetric analysis

	Correct	Incorrect
Burette Pipette	The final rinse should be with the acid or base they are to be filled with.	Rinsing with water only would dilute the acid or base solution.
Volumetric flask Titration flask (conical flask)	Should only be rinsed with deionised water.	Rinsing with acidic or basic solutions will introduce unmeasured amounts of acids or bases into the flask, which can react and affect the results.

A measurement that involves a mistake must be rejected and neither included in any calculations nor averaged with other measurements of the same quantity. Mistakes are not generally referred to as errors.

7.5 Review

SUMMARY

- 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 amount, in mol, of a species in the equation to be calculated from the amount, in mol, 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 a chance of being greater or lower than the true value.

KEY QUESTIONS

1 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.

2 The concentration of ethanoic acid (CH_3COOH) in vinegar was determined by titration with a standardised solution of sodium hydroxide. A 25.00 mL aliquot of vinegar required 21.56 mL of 0.995 mol L^{-1} NaOH to reach the end point.

a Write an equation for the reaction between ethanoic acid and sodium hydroxide.

b Calculate the amount, in mol, of NaOH used in the titration.

c Calculate the amount, in mol, of ethanoic acid that reacted.

d Calculate the concentration of ethanoic acid in the vinegar.

3 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 red when 23.92 mL of the diluted cleaner had been added.

The equation for the reaction is:

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

Calculate the concentration of hydrochloric acid in the concrete cleaner.

4 Determine the concentration of ammonia in a cloudy ammonia cleaning solution, given the following laboratory notes recorded by a student.

Pipetted 25.00 mL of the cloudy ammonia solution into a 250.0 mL conical flask.

Reacted the ammonia in the conical flask with 50.00 mL of 0.102 mol L^{-1} HCl(aq).

Titrated the excess HCl(aq) in the conical flask with 0.050 mol L^{-1} $Na_2CO_3(aq)$.

After three trials, I calculated an average volume of 21.50 mL of $Na_2CO_3(aq)$ was required.

Chapter review

07

KEY TERMS

accurate
acid rain
aliquot
anhydrous
average titre
back titration
burette
concordant titres
dilution factor
end point
equivalence point
indicator
mistake
parallax error
pH curve
pipette
precise
primary standard
quantitative analysis
random errors
standard solution
systematic error
titration
titration curve
titre
uncertainty
volumetric analysis
volumetric flask

Acids and bases in water

1 What are the main gases that contribute to acid rain, and what are the sources of these gases?

2 The following reactions can occur in unpolluted river water:

$$CO_2(g) + 2H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$
$$CaCO_3(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + HCO_3^-(aq) + OH^-(aq)$$

A sample of river water has pH 8.0. Which one of the following statements is true?

A The first reaction is the only reaction occurring.
B The second reaction is the only reaction occurring.
C The first reaction occurs to a greater extent than the second.
D The second reaction occurs to a greater extent than the first.

3 Name two weak acids present in wine.

4 Explain why control and monitoring of the acidity in wine is an important part of the manufacturing process.

Calculations involving acids and bases

5 What volume of 0.200 mol L^{-1} KOH is required to react with 30.0 mL of 0.100 mol L^{-1} HNO_3?

6 What volume of 0.100 mol L^{-1} of NaOH is required to react with 20.00 mL of 0.200 mol L^{-1} HCl?

Standard solutions

7 Sodium borate ($Na_2B_4O_7{\cdot}10H_2O$) is used as a primary standard in volumetric analysis. Some properties of $Na_2B_4O_7.10H_2O$ are listed below. Which one of these properties is not important in its use 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}.

8 Calculate the concentration of a standard solution of hydrated oxalic acid ($H_2C_2O_4{\cdot}2H_2O$) prepared by dissolving 25.21 g of hydrated oxalic acid in 250.0 mL of deionised water.

9 Calculate the mass of Na_2CO_3 required to make a 500 mL standard solution of 0.400 mol L^{-1} Na_2CO_3.

Volumetric analysis

10 Explain the use of each of the following pieces of equipment during a titration.

a burette
b pipette
c volumetric flask

11 Explain the difference between the end point and the equivalence point of a titration.

12 Why is it important to select an indicator with an end point close to the equivalence point for the reaction?

Calculations in volumetric analysis

13 A standard solution of potassium carbonate 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 Write the equation for the reaction.
b Calculate the concentration of the K_2CO_3 solution.
c Calculate the concentration of the sulfuric acid solution.

14 A chemistry student is required to accurately determine the concentration of a solution of hydrochloric acid. First she makes up 250.0 mL of a standard solution of sodium carbonate. This solution contains 1.358 g of Na_2CO_3. She then takes a 20.00 mL aliquot of this standard solution and titrates it against the acid. An average titre of 20.24 mL of acid was required to reach the end point.

a Write a balanced equation for the reaction involving the titration.
b Calculate the concentration of the sodium carbonate solution.
c Find the concentration of the 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, what effect would this have had on the volume of acid required for the titration?

15 1.104 g of sodium carbonate (Na_2CO_3) is dissolved in water in a 250.0 mL volumetric flask. 20.00 mL aliquots of this solution were titrated with nitric acid. An average titre of 23.47 mL was found.
- **a** What is the concentration of the Na_2CO_3 solution?
- **b** What is the concentration of the nitric acid?

16 A student added 50.00 mL of 0.100 mol L^{-1} HCl(aq) to 25.00 mL of a commercial ammonia-based cleaner. The excess hydrochloric acid was titrated against a standardised sodium hydroxide solution. It was neutralised by 21.50 mL of the 0.100 mol L^{-1} NaOH(aq). Calculate the concentration of ammonia in the cleaner.

17 A 3.86 g sample of limestone was analysed using a back titration in order to determine the percentage of calcium carbonate in the rock. The sample was dissolved in 50.00 mL of 2.00 mol L^{-1} HCl(aq). The reaction mixture of excess HCl was made up to 250.00 mL in a volumetric flask. 25.0 mL aliquots of this solution of excess HCl(aq) were titrated using standardised solution of 0.100 mol L^{-1} NaOH(aq) using phenolphthalein indicator. The average NaOH(aq) titre was 38.15 mL. Calculate the:
- **a** number of moles of excess HCl(aq) as determined by the titration
- **b** number of moles of HCl(aq) added to dissolve the calcium carbonate in the sample
- **c** mass, in grams, of $CaCO_3$
- **d** percentage mass of $CaCO_3$ in the limestone sample.

Connecting the main ideas

18 A manufacturer wants to know the exact concentration of hydrochloric acid in the concrete cleaner it produces.
- **a** What substance would you use to make a standard solution for use in this titration and why have you chosen this substance?
- **b** How would you prepare this standard solution for volumetric analysis?
- **c** How should each piece of glassware used in a titration 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** Would the concentration calculated be different if you used a standard solution of another base other than potassium carbonate? Explain.

19 A particular brand of indigestion tablet has magnesium oxide as its active ingredient. Determine the mass, in grams, and percentage mass of magnesium oxide in the tablet. A back titration method was used to analyse one of the tablets. The procedure and results are recorded below.

Mass of tablet = 1.75 g

The tablet was dissolved in 45.00 mL of 2.00 mol L^{-1} HCl solution

The reaction mixture was then made up to 250 mL in a volumetric flask

20.00 mL aliquots were titrated against a 0.100 mol L^{-1} standardised solution of sodium hydroxide using phenolphthalein indicator

The average NaOH titre used was 18.60 mL.
- **a** Write an equation for the reaction of the MgO(s) in the tablet with the HCl solution.
- **b** Write an equation for the titration reaction of the excess HCl solution with the standardised NaOH solution.
- **c** Explain why phenolphthalein indicator was used and describe the colour change observed.
- **d** Calculate the average number moles of NaOH used in the titration.
- **e** Calculate the moles of excess HCl found by titration.
- **f** Calculate the moles of HCl that reacted with the MgO.
- **g** Calculate the mass of MgO in the tablet.
- **h** Determine the percentage of MgO in the tablet.

CHAPTER

08 Redox reactions

Some of the most colourful and exothermic reactions are classified as redox reactions. This group of reactions includes some that are vitally important for the functioning of the human body. Redox reactions also provide the energy and produce key materials for our modern lifestyle.

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 find out how to write balanced half-equations that describe the transfer of electrons, and then how to combine these half-equations to create an overall equation for the reaction. You will also become familiar with redox reactions such as metal displacement reactions.

Science understanding

- oxidation–reduction (redox) reactions involve the transfer of one or more electrons from one species to another
- oxidation involves the loss of electrons from a chemical species, and reduction involves the gain of electrons by a chemical species; these processes can be represented using half-equations and redox equations (acidic conditions only)
- a range of reactions involve the oxidation of one species and reduction of another species, including metal and halogen displacement reactions, combustion and corrosion
- the species being oxidised and reduced in a redox reaction can be identified using oxidation numbers

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8.1 Oxidation and reduction

FIGURE 8.1.1 When glycerol is added to potassium permanganate, a vigorous reaction occurs in which the glycerol is oxidised by the potassium permanganate.

FIGURE 8.1.2 Molten iron from a blast furnace being poured into a bucket

Every day, you depend on a large number of chemical reactions. Many of these are redox reactions (*red*-uction; *ox*-idation). The bleaching of hair, corrosion of metals, extraction of metals from their ores, combustion of fuels, and reactions in batteries that produce electrical energy, as well as respiration and photosynthesis, are all redox reactions. The highly exothermic reaction between glycerol and potassium permanganate shown in Figure 8.1.1 is a spectacular example of a redox reaction.

In this section, you will learn how redox reactions are defined in terms of electron transfer and how to represent this transfer of electrons using half-equations.

INTRODUCING REDOX REACTIONS

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. Pouring the molten iron from the blast furnace is shown in Figure 8.1.2.

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 loses oxygen and the carbon monoxide gains oxygen. The iron(III) oxide is described as having been **reduced** and the carbon monoxide is described as having been **oxidised**.

Oxidation and reduction always occur simultaneously; hence the term 'redox reaction'.

CHEMFILE

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 combining them 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 8.1.3. Some fine particles of copper escape with the gas, causing the green flame.

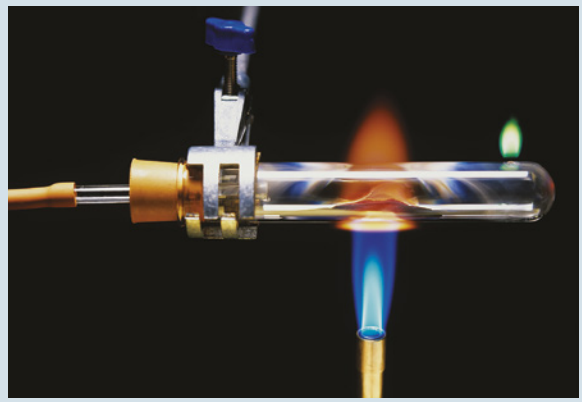

FIGURE 8.1.3 The reduction of copper(II) oxide to form copper powder occurs when copper(II) oxide is heated in the presence of hydrogen or methane gas.

Transfer of electrons

Development of the atomic theory allowed chemists to understand oxidation and reduction reactions as electron transfer processes. The older, limited view of oxidation as the gain of oxygen was replaced by an electron transfer model that defined oxidation as the loss of electrons.

If you heat a piece of magnesium ribbon in an experiment, as shown in Figure 8.1.4, it burns with a brilliant white flame. Magnesium oxide powder is formed.

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 ion (Mg^{2+}). The half-equation for this part of the overall reaction is:

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

Notice that when electrons are lost, they appear as products 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):

$$O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$$

Notice that when electrons are gained, they appear as reactants in the half-equation. The electrons that are gained by the oxygen come from the magnesium atoms.

The burning of magnesium involves the transfer of electrons from magnesium atoms to oxygen atoms. Atoms also lose and gain electrons in many other reactions, and this transfer of electrons provides a definition of oxidation and reduction.

Redox reactions involve the transfer of electrons from one chemical species to another. Redox reactions can be considered as occurring in two halves, both happening simultaneously.

In these reactions:

- one of the reactants *loses* electrons in a process called **oxidation**
- one of the reactants *gains* electrons in a process called **reduction**.

The mnemonic OIL (Oxidation Is Loss) RIG (Reduction Is Gain) is a way to remember the difference between oxidation and reduction processes in terms of electron movement (Figure 8.1.5).

The mnemonic OIL RIG reminds you that:

- oxidation is defined as the loss of electrons
- reduction is defined as the gain of electrons.

FIGURE 8.1.4 Magnesium ribbon burns brightly when heated in air to form a white powder, magnesium oxide.

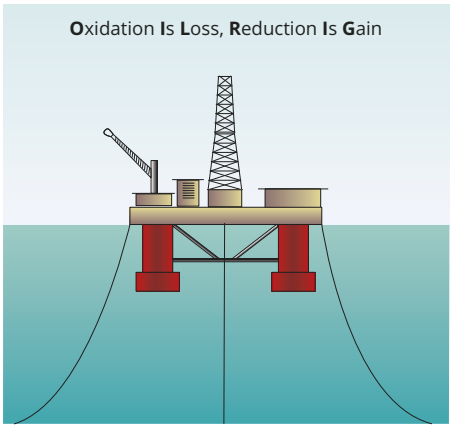

FIGURE 8.1.5 The mnemonic OIL RIG is a useful way to remember that Oxidation Is the Loss of electrons and Reduction Is the Gain of electrons.

Other examples of redox reactions

Many redox reactions do not involve a reaction with oxygen. The reaction between potassium and chlorine, shown in Figure 8.1.6, 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 **halogen displacement reaction** between chlorine gas and potassium bromide solution:

$$Cl_2(g) + 2KBr(aq) \rightarrow Br_2(aq) + 2KCl(aq)$$

Oxidation half-equation: $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$

Reduction half-equation: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$

FIGURE 8.1.6 Potassium burning in chlorine gas is a spectacular example of a redox reaction.

Worked example 8.1.1

IDENTIFYING OXIDATION AND REDUCTION

Write the oxidation and reduction half-equations for the reaction with the overall equation:

$$2NaI(aq) + Br_2(aq) \rightarrow 2NaBr(s) + I_2(aq)$$

Thinking	Working
Identify the ions in the product.	NaBr is made up of Na^+ and Br^- ions.
Write the half-equation for the oxidation of the reactant that forms positive ions and balance the equation with electrons.	$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$
Write the half-equation for the reduction of the reactant and balance the equation with electrons.	$2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Note that this is an example of a halogen displacement reaction in which one halogen is oxidised (the halide ions lose electrons to produce the elemental halogen) and the other halogen is reduced to produce the halide ions. In this situation, the bromine is reduced to bromide ions.

Worked example: Try yourself 8.1.1

IDENTIFYING OXIDATION AND REDUCTION

Write 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

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 8.1.7, 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.

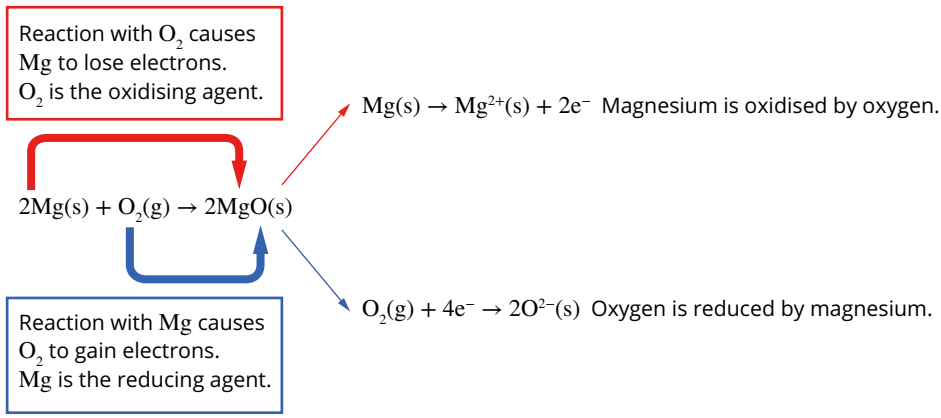

FIGURE 8.1.7 In the reaction between magnesium and oxygen, magnesium is the reducing agent and oxygen is the oxidising agent.

Since metals tend to lose electrons, they act as reducing agents, donating electrons to the substance being reduced.

Figure 8.1.8 summarises the list of redox terms introduced in this section.

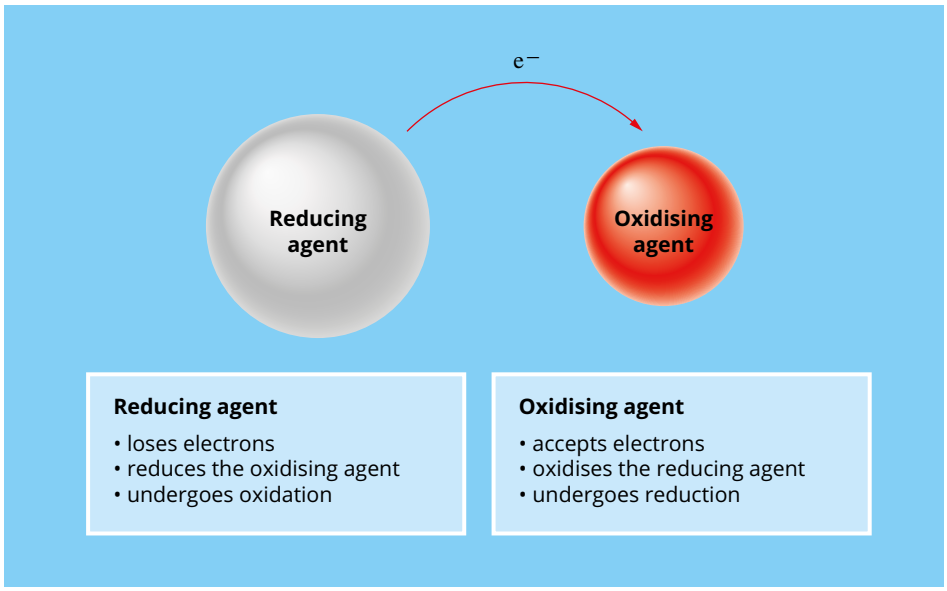

FIGURE 8.1.8 Summary of redox reaction terms

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.

REDOX EQUATIONS

Writing simple half-equations

Half-equations show what is happening as electrons are transferred 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 overall equations should also indicate states.

In an oxidation half-equation, the electrons are 'lost' or produced, so they are always written on the right-hand side of the equation.

The half-equation for the oxidation of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$ is written as:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

Charge is balanced by adding an electron to the right-hand side of the equation.

The half-equation for the reduction of $Cl_2(g)$ to $Cl^-(aq)$ is written as:

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$$

Charge is balanced by adding two electrons to the left-hand side of the equation.

For a reduction process, electrons are 'gained' by the reactant. For this to happen, the electrons must appear on the left-hand side of the equation.

Checking which side of the equation the electrons appear on allows you to determine whether a process is oxidation or reduction.

Worked example 8.1.2

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.
Write these half-equations and identify the substances that are oxidised and reduced.

Thinking	Working
Identify one reactant and the product it forms and write 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 write 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.

Worked example: Try yourself 8.1.2

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 solution.
The oxidation and reduction reactions can be represented by two half-equations.
Write these half-equations and identify the substances that are oxidised and reduced.

FIGURE 8.1.9 The reaction between chlorine and iron is a redox reaction. It is so exothermic that the iron burns as it reacts.

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, or full, equation.

The overall equation does not show any electrons transferred; that is, no electrons appear in a properly balanced full equation. All the electrons lost in the oxidation reaction are gained in the reduction reaction. You may need to multiply one, or perhaps both, of the half-equations by a factor to ensure that the electrons balance and can be cancelled out in the overall equation.

States must be included in both redox half-equations and full equations for each species. Electrons do not have a state and should always cancel in the overall equation.

Consider the reaction of iron and chlorine shown in Figure 8.1.9. In this reaction, each Fe atom is oxidised and loses three electrons. Each Cl_2 molecule is reduced and gains two electrons:

$$Fe(s) \rightarrow Fe^{3+}(s) + 3e^-$$
$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$$

To write an overall equation for this reaction, the number of electrons lost during oxidation must equal the number of electrons gained during reduction. Three electrons are produced by the oxidation of an iron atom, but only two electrons are required to reduce a chlorine molecule.

The lowest common multiple of 3 and 2 is 6. The half-equation involving the oxidation of Fe is multiplied by a factor of 2 to bring the total number of electrons to 6, and the half-equation involving the reduction of Cl_2 is multiplied by a factor of 3 to also bring the total number of electrons to 6:

$$2Fe(s) \rightarrow 2Fe^{3+}(s) + 6e^-$$
$$3Cl_2(g) + 6e^- \rightarrow 6Cl^-(s)$$

When multiplying half-equations, it is essential to multiply the coefficients of all of the species in the equation by the same factor.

The two half-equations are then added to find the overall equation:

$$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$$

You can see that the electrons have been cancelled from each side of the equation to give the overall equation with no electrons.

Worked example 8.1.3

WRITING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Sodium metal is oxidised by oxygen gas in air to form solid sodium oxide. Write the half-equations for the reaction and hence write the balanced overall equation.	
Thinking	**Working**
Identify one reactant and the product it forms, and write 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 write 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.	$(Na(s) \rightarrow Na^+(s) + e^-) \times 4$ $4Na(s) \rightarrow 4Na^+(s) + 4e^-$
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: $4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

Worked example: Try yourself 8.1.3

WRITING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Potassium metal is oxidised by oxygen gas in air to form solid potassium oxide. Write the half-equations for the reaction and hence write the balanced overall equation.

CHEMISTRY IN ACTION

Photochromic sunglasses

Some people wear glasses fitted with photochromic lenses, such as the glasses in Figure 8.1.10. These glasses darken in bright sunlight and become more transparent when the light intensity drops. People who wear these glasses don't need sunglasses because the photochromic lenses can reduce the amount of transmitted light by up to 80%.

Many silver compounds, including silver chloride, are sensitive to light. Tiny crystals of silver chloride are incorporated into the complex silicate-based structure of the glass used to make the photochromic lenses. On exposure to ultraviolet light, which is present in sunlight, the chloride ions are oxidised to chlorine atoms:

$$Cl^- \rightarrow Cl + e^-$$

Electrons produced from this reaction are transferred to silver ions, reducing the silver ions to metallic silver:

$$Ag^+ + e^- \rightarrow Ag$$

The silver metal formed reflects light, causing the lenses to darken, and reducing the intensity of light reaching the wearer's eyes. To prevent the silver metal and chlorine atoms immediately forming silver chloride again, tiny amounts of copper(I) chloride are also added to the glass. Copper(I) chloride reacts with the chlorine atoms, reducing the rate at which silver chloride can be re-formed:

$$Cl + Cu^+ \rightarrow Cl^- + Cu^{2+}$$

The darkening process must be reversible for the glasses to be effective. In the absence of strong sunlight, silver ions are re-formed by a redox reaction involving the silver metal and Cu^{2+} ions:

$$Cu^{2+} + Ag \rightarrow Cu^+ + Ag^+$$

As a consequence, the lenses of the glasses recover their transparency.

FIGURE 8.1.10 The lenses of these photochromic glasses darken in sunlight as a result of redox reactions involving silver chloride.

8.1 Review

SUMMARY

- Redox (reduction–oxidation) reactions involve the transfer of electrons from one species to another.
- Oxidation and reduction always occur at the same time.
- Half-equations are used to represent oxidation and reduction.
- Oxidation is defined as the loss of electrons, e.g. $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$.
- Reduction is defined as the gain of electrons, e.g. $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$.
- The reducing agent (reductant) donates electrons to another substance, causing that substance to be reduced. The reductant is itself oxidised.
- The oxidising agent (oxidant) accepts electrons from another substance, causing that substance to be oxidised. The oxidant is itself reduced.
- Half-equations are added together to obtain the overall equation. Before adding the half-equations, it may be necessary to multiply them by a factor to balance the electrons.
- Halogen displacement reactions occur in which one halogen is oxidised (the halide ions lose electrons to produce the elemental halogen) and the other halogen is reduced to produce the halide ions.

KEY QUESTIONS

1 Complete the summary about redox reactions by using the following terms: 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.

2 Classify each of the following half-equations as oxidation or reduction.

a $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$

b $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

c $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

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

e $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$

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

3 Iron reacts with hydrochloric acid according to the ionic equation:

$Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$

a What has been oxidised in this reaction? What is the product?

b Write a half-equation for the oxidation reaction.

c Identify the oxidising agent.

d What has been reduced in this reaction? What is the product?

e Write a half-equation for the reduction reaction.

f Identify the reducing agent.

4 Balance the following half-equations and then identify 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 $O_2(g) \rightarrow O^{2-}(s)$

5 Name the chemicals that undergo oxidation in the following reactions.

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

b $Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$

c $Cl_2(g) + 2NaI(aq) \rightarrow I_2(aq) + 2NaCl(aq)$

6 Identify each oxidising and reducing agent in Question **5**.

7 When nickel metal reacts with copper(II) ions in an aqueous solution, nickel(II) ions are formed. Write the oxidation half-equation for the reaction.

8 The overall equation for the reaction between aluminium metal and liquid sulfur is:

$$2Al(s) + 3S(l) \rightarrow Al_2S_3(s)$$

From the overall equation, write the half-equations for the redox process and label each one as either reduction or oxidation.

9 Metal M is found to react with oxygen to form the compound M_2O_3. In a separate reaction, metal M reacted with an aqueous solution of silver nitrate ($AgNO_3$). The unbalanced and incomplete equations for the reaction between metal M and $AgNO_3$ are given below.

$Ag^+(aq) + _____ \rightarrow Ag(s)$

$M(s) \rightarrow _____(aq) + ___e^-$

$M(s) + _____(aq) \rightarrow _____(aq) + ____Ag(s)$

a Complete the half-equations and the overall equation for the reaction between metal M and silver ions, $Ag^+(aq)$.

b Identify each half-equation as either reduction or oxidation.

c Identify the oxidising and reducing agents for the reaction.

10 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 Write a half-equation for the oxidation reaction.

c Write a half-equation for the reduction reaction.

d Write 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.

11 Some ions, such as Cu^+, can be either oxidised or reduced.

a Write the formula for the product of the oxidation of Cu^+.

b Write the formula for the product of the reduction of Cu^+.

12 Calcium metal that is exposed to the air forms an oxide coating.

a What is the formula of calcium oxide?

b What has been oxidised in this reaction?

c Write a balanced half-equation for the oxidation reaction.

d What has been reduced in this reaction?

e Write a balanced half-equation for the reduction reaction.

f Write an overall equation for this redox reaction.

g Copy the following statement and fill in the blank spaces with the appropriate words.

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 _____.

8.2 Oxidation numbers

FIGURE 8.2.1 Many redox reactions involve colour changes. It is convenient to assign individual oxidation numbers to the atoms involved in redox reactions such as this.

In this section, you will learn the set of rules that chemists use to classify redox reactions. This involves assigning **oxidation numbers** to the atoms in a reaction.

You will see how oxidation numbers can be used to determine whether a reaction that does not involve the formation of ions could be classified as a redox reaction and which substances in a redox reaction have been oxidised or reduced.

You will also discover that many transition metals have multiple oxidation states and that many of these compounds can be coloured, such as in the reaction shown in Figure 8.2.1.

OXIDATION NUMBERS

In section 8.1 you looked at redox reactions that involved the production of ionic compounds from their elements. In these cases, it was relatively easy to deduce which element gained or lost electrons by considering the charge on the ions produced in the reaction. A species that was reduced gained electrons, becoming less positive, whereas the oxidised species lost electrons, becoming more positive.

For some redox reactions, it is more difficult to identify the species that are oxidised and reduced. For example, the reaction that occurs during the wet corrosion of iron metal can be represented by the half-equations:

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

The first half-equation shows that the iron loses electrons and is oxidised. The second half-equation represents a reduction reaction because electrons have been gained. However, it is not obvious if oxygen or hydrogen has gained these electrons.

It is possible to determine which element has been oxidised and which has been reduced in this reaction by comparing oxidation numbers before and after the reaction. Oxidation numbers can also be called oxidation states.

Oxidation numbers have no real physical meaning. However, they are a useful tool for identifying which atoms have been oxidised and which atoms have been reduced.

Oxidation number rules

Oxidation numbers are assigned to elements involved in a reaction by following a specific set of rules.

Table 8.2.1 describes the rules for determining oxidation numbers. In the examples, 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.

Common oxidation states of the first 36 elements in their compounds are shown in the periodic table in Figure 8.2.2. 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. Appendix D on page 554 includes a list of ions for which you should know the names and formulas.

TABLE 8.2.1 Rules for determining oxidation numbers of elements in compounds

Rule	Examples
1 The oxidation number of a free (uncombined) 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.	Ionic compounds: $\overset{+1}{K}Cl$, $\overset{+2}{Mg}SO_4$
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.	Compounds of H: $\overset{+1}{H_2}O$ Metal hydrides: $Na\overset{-1}{H}$, $Ca\overset{-1}{H_2}$
c Oxygen usually has an oxidation number of –2. Exceptions: In compounds with fluorine, oxygen has a positive oxidation number (because fluorine is more electronegative than oxygen—see rule 6). In peroxides, oxygen has an oxidation number of –1.	Compounds of O: $H_2\overset{-2}{O}$ Peroxides: $H_2\overset{-1}{O_2}$, $Ba\overset{-1}{O_2}$
4 The sum of the oxidation numbers in a neutral compound is zero.	$\overset{+4}{C}\overset{-2}{O_2}$
5 The sum of the oxidation numbers 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.	$\overset{+2}{O}\overset{-1}{F_2}$

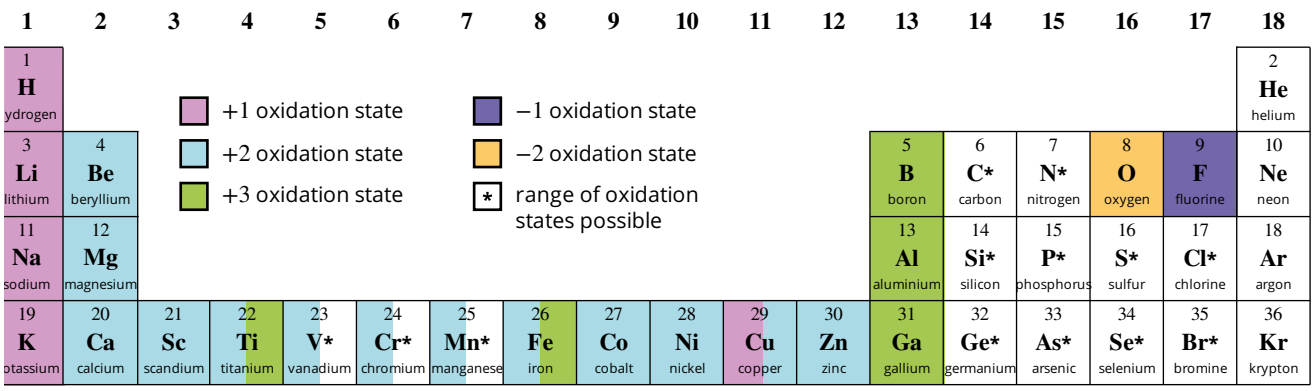

FIGURE 8.2.2 Part of the periodic table showing the most common oxidation states of some elements

Calculating oxidation numbers

For a compound containing several elements, you can use algebra and the rules given in Table 8.2.1 to calculate the oxidation number of an element.

For example, to find the oxidation number of sulfur in H_2SO_4, there is a rule for hydrogen and for oxygen, which leaves sulfur as the only unknown. If you let the oxidation number of S equal x, the following expression can be written to solve for x:

$$\begin{aligned}(2 \times +1) + x + (4 \times -2) &= 0\\ 2 + x - 8 &= 0\\ x - 6 &= 0\\ x &= +6\end{aligned}$$

You will learn later on in this section how to use oxidation numbers to determine if a substance has been oxidised or reduced.

Worked example 8.2.1

CALCULATING OXIDATION NUMBERS

Use the rules in Table 8.2.1 to determine the oxidation number of each element in $KClO_4$.

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: $+1 + x + (4 \times -2) = 0$ $+1 + x - 8 = 0$ $x - 7 = 0$ $x = +7$
Write oxidation numbers above the elements in the formula.	$\overset{+1+7-2}{KClO_4}$

Worked example: Try yourself 8.2.1

CALCULATING OXIDATION NUMBERS

Use the rules in Table 8.2.1 to determine the oxidation number of each element in $NaNO_3$.

USING OXIDATION NUMBERS

Using oxidation numbers to name chemicals

Transition elements can form ions with a number of different charges. For example, there are two compounds that can be called iron chloride: $FeCl_2$ and $FeCl_3$.

Using the rules in Table 8.2.1, 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, insert Roman numerals representing the appropriate oxidation number in the name.

- $FeCl_2$ is named iron(II) chloride. (Note that the old name of this substance is ferrous chloride.)
- $FeCl_3$ is named iron(III) chloride. (Note that the old name of this substance is ferric chloride.)

When naming non-metal compounds, you can also use Roman numerals to show the oxidation number of an element such as nitrogen, which has several possible oxidation states. Nitrogen dioxide (NO_2) is called nitrogen(IV) oxide, while nitric oxide (NO) is called nitrogen(II) oxide. This method of naming makes it much easier to determine the formula from the name of the oxide.

> 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 oxidation and reduction

You can use the concept of oxidation numbers to extend the definition of oxidation and reduction.

In this definition, a change in oxidation numbers indicates that a redox reaction has taken place. This can be used as an alternative definition of oxidation and reduction to the earlier definition involving loss and gain of electrons. It is particularly useful for non-ionic compounds when it is difficult to determine whether electrons have been transferred.

It can be stated that:

- oxidation involves an increase in oxidation number (as electrons are lost)
- reduction involves a decrease in oxidation number (as electrons are gained).

Remember that oxidation and reduction always occur together in a redox reaction.

If there is no change of oxidation number for all elements in a reaction, then the reaction is not a redox reaction.

Oxidation numbers can be used to analyse the equation of a reaction and determine whether it represents a redox process.

> An increase in oxidation number indicates the element was oxidised.
> A decrease in oxidation number indicates the element was reduced.

At the beginning of this chapter, you were introduced to a number of everyday redox reactions. Combustion reactions are very important redox reactions: fuel is burnt in order to produce heat while giving off CO_2 and water. The equation for the burning of carbon in excess oxygen is:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

Using oxidation numbers, you can identify both an oxidation process and a reduction process for the reaction.

$$\overset{0}{C}(s) + \overset{0}{O}_2(g) \rightarrow \overset{+4\ -2}{C}O_2(g)$$

CHEMFILE

Colourful oxidation states

A characteristic property of the transition elements is that they form brightly coloured compounds. Different oxidation states can result in different colours for the same transition metal.

Vanadium is a very colourful transition element that has a wide variety of colours depending on its oxidation state. You can see this in Figure 8.2.3. When its oxidation state is +5, vanadium is yellow; when its oxidation state is +4, it is light blue; when its oxidation state is +3, it is green; and when its oxidation state is +2, it is magenta.

FIGURE 8.2.3 These colourful solutions have been made by adding a reducing agent (mercury–zinc amalgam) to a yellow solution containing vanadium(V) ions. The amalgam reduces the oxidation state of the vanadium by one each time it is shaken, producing, in order: blue (+4), green (+3) and magenta (+2) solutions.

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.

The use of oxidation numbers allows you to look at a chemical reaction and determine whether it is a redox process.

Worked example 8.2.2

USING OXIDATION NUMBERS TO IDENTIFY OXIDATION AND REDUCTION IN AN EQUATION

Use oxidation numbers to determine which element has been oxidised and which has been reduced in the following equation:

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

Thinking	Working
Determine the oxidation numbers of one of the elements on each side of the equation.	Choose C as the first element. $\overset{-4}{C}H_4(g) + 2O_2(g) \rightarrow \overset{+4}{C}O_2(g) + 2H_2O(l)$
Assess if the oxidation number 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 carbon in CH_4 has been oxidised.
Determine the oxidation numbers of a second element on the left-hand and the right-hand side of the equation.	Choose oxygen as the second element. $CH_4(g) + 2\overset{0}{O}_2(g) \rightarrow \overset{-2}{C}O_2(g) + 2\overset{-2}{H_2}O(l)$
Assess if the oxidation number has changed. If so, identify if it has increased (oxidation) or decreased (reduction).	The oxidation number of O has decreased from 0 to –2, so O_2 has been reduced.
Continue this process until the oxidation numbers of all elements have been determined.	Determine the oxidation numbers of hydrogen. $\overset{+1}{C}H_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2\overset{+1}{H_2}O(l)$ The oxidation number of H has not changed (so H has not been oxidised or reduced).

Worked example: Try yourself 8.2.2

USING OXIDATION NUMBERS TO IDENTIFY OXIDATION AND REDUCTION IN AN EQUATION

Use oxidation numbers to determine which element has been oxidised and which has been reduced in the following equation:

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l)$$

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 this reactant and product as a **conjugate redox pair**.

For example, in the half-equation for the oxidation of zinc:

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

zinc metal (Zn) is a reducing agent and it forms $Zn^{2+}(aq)$, an oxidising agent. Zn(s) and $Zn^{2+}(aq)$ form a conjugate redox pair $Zn(s)/Zn^{2+}(aq)$.

When listing conjugate redox pairs, it is best to include the states of both the oxidising and reducing agent.

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.

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 8.2.4. One conjugate redox pair is red and the other one is blue.

You will notice that this type of relationship is similar to the conjugate acid–base pairs that you encountered in Chapter 4. In conjugate acid–base pairs, protons are transferred. In conjugate redox pairs, electrons are transferred.

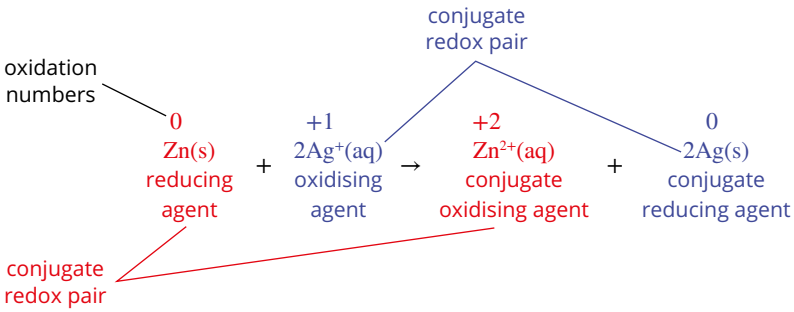

FIGURE 8.2.4 The change in oxidation numbers seen in conjugate redox pairs. For each redox reaction, there are two conjugate redox pairs.

8.2 Review

SUMMARY

- Oxidation numbers are calculated according to a set of rules.
  - 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.
  - Oxygen in a compound usually has an oxidation number of –2.
  - Hydrogen in a compound usually has an oxidation number of +1.
  - 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.
- Transition metals and some non-metals have variable oxidation numbers that can be calculated using the rules above.
- 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 all elements in the equation for a reaction, then the reaction is not a redox reaction.

8.2 Review *continued*

- 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 this case, the oxidation number of the oxidising agent decreases.
- The other conjugate redox pair in a redox reaction is made up of a reducing agent (a reactant) and the oxidising agent (a product) that is formed when the reducing agent loses electrons. In this case, the oxidation number of the reducing agent increases.
- Figure 8.2.5 summarises the redox terms that you need to understand from this section.

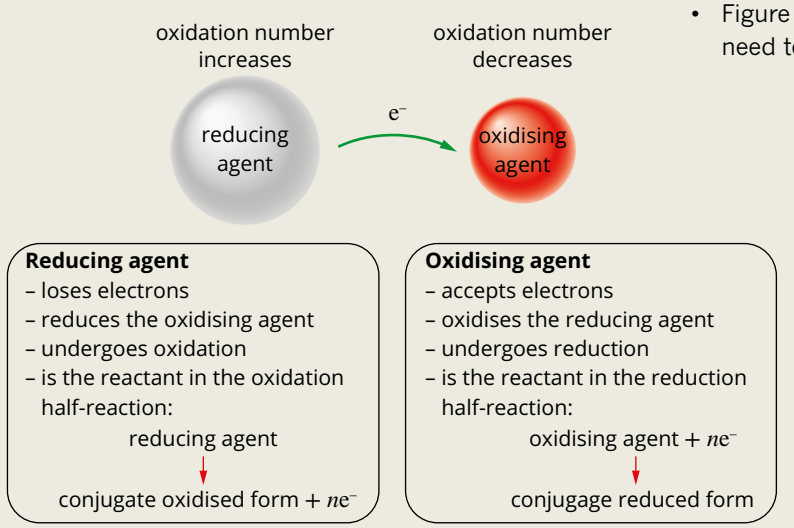

FIGURE 8.2.5 Summary of redox reaction terms

KEY QUESTIONS

1 State the oxidation number of carbon in:
- **a** CO
- **b** CO_2
- **c** CH_4
- **d** C (graphite)
- **e** HCO_3^-

2 Which one or more of the following substances contain manganese in the +6 oxidation state: $MnCl_2$, $MnCl_3$, MnO_2, K_2MnO_4, $KMnO_4$?

3 Find the oxidation numbers of each element in the following compounds or ions. Hint: For ionic compounds, use the charge on each ion to help you.
- **a** CaO
- **b** $CaCl_2$
- **c** HSO_4^-
- **d** MnO_4^-
- **e** F_2
- **f** SO_3^{2-}
- **g** $NaNO_3$
- **h** $K_2Cr_2O_7$

4 Assign oxidation numbers to each element in these equations, and hence 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** $2Fe^{2+}(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$

5 For each of the following redox reactions, identify the conjugate redox pairs.

Redox reaction	Conjugate redox pair (oxidation process)	Conjugate redox pair (reduction process)
$Na(s) + Ag^+(aq) \rightarrow Na^+(aq) + Ag(s)$		
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$		
$2K(s) + Cl_2(g) \rightarrow 2K^+(s) + 2Cl^-(s)$		

8.3 More complex redox equations

Not all oxidation and reduction half-equations involve simple ions and their elements. Many interesting redox reactions, such as the iodine clock reaction shown in Figure 8.3.1, involve reactants and products that have oxygen and hydrogen in their formulas. In this section, you will learn how to balance more complex half-equations in a few simple steps.

FIGURE 8.3.1 This redox reaction involving colour changes is known as the iodine clock reaction. The black compound is a starch–iodine complex.

BALANCING OXYGEN AND HYDROGEN IN HALF-EQUATIONS

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 write the half-equation as:

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

However, half-equations involving polyatomic ions are usually less obvious. For example, 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 hydrogen and oxygen in the half-equation:
$2NO_3^- \rightarrow N_2O$

2 Balance the oxygen atoms by adding water molecules to the side with fewer oxygen atoms:
$2NO_3^- \rightarrow N_2O + 5H_2O$

3 Balance the hydrogen atoms by adding H^+ ions (which are always present in acidic solution) to the side with fewer H^+ ions:
$2NO_3^- + 10H^+ \rightarrow N_2O + 5H_2O$

4 Balance the charge in the equation by adding electrons to the side that has the most positive charge:
$2NO_3^- + 10H^+ + 8e^- \rightarrow N_2O + 5H_2O$
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 0. Adding the 8 electrons lowers the charge of the left-hand side to match the charge on the right-hand side.

5 Add state symbols to complete the half-equation:
$2NO_3^-(aq) + 10H^+(aq) + 8e^- \rightarrow N_2O(g) + 5H_2O(l)$

CHEMFILE

Vinegary wine or winey vinegar?

The oxidation of ethanol forms ethanoic (acetic) acid. You will learn more about this reaction in Chapter 14. Ethanoic acid is the main ingredient of vinegar and is responsible for its sourness. If a bottle of wine is left open to the atmosphere for a few days, it becomes 'vinegary' and undrinkable.

This reaction is put to good use when specialist vinegars such as apple cider vinegar, red wine vinegar and even beer vinegar (Figure 8.3.3) are made by deliberately oxidising the appropriate alcoholic beverage under the right conditions.

The oxidation half-equation for the production of ethanoic acid from ethanol is given by:

$C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$

FIGURE 8.3.3 This selection of vinegars includes, from left to right: distilled malt vinegar, cider vinegar, white wine vinegar and malt vinegar.

i The steps outlined are for balancing redox half-equations in acidic solution only.

When writing half-equations and overall equations, it is important that they are fully balanced in terms of number of atoms and the amount of charge. Remember that the charges being equal does not mean they must be zero (Figure 8.3.2).

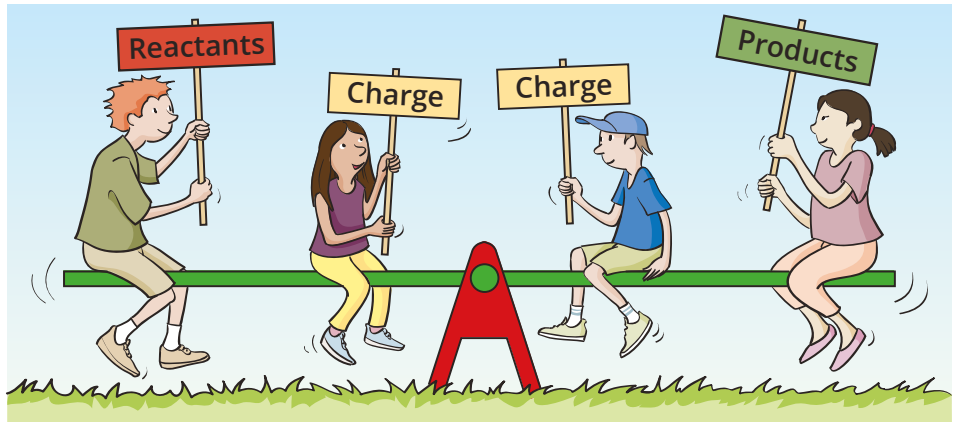

FIGURE 8.3.2 In balanced half-equations and overall equations, the number of atoms of each element is equal on both sides and the total charge on each side is equal.

i The steps for balancing complex redox half-equations must be carried out in sequence for the process to work.

Worked Example 8.3.1 shows how to balance a complex redox half-equation. The final equation in this example has an overall charge of +6 for each side.

Worked example 8.3.1

BALANCING A HALF-EQUATION IN ACIDIC SOLUTION

Write the half-equation for the reduction of an acidified solution of $Cr_2O_7^{2-}$ to aqueous Cr^{3+}.

Thinking	Working
Balance all elements except hydrogen and oxygen in the half-equation.	There are 2 Cr atoms in $Cr_2O_7^{2-}$, so 2 Cr atoms are needed on the right-hand side (RHS). $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$
Balance the oxygen atoms by adding water.	There are 7 O atoms in $Cr_2O_7^{2-}$, so 7 H_2O molecules must be added to the RHS. $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$
Balance the hydrogen atoms by adding H^+ ions. Acids provide a source of H^+ ions.	There are now 14 H atoms on the RHS and none on the left-hand side (LHS), so 14 H^+ ions must be added to the LHS. $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$
Balance the charge in the equation by adding electrons.	The charge on the LHS is (–2) + (+14) = +12 and the charge on the RHS is 2 × +3 = +6, so 6 electrons must be added to the LHS to make the charges equal. $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
Add states to complete the half-equation.	All states are (aq) except for water, which is (l). $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

Worked example: Try yourself 8.3.1

BALANCING A HALF-EQUATION IN ACIDIC SOLUTION

Write the half-equation for the reduction of an acidified solution of MnO_4^- to solid MnO_2.

OVERALL REDOX EQUATIONS UNDER ACIDIC CONDITIONS

To write an overall redox equation, you add the oxidation half-equation to the reduction half-equation, making sure that the number of electrons used in reduction equals the number of electrons released during oxidation. In addition, for redox reactions under acidic conditions, H^+ ions and H_2O molecules are also present as reactants and products, which need to be cancelled down.

Worked example 8.3.2

COMBINING HALF-EQUATIONS TO WRITE OVERALL REDOX EQUATIONS UNDER ACIDIC CONDITIONS

Write balanced oxidation and reduction half-equations for the reaction in which $C_2H_5OH(aq)$ and $Cr_2O_7^{2-}(aq)$ react to form $CH_3COOH(aq)$ and $Cr^{3+}(aq)$. Then write the overall redox equation for the reaction.

Thinking	Working
Identify one reactant and the product it forms, and write the balanced half-equation.	$C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$
Identify the second reactant and the product it forms, and write the balanced half-equation.	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
Multiply one or both equation(s) by a suitable factor to ensure that the number of electrons on both sides of the arrow is equal.	Lowest common multiple = 12 $3 \times [C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-]$ $2 \times [Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)]$ $3C_2H_5OH(aq) + 3H_2O(l) \rightarrow 3CH_3COOH(aq) + 12H^+(aq) + 12e^-$ $2Cr_2O_7^{2-}(aq) + 28H^+(aq) + 12e^- \rightarrow 4Cr^{3+}(aq) + 14H_2O(l)$
Add the oxidation and the reduction half-equations together, cancelling electrons so that none appear in the final equation. Also cancel H_2O and H^+ if these occur on both sides of the arrow.	$3C_2H_5OH(aq) + \cancel{3H_2O(l)} \rightarrow 3CH_3COOH(aq) + \cancel{12H^+(aq)} + \cancel{12e^-}$ $2Cr_2O_7^{2-}(aq) + \cancel{28}\,^{16}\cancel{H^+(aq)} + \cancel{12e^-} \rightarrow 4Cr^{3+}(aq) + \cancel{14H_2O}\,^{11}\,O(l)$ $3C_2H_5OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$

Worked example: Try yourself 8.3.2

COMBINING HALF-EQUATIONS TO WRITE OVERALL REDOX EQUATIONS UNDER ACIDIC CONDITIONS

Write balanced oxidation and reduction half-equations for the reaction in which $SO_3^{2-}(aq)$ and $ClO^-(aq)$ react to form $H_2S(g)$ and $ClO_3^-(aq)$. Then write the overall equation for the reaction.

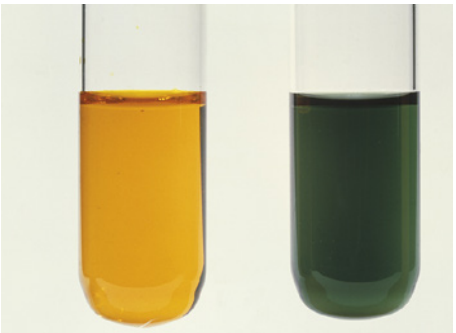

FIGURE 8.3.4 The oxidation of ethanol, described in Worked Example 8.3.2, was the basis of an older form of the breathalyser. The presence of alcohol in a motorist's breath was identified by a colour change in the oxidising agent, potassium dichromate. During the reaction, the yellow-orange colour of dichromate ions changed to the green colour of chromium(III) ions as the alcohol was oxidised.

Some strong oxidising agents, such as potassium dichromate, are highly coloured. The change in colour that occurs as the redox process proceeds can be used for a number of chemical analyses.

The reaction of an alcohol with acidified dichromate, as seen in Worked Example 8.3.2, can be followed by the colour change of the solution from orange to green (Figure 8.3.4). This colour change was the basis for older forms of handheld breathalysers used for testing the blood alcohol level of drivers.

CHEMISTRY IN ACTION

Alcohol and the road toll

Drinks such as wine, beer, vodka and bourbon 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.

Because ethanol slows reaction time, it seriously affects a person's driving skills. It is estimated that nationally, 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) (mass in grams dissolved in 100 mL of solution, or 0.05 g of alcohol in 100 mL of blood). Probationary or P-plate drivers are required to have a zero blood alcohol level.

It is difficult to determine your blood alcohol concentration because it is affected by how much alcohol you drink, how quickly or slowly you have consumed alcohol, how much you have eaten, your body mass and level of fitness and even how healthy your liver is. As a guide, to keep within a safe limit, men should not drink more than two standard drinks in the first hour and one standard drink every following hour, while women should not drink more than one standard drink every hour.

The ethanol content of alcoholic drinks varies, so it can be difficult to determine what a standard drink is. Regulations require that the ethanol content of alcoholic drinks be specified on their labels, because ethanol content determines how much drink can be consumed without adverse effects. The relationships between the type of alcoholic beverage, its ethanol content and the number of standard drinks are shown in Table 8.3.1.

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. However, despite 20 years of anti-drink driving messaging, alcohol still remains a factor in a quarter of fatal crashes in Western Australia.

TABLE 8.3.1 Typical ethanol contents of some alcoholic beverages, and a standard drink

Drink	Volume (mL)	Ethanol content (%v/v)	Number of standard drinks
Mid-strength beer, glass	285	3–4	0.8
Mid-strength beer, can	375	3–4	1
Full-strength beer, glass	285	4–6	1
Full-strength beer, can	375	4–6	1.5
Pre-mixed drink	375	5	1.5
Wine	100	10–14	1
Spirits (brandy, whisky, gin, vodka etc.)	30	37–43	1

WA Road Safety Commission

FIGURE 8.3.5 Breathalysers are used to analyse the blood alcohol content of motorists. The sensor detects the change in colour as the ethanol is oxidised to ethanoic acid in the presence of acidified potassium dichromate.

Chemists were involved in the invention of the breathalyser, an instrument designed for police to use to estimate blood alcohol content (Figure 8.3.5). 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. The blood alcohol content may then be confirmed by instrumental techniques, such as infrared spectroscopy or gas–liquid chromatography. Some police departments also use alcohol fuel cell sensors.

The first breathalysers operated by detecting the colour change that occurs when ethanol reacts with an acidified solution of potassium dichromate ($K_2Cr_2O_7$), forming Cr^{3+} ions and ethanoic acid. The redox reaction can be represented by the equation:

$$2Cr_2O_7^{2-}(aq) + 3CH_3CH_2OH(g) + 16H^+(aq) \rightarrow 4Cr^{3+}(aq) + 3CH_3COOH(aq) + 11H_2O(l)$$

orange → green

CHEMFILE

Elephant's toothpaste

Hydrogen peroxide is such a strong oxidising agent that it can even oxidise itself, decomposing to form water and oxygen gas:

$$H_2O_2(aq) + H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

In this reaction the two half-equations are:

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$$

$$H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$$

The decomposition reaction of hydrogen peroxide is the basis for the impressive 'foam column' or 'elephant's toothpaste' demonstration.

When detergent and a catalyst are added to concentrated hydrogen peroxide solution, a column of foam is formed (Figure 8.3.6).

FIGURE 8.3.6 The 'elephant's toothpaste' demonstration involves a redox reaction in which hydrogen peroxide reacts with itself to form water and oxygen gas. In this reaction, the hydrogen peroxide is both the reducing agent and the oxidising agent. In this image, solid potassium iodide catalyst is added to hydrogen peroxide solution. Red colouring has also been added for effect.

8.3 Review

SUMMARY

- Half-equations are used to represent oxidation and reduction.
- Half-equations are added together to obtain the overall equation. Before adding the half-equations, you may need to multiply them by a factor to balance the electrons.
- State symbols should always be included in half-equations and balanced equations for overall redox reactions.
- To balance redox half-equations under acidic conditions:
  1 Balance all atoms except hydrogen and oxygen.
  2 Balance the oxygen atoms by adding water molecules.
  3 Balance the hydrogen atoms by adding H^+ ions.
  4 Balance the charge by adding electrons.
  5 Add states.
- To write 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

1 Write 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-}.

2 When zinc powder is sprinkled into an acidified solution of potassium dichromate, a reaction occurs that produces zinc ions and chromium(III) ions in solution.
- **a** Write the oxidation half-equation for the reaction.
- **b** Write the reduction half-equation for the reaction.
- **c** Use your answers to parts **a** and **b** to write a balanced equation for the overall reaction.

3 Write the half-equations and the balanced overall equation for the reaction in which a solution containing:
- **a** 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** 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.

4 The following equations are not balanced. For each equation:
- **i** identify the species that has been reduced and the species that has been oxidised
- **ii** write balanced half-equations for the oxidation and reduction reactions
- **iii** combine the half-equations to write 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 $MnO_2(s) + H^+(aq) + S(s) \rightarrow Mn^{2+}(aq) + H_2O(l) + SO_2(g)$

8.4 The reactivity series of metals

When metals undergo corrosion, some react quickly with oxygen and water, and even more vigorously with acids. For example, magnesium ribbon reacts vigorously in acid. Other metals react quite slowly with oxygen. For example, copper pipes oxidise slowly in air, producing a brown-black copper(II) oxide coating. These are both redox reactions.

In this section, you will examine the reactivity of different metals and learn how to write equations for the displacement 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. For example, in 2008, corroded pipelines caused an explosion at a gas processing plant on Varanus Island. This crisis resulted in 35% of Western Australia's gas supply being lost for 2 months.

Other metals do not corrode as readily. For example, platinum and gold are sufficiently inert to exist as pure elements in nature.

Figure 8.4.1 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.

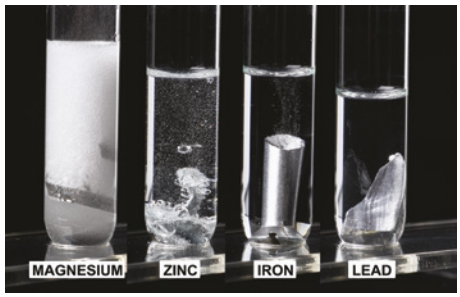

FIGURE 8.4.1 Some metals react with dilute acid to form a salt and hydrogen gas. The reaction between magnesium and dilute acid is extremely vigorous. The reaction between zinc and dilute acid is less vigorous. The reaction between iron and dilute acid is very slow. There is no reaction between lead and dilute acid. This information can be used to determine that the order of metal reactivity from most reactive to least reactive is magnesium, zinc, iron and lead.

The metals can be ranked in a list according to their reactivity, or ability to act as reducing agents. Figure 8.4.2 shows such a ranking, which is also known as a **reactivity series**. The series shows the reduction half-equations for the metal cations as each cation gains electrons to form the corresponding metal.

The metals are listed on the right-hand side of the series, from the least reactive (Au) at the top to the most reactive (K and Li) at the bottom. The lower down the table a metal is placed, the more reactive it is.

Metals, with their small number of valence electrons, 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.

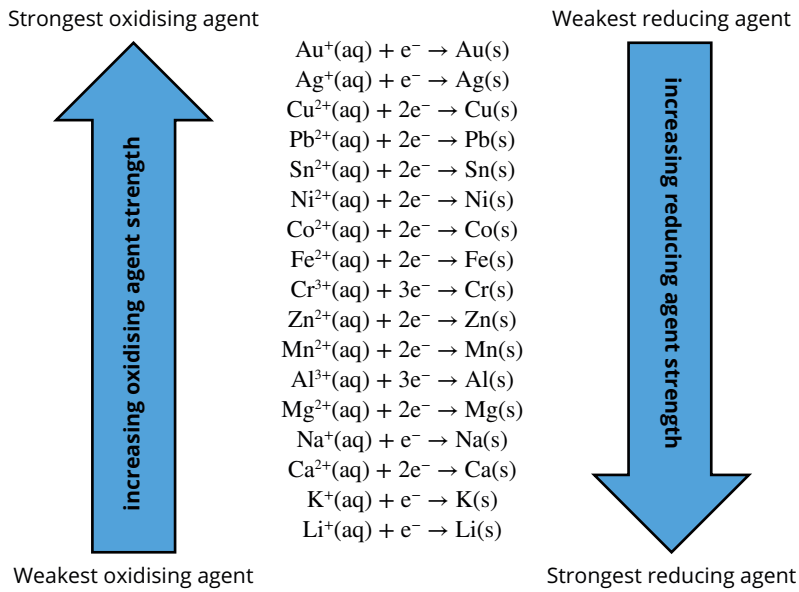

FIGURE 8.4.2 The reactivity series of metals

As you go down the reactivity series of metals in Figure 8.4.2, the:

- metals, which are on the right-hand side, become more reactive. This means the metals lower in the series are easier to oxidise and are therefore stronger reducing agents
- metal cations, which are on the left-hand side, become increasingly harder to reduce and are therefore less reactive. Cations higher in the series have a greater attraction for electrons, so they are easier to reduce and are therefore relatively strong oxidising agents.

CHEMISTRY IN ACTION

The ages of discovery

Since the beginning of civilisation, human progress has depended on the discovery and development of materials. The epochs of civilisation are commonly described as:

- Stone Age
- Bronze Age
- Iron Age
- Modern Age.

As the electrochemical reactivity series shows, the first metals discovered are low in reactivity and are found as pure elements. With the discovery of fire, small samples of metals such as copper and tin, which were reduced from their ores, were found in the ashes of campfires. The mixture of copper and tin, which produced the hard alloy bronze, initiated the Bronze Age. Copper could be beaten into shapes for tools and weapons that held a sharper edge, and was easily resharpened once blunt. The Trojan War was conducted by bronze-shielded warriors throwing bronze-tipped spears.

Lead and iron, which are more reactive metals, require higher temperatures to extract them from their ores, and efficient production methods were invented much later. Wood fires could not reach high enough temperatures. It was only when charcoal was used that the manufacture of iron was possible and iron weapons could be produced at a fraction of the cost of those made from bronze.

Highly reactive metals, such as aluminium and sodium, are so easily oxidised and have such stable cations that it was not until electricity was invented in the late 1800s that they could be extracted from their mineral ores.

It was so difficult to extract aluminium metal that Napoleon III proudly displayed a small bar of the metal with his crown jewels in 1855. Modern electrolytic production methods use direct current electricity to produce the metals from molten minerals. (You will encounter some of these processes in Chapter 10.) Consequently, these metals tend to be expensive to produce. Aluminium is produced using the electrolytic cells shown in Figure 8.4.3.

Historians may one day label our Modern Age as the Silicon, Aluminium, Plastics, Ceramics or Nanoparticle Age in recognition of the influence that these technologically advanced materials have had on our modern lives. Further developments in materials technology will no doubt see the production of new materials to meet the demands of our modern culture.

FIGURE 8.4.3 A row of electrolytic cells used for the modern production of aluminium

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 above the other metal in the reactivity series, as shown in Figure 8.4.4. The more reactive metal acts as the reducing agent, and the metal ions of the other metal act as the oxidising agent.

In Chapter 9 you will see how this idea of predicting whether reactions will occur can be extended to other oxidising and reducing agents by using a more wide-ranging electrochemical series.

A metal ion higher in the reactivity series (an oxidising agent) will react with a metal lower in the reactivity series (a reducing agent).

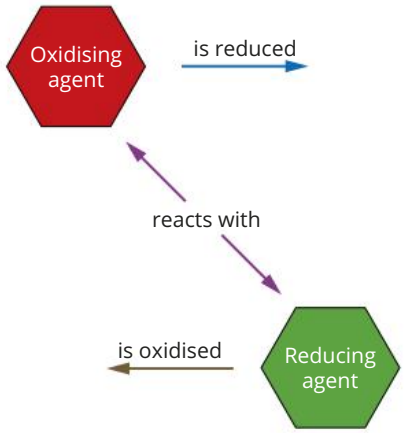

FIGURE 8.4.4 Predicting the reaction between an oxidising agent and a reducing agent

When copper wire is placed in a solution of silver nitrate, as shown in Figure 8.4.5, 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 8.4.6. The overall redox reaction can be represented by the equation:

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

FIGURE 8.4.5 In the flask on the left, copper wire is suspended in a solution of silver nitrate. In the flask on the right, long crystals of silver metal have formed and the copper has displaced the silver from the solution.

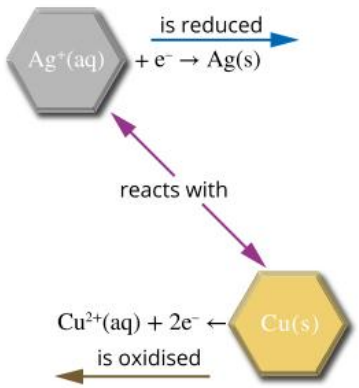

FIGURE 8.4.6 A spontaneous redox reaction occurs when copper is added to a solution of silver nitrate. Silver ions oxidise copper atoms.

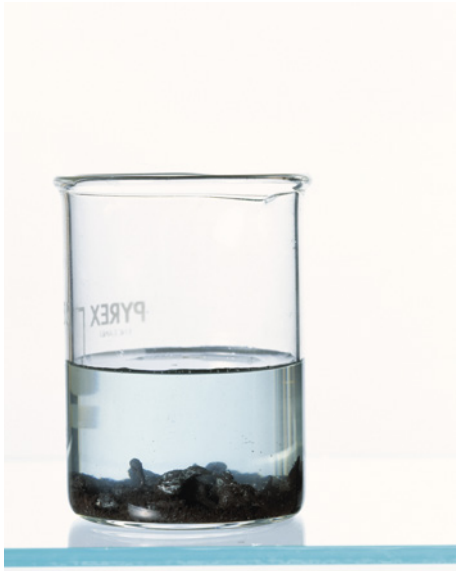

FIGURE 8.4.7 When zinc is added to copper(II) sulfate solution, a salmon pink deposit of copper metal is observed forming on the zinc and the blue copper(II) sulfate solution gradually becomes colourless as the concentration of Cu^{2+} ions decreases.

Worked example 8.4.1

PREDICTING METAL DISPLACEMENT REACTIONS

Predict whether zinc will displace copper from a solution containing copper(II) ions. If appropriate, write the overall redox 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 on the left-hand side of the reactivity series. $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $Sn^{4+}(aq) + 2e^- \rightarrow Sn(aq)$ $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $Co^{2+}(aq) + 2e^- \rightarrow Co(s)$ $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$ $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$
Determine whether the metal element is below 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 below Cu^{2+}, so there will be a reaction as shown in Figure 8.4.7.
Write the reduction half-equation for the metal ion directly as it is written in the reactivity series. Include state symbols.	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Write the oxidation half-equation for the metal with the metal on the left-hand side of the arrow (as a reactant). Include state symbols.	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
Combine the two half-equations, balancing electrons, to give the overall equation for the reaction.	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Worked example: Try yourself 8.4.1

PREDICTING METAL DISPLACEMENT REACTIONS

Predict whether copper will displace gold from a solution containing gold ions. If appropriate, write the overall redox equation for the reaction.

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 8.4.7.

8.4 Review

SUMMARY

- The reactivity series lists half-equations involving metals and their corresponding cations.
- The half-equations involving stronger oxidising agents (the ones more easily reduced) appear higher in the reactivity series than those involving weaker oxidising agents.
- The half-equations involving stronger reducing agents (the ones more easily oxidised) appear lower in the reactivity series.
- 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.

KEY QUESTIONS

1 Refer to the reactivity series and predict whether each of 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 The element 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.

2 Use the reactivity series to predict whether a reaction will occur in each of the following situations. Write an overall redox 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.

3 Solutions of zinc nitrate, tin(II) nitrate and copper(II) nitrate have been prepared in a laboratory, but are unlabelled. Name two metals that could be used to identify each solution.

Chapter review

08

KEY TERMS

conjugate redox pair
displace
half-equation
halogen displacement reaction
main group metal
metal displacement reaction
oxidant
oxidation
oxidation number
oxidised
oxidising agent
reactivity series
redox reaction
reduced
reducing agent
reductant
reduction
spontaneous redox reaction
transition element

Oxidation and reduction

1 Define oxidation and reduction in terms of the transfer of:
- **a** oxygen
- **b** electrons.

2 State whether each of the statements is true or false.
- **a** Groups 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.

3 Complete the following sentences, which describe oxidation and reduction.
Oxidation and reduction occur together. Oxidation occurs when an atom _____ electrons to form a _____ ion, such as happens 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 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.

4 Lead metal is oxidised to form Pb^{2+} ions by reaction with silver ions in solution. Write half-equations for the reaction and then write the balanced overall equation.

5 Classify each of the following half-equations as either oxidation or reduction half-equations.
- **a** $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$
- **b** $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$
- **c** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
- **d** $K(s) \rightarrow K^+(aq) + e^-$
- **e** $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$
- **f** $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$

6 Each of the following half-equations have a mistake in them. For each half-equation, state what the error is and then write 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** $Na^+(aq) - e^- \rightarrow Na(s)$

7 Identify the reducing agent in each of these redox reactions.
- **a** $2Cu(s) + O_2(g) \rightarrow 2CuO(s)$
- **b** $F_2(g) + 2LiBr(aq) \rightarrow Br_2(aq) + 2LiF(aq)$
- **c** $2Fe^{3+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$
- **d** $2Ag^+(aq) + Ni(s) \rightarrow Ni^{2+}(aq) + 2Ag(s)$

8 Balance these half-equations.
- **a** $Ag^+(aq) \rightarrow Ag(s)$
- **b** $Cu(s) \rightarrow Cu^{2+}(aq)$
- **c** $Zn(s) \rightarrow Zn^{2+}(aq)$

9 Which one of the following redox equations has not been balanced correctly?
- **A** $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$
- **B** $Fe^{2+}(aq) + Zn(s) \rightarrow Fe(s) + Zn^{2+}(aq)$
- **C** $Ag^+(aq) + Cu(s) \rightarrow Ag(s) + Cu^{2+}(aq)$
- **D** $Zn^{2+}(aq) + Mg(s) \rightarrow Zn(s) + Mg^{2+}(aq)$

Oxidation numbers

10 What is 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** $Na_2S_2O_3$

11 Complete the following table.

Compound	Element	Oxidation number
$CaCO_3$	Ca	
HNO_3	O	
H_2O_2		–1
HCO_3^-		+4
HNO_3	N	
$KMnO_4^-$	Mn	
H_2S	S	
Cr_2O_3	Cr	
N_2O_4	N	

12 Place the following substances in order of increasing oxidation number of nitrogen.
NO, K_3N, N_2O_4, N_2O, $Ca(NO_3)_2$, N_2O_3, N_2

13 Which of the following reactions are redox reactions? Give reasons for each of your answers.

a $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$
b $2Ag + Cl_2 \rightarrow 2AgCl$
c $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$
d $ZnCO_3 \rightarrow ZnO + CO_2$
e $HPO_3^{2-} + I_2 + OH^- \rightarrow H_2PO_4^- + 2I^-$
f $2Cu^+ \rightarrow Cu^{2+} + Cu$
g $CaF_2 \rightarrow Ca^{2+} + 2F^-$
h $P_4 + 6H_2 \rightarrow 4PH_3$

14 Determine the oxidation numbers of the underlined atom in the following compounds and ions.

a $\underline{Cu}O$
b $\underline{Fe}(OH)_3$
c $H\underline{Cl}O_2$
d $\underline{Mn}O_4^-$
e $\underline{Cr}_2O_7^{2-}$

15 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 What is the oxidation number of copper:
i before the reaction?
ii after the reaction?
b What is the oxidation number of nitrogen:
i before the reaction?
ii after the reaction?
c Name the oxidising agent and reducing agent in this process.

16 Complete the following table, giving the conjugate redox pairs for each of the reactions.

Equation	Conjugate redox pair (oxidation)	Conjugate redox pair (reduction)
$Fe(s) + I_2(aq) \rightarrow FeI_2(aq)$		
$Mg(s) + FeCl_2(aq) \rightarrow MgCl_2(aq) + Fe(s)$		
$10Br^-(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Br_2(aq)$		
$Cu(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$		

More complex redox equations

17 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 the 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.	

18 The unbalanced half-equation for the reduction of the iodate ion (IO_3^-) is:

$$2IO_3^-(aq) + xH^+(aq) + ye^- \rightarrow I_2(aq) + zH_2O(l)$$

Complete the equation by inserting the correct coefficients for *x*, *y* and *z*. (Hint: You will need to write the relevant half-equations first.)

19 When sulfur dioxide is bubbled through an acidified solution of sodium dichromate, sulfate ions and green chromium(III) ions are formed. Write the half-equations for this reaction and then deduce the balanced overall equation.

20 In dry cells commonly used to power torches, energy is produced from the reaction of zinc metal with solid MnO_2. During this reaction, Zn^{2+} ions and solid Mn_2O_3 are formed. Write half-equations, and hence an overall equation, for the reaction.

21 Answer the following questions about the reaction of $H_3AsO_4(aq)$ with $I^-(aq)$. The unbalanced equation for the reaction is:

$H_3AsO_4(aq) + I^-(aq) \rightarrow As_2O_3(s) + IO_3^-(aq) + H_2O(l)$

- **a** Write the two half-equations for the reaction.
- **b** Write a balanced overall equation using your two half-equations from part **a**.

The reactivity series of metals

You may need to refer to the reactivity series of metals to answer Questions 22–27.

22 List the following in order of increasing reducing strength.

Mg, Ag, Ni, Sn, Li, Cu

23 Predict whether the following mixtures would result in spontaneous reactions. Write an overall equation for each reaction that you predict will occur.

- **a** Zinc metal is added to a solution of silver nitrate.
- **b** Copper metal is placed in an aluminium chloride solution.
- **c** Tin(II) sulfate is placed in a copper container.
- **d** Magnesium metal is added to a solution of lead nitrate.
- **e** Silver metal is added to nickel chloride solution.
- **f** Solutions of potassium chloride and copper(II) chloride are mixed.
- **g** Potassium nitrate solution is added to a silver container.
- **h** Elemental lead is placed in a solution of silver nitrate.

24 Would you expect a reaction when a piece of zinc metal is added to solutions of the following compounds? If so, write a fully balanced chemical equation for the reaction.

- **a** $AlCl_3$
- **b** $AgNO_3$
- **c** $SnCl_2$
- **d** $CuSO_4$

25 You are given three colourless solutions (A, B and C) known to be sodium nitrate, silver nitrate and lead(II) nitrate, but not necessarily in this order. You also have some pieces of magnesium ribbon and copper wire. Describe how you could identify each of the solutions using only the chemicals supplied.

26 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. Suggest the name of the unknown metal.

27 Iron nails are placed into solutions of $CuSO_4$, $MgCl_2$, $Pb(NO_3)_2$ and $ZnCl_2$. In which solutions would you expect a coating of another metal to appear on the nail? Explain your answer.

Connecting the main ideas

28 Construct a concept map that shows the links between the following terms:

oxidising agent, reducing agent, electrons, oxidation, reduction

29 As a result of a traffic accident, residents in a Perth 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** Write half-equations for the oxidation and reduction reactions that occur when sodium dithionite is mixed with water.

30 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** Write the balanced overall equation for the reaction that occurs.
- **e** Identify the conjugate redox pairs for the reaction.

31 The thermite process can be used to weld lengths of railway track together. A mould placed over the ends of the two rails to be joined is filled with a charge of aluminium powder and iron(III) oxide. When the mixture is ignited, a redox reaction occurs to form molten iron, which joins the rails together, and aluminium oxide.

a Write a half-equation for the conversion of iron(III) oxide to metallic iron and oxide ions.

b Is the half-equation you wrote for part **a** an oxidation or a reduction process?

c Write the overall equation for the thermite process.

d What mass of iron(III) oxide must be present in the charge if each joint requires 3.70 g of iron to weld it together?

32 The following equations form part of the reactivity series. They are ranked in the order shown.

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

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

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

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

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

a Which species is the strongest oxidising agent and which is the weakest oxidising agent?

b Which species is the strongest reducing agent and which is the weakest reducing agent?

c Lead rods are placed in solutions of silver nitrate, iron(II) sulfate and magnesium chloride. In which solutions would you expect to see a coating of another metal form on the lead rod? Explain.

d Which of the metals silver, zinc or magnesium might be coated with lead when immersed in a solution of lead(II) nitrate?

33 Consider the following information relating to metals, R, S and T, and solutions of their salts, $T(NO_3)_2$, RNO_3 and $S(NO_3)_2$.

Three experiments are carried out with these metals to determine their order of reactivity. Equations representing what happened in these experiments are listed below.

Experiment 1: $T(s) + 2RNO_3(aq) \rightarrow T(NO_3)_2(aq) + 2R(s)$

Experiment 2: $T(NO_3)_2(aq) + S(s) \rightarrow$ no reaction

Experiment 3: $S(s) + RNO_3(aq) \rightarrow$ no reaction

Determine the order of reactivity of the three metals, from least reactive to most reactive.

CHAPTER

09 Galvanic cells

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 the many types of galvanic cells.

Finally, you will investigate how different types of galvanic cells are used as a source of power for a range of uses.

Science as a human endeavour

Spontaneous redox reactions can be used as a source of electrical energy, including primary, secondary and fuel cells. Fuel cells are a potential lower-emission alternative to the internal combustion engine and are already being used to power various modes of transport. Organisations, including the International Partnership for Hydrogen and Fuel Cells in the Economy, have been created to foster global cooperation on research and development, common codes and standards, and information sharing on infrastructure development.

Science understanding

- electrochemical cells, including galvanic and electrolytic cells, consist of oxidation and reduction half-reactions connected via an external circuit through which electrons move from the anode (oxidation reaction) to the cathode (reduction reaction)
- galvanic cells produce an electric current from a spontaneous redox reaction
- electrochemical cells can be described in terms of the reactions occurring at the anode and cathode, the role of the electrolyte, salt bridge (galvanic cell), ion migration, and electron flow in the external circuit
- cell diagrams can be used to represent electrochemical cells
- the relative strength of oxidising and reducing agents can be determined by comparing standard electrode potentials, and can be used to predict reaction tendency
- the electric potential difference of a cell under standard conditions can be calculated from standard electrode potentials; these values can be used to compare the voltages generated by cells constructed from different materials
- a range of reactions involve the oxidation of one species and reduction of another species, including metal and halogen displacement reactions, combustion and corrosion

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9.1 Galvanic cells

FIGURE 9.1.1 Your way of life depends on cells and batteries.

Electronic devices, such as mobile phones, notebook computers, cameras and hearing aids, all depend on small portable sources of electricity: cells and batteries (Figure 9.1.1). Portable energy in the form of cells and batteries enables you to operate electrical equipment without the restriction 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 the convenience.

In this section, you will find out how cells are constructed, and how they provide you with a source of electrical energy.

CHEMISTRY IN ACTION

A technological leap beginning with a frog's leg

The history of electrochemistry began in 1791 when Italian biologist Luigi Galvani and his assistant were experimenting with dissected frogs. They hung a frog's leg on a copper hook and were startled to see the leg twitch when it touched an iron rail. The muscles of the frog were stimulated by an electric shock. Galvani had just discovered how to generate a current. His 'error' was in thinking that the current was some sort of life force, a perfectly reasonable idea for the time.

Other scientists set out to investigate the possibility that metals were involved in this phenomenon. After several years' work, in 1800, Alessandro Volta developed a device that used a chemical reaction to produce an electric current. Figure 9.1.2 shows the device, now called a 'voltaic pile'. It consisted of a stack of alternating copper and zinc discs separated by cardboard soaked in salt water.

FIGURE 9.1.2 An original voltaic pile. The pile is 15 cm high and contains alternating copper and zinc discs separated by cardboard.

INTRODUCING GALVANIC CELLS

An **electrochemical cell** is a device in which chemical energy is converted into electrical energy, and vice versa. A **galvanic cell** (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 you 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 9.1.3 shows how you can produce a galvanic cell from simple laboratory equipment.

FIGURE 9.1.3 Construction of a galvanic cell from simple laboratory equipment.

In Figure 9.1.4, you can see a diagram of a Daniell cell, named after the scientist who invented it in 1836, John Daniell. The Daniell 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.

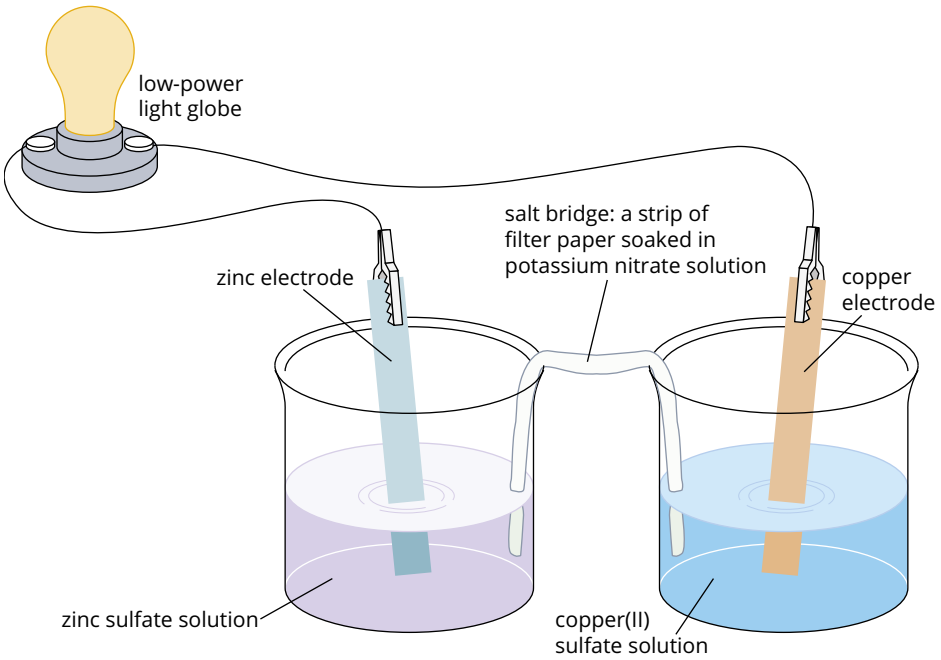


FIGURE 9.1.4 The Daniell cell is a type of galvanic cell.

CHEMFILE

The Daniell cell

In 1836, English chemist John Daniell invented a device that could supply a useful electric current. The device, which became known as the Daniell cell, was used almost exclusively to power the early English and US telegraph systems because of its reliable output.

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:

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

- The copper metal that is formed deposits on the electrode as a dark brown coating.

In this cell, chemical energy is transformed into electrical energy. Figure 9.1.5 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 would be the same number of electrons (two) on each side of the equation, so they are cancelled out and don't appear in the final equation.

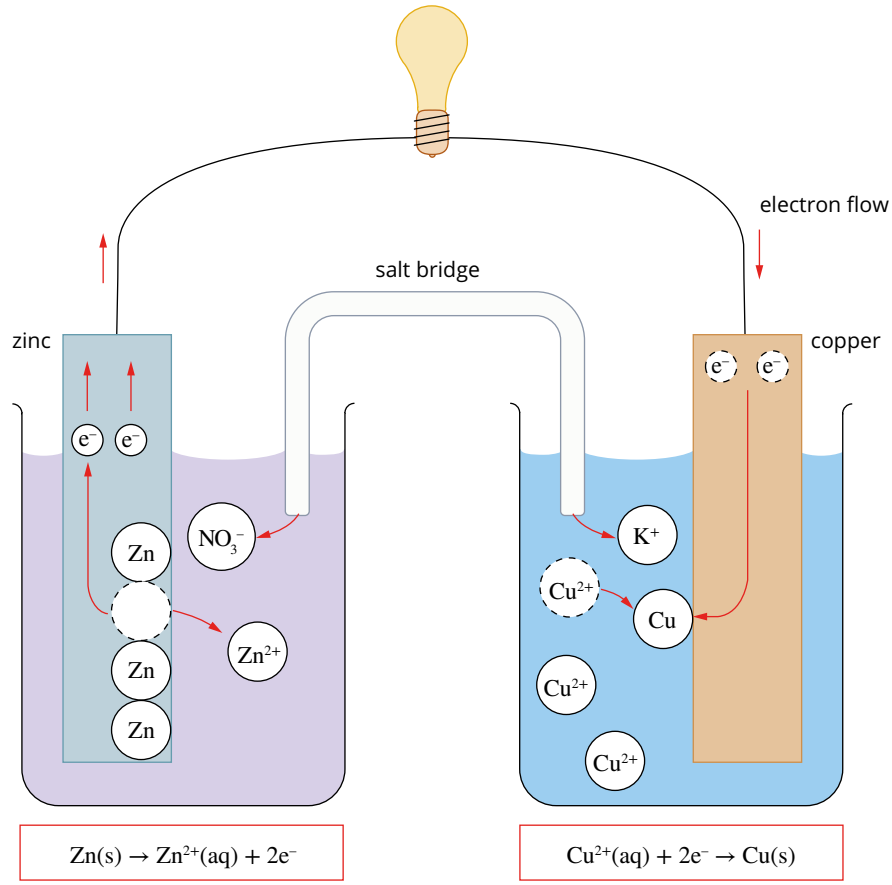


FIGURE 9.1.5 A representation of the electrode reactions in a Daniell cell. The salt bridge contains potassium nitrate solution.

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**.

> A chemical that causes another substance to be oxidised is called an oxidising agent and is itself reduced in the 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 9.1.6 $Cu^{2+}(aq)$ ions in blue-coloured copper(II) sulfate solution reacting directly with a strip of zinc metal

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 (Figure 9.1.6).

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 into thermal energy. However, in a galvanic cell, the half-reactions occur in separate containers, and the electrons are transferred through 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 9.1.7.

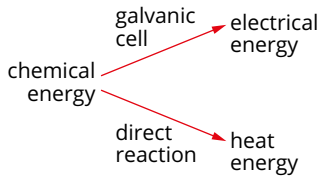


FIGURE 9.1.7 Energy transformations that occur when reactants are separated in a galvanic cell and when the reactants react directly

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.

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 9.1.8). 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 forms 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 $Br_2(aq)/Br^-(aq)$ 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, as shown in Figure 9.1.8.

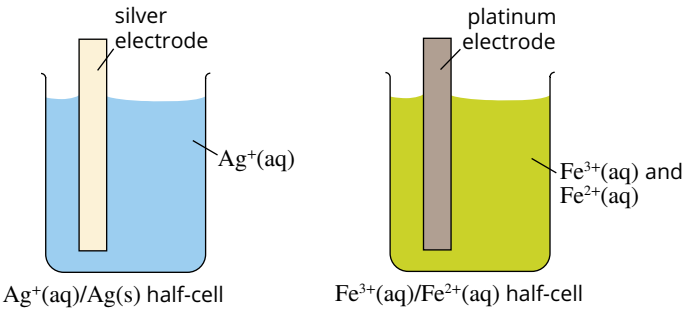


FIGURE 9.1.8 Typical half-cells. The $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell on the right does not contain a solid metal to act as an electrode, so an inert platinum electrode has to be added.

In some half-cells, one of the conjugate pairs may be a gas. In such cases, the special 'gas electrode', like the one shown in Figure 9.1.9 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.

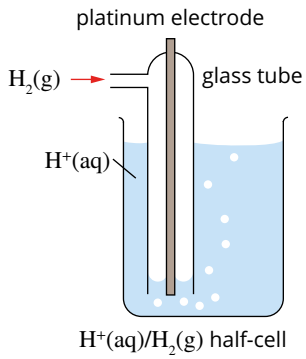


FIGURE 9.1.9 A $H^+(aq)/H_2(g)$ half-cell consists of a platinum rod in a solution of $H^+(aq)$ with H_2 gas bubbling through the solution.

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 compartments. *Cat*ions move towards the *cat*hode and *an*ions move towards the *an*ode.

> Cations in the salt bridge move towards the cathode and anions in the salt bridge move towards the anode.

Without a salt bridge, as the reaction proceeded, the solution in one compartment in the galvanic cell would accumulate negative charge and the solution in the other compartment would accumulate positive charge. Such accumulation of charge would stop the reaction very quickly and, hence, prevent further reaction.

The salt bridge is also called the **internal circuit**.

WRITING HALF-CELL EQUATIONS

> In balanced half-equations and overall equations, the:
>
> - number of atoms of each element is equal on both sides
> - total charge on each side is equal.

If a conjugate redox pair consists of an element and its corresponding ion, then the half-equation is relatively easy to write. For example, knowing that a reduction reaction involves the conjugate redox pair of Zn^{2+} ions and Zn, you can simply 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 write half-equations such as these in Chapter 8.

Writing an overall equation for a cell reaction

> The number of electrons lost in the oxidation reaction must equal the number of electrons gained in the reduction 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.

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. The diagram will identify key features, such as the anode, cathode, electrode polarity, direction of electron flow in the external circuit and direction of the flow of ions in the solutions and the salt bridge.

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 is oxidised and oxidation occurs at the anode)
- chlorine gas is present at the cathode (because 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 9.1.10.

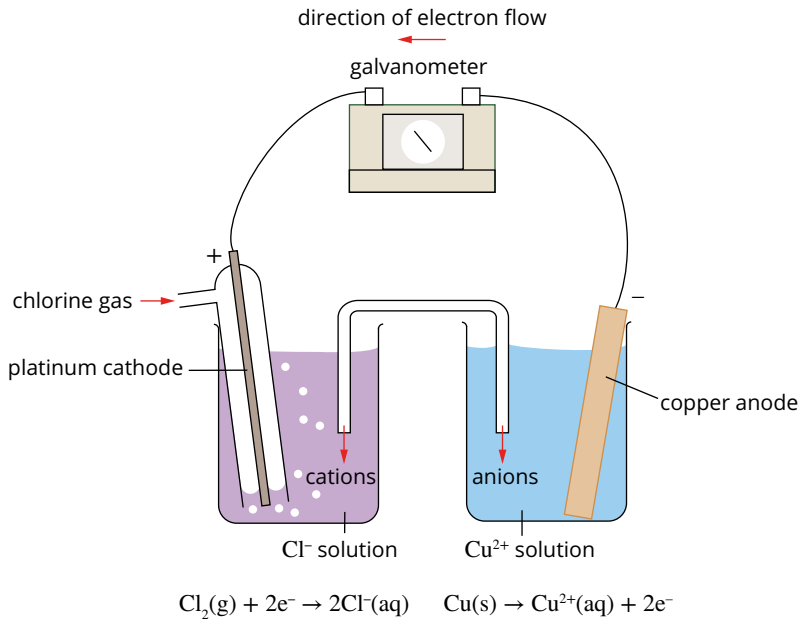


FIGURE 9.1.10 A diagram of the cell containing $Cl_2(g)/Cl^-(aq)$ and $Cu^{2+}(aq)/Cu(s)$ half-cells

Shorthand cell notation

A useful shorthand notation can be used to describe the components of a galvanic cell. For example, the Daniell cell shown earlier (Figure 9.1.4), can be represented as shown in Figure 9.1.11.

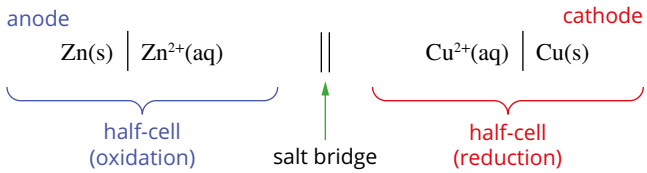


FIGURE 9.1.11 A shorthand representation of the Daniell cell, which contains $Zn^{2+}(aq)/Zn(s)$ and $Cu^{2+}(aq)/Cu(s)$ half-cells

The components of the half-cell that contains the anode, and undergoes oxidation, are shown on the left. The components of the half-cell that contains the cathode, and undergoes reduction, are shown on the right. A double vertical line represents the salt bridge and single vertical lines are used to separate chemicals in different physical states.

The cell shown in Figure 9.1.10 is represented as:

$$Cu(s) \mid Cu^{2+}(aq) \parallel Cl^-(aq) \mid Cl_2(g) \mid \text{platinum}$$

Note that the electrode that is negatively charged is on the far left and the electrode that is positively charged is on the far right.

9.1 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.
- Galvanic cells can be represented by cell diagrams and by a shorthand notation.
- Key concepts about a galvanic cell are summarised in Figure 9.1.12.

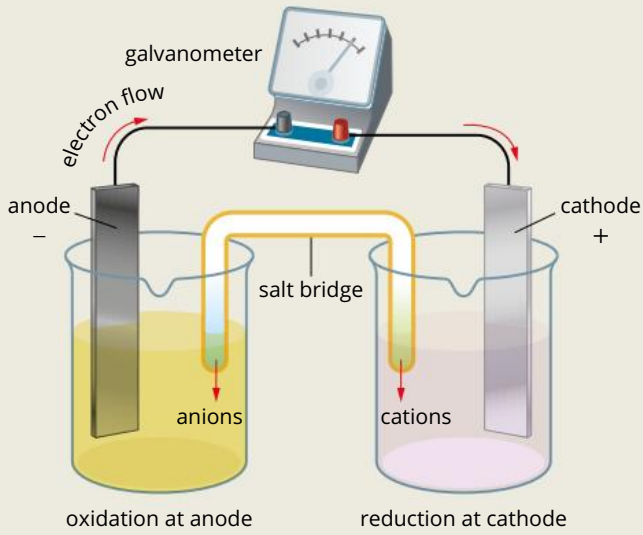


FIGURE 9.1.12 Key concepts of how a galvanic cell works

KEY QUESTIONS

1 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 Anions flow into the half-cell containing the electrode where reduction occurs.

D The electrode where oxidation occurs has a negative polarity.

2 Draw labelled diagrams of the following half-cells.

a $Ni^{2+}(aq)/Ni(s)$

b $Sn^{4+}(aq)/Sn^{2+}(aq)$

c $H^{+}(aq)/H_2(g)$

3 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:

$$2Al(s) + 3Sn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Sn(s)$$

Write half-equations for the reaction occurring at the:

a cathode

b anode.

4 Draw a diagram of the cell from Question **3** and label the:

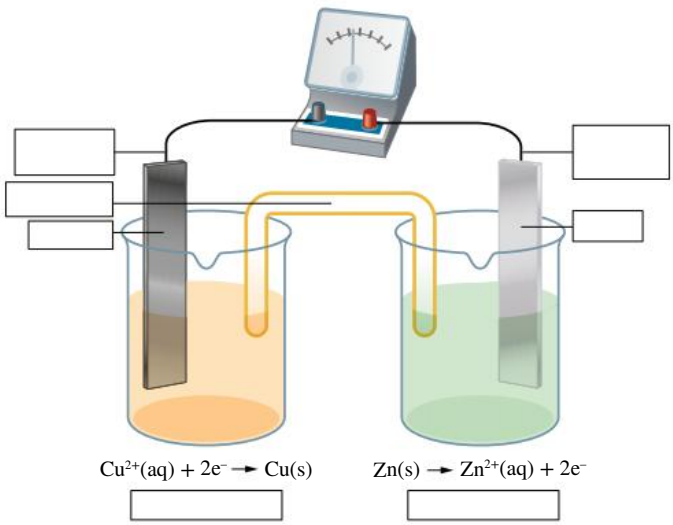
- half-equation for the reaction occurring in each half-cell
- anode and cathode
- direction of electron flow
- electrode polarities (which electrode is positive and which is negative)
- direction of anion and cation flow from the salt bridge.

5 Write the cell equation from Question **3** using shorthand cell notation.

6 In the spaces provided, label the following galvanic cell with:

- anode
- cathode
- positive electrode
- negative electrode
- reduction
- oxidation
- salt bridge.

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



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

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

9.2 The electrochemical series

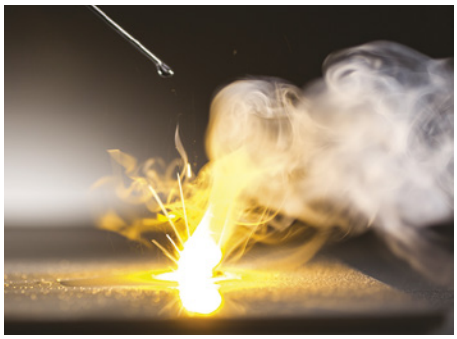


FIGURE 9.2.1 Sodium is highly reactive. When water is dropped onto sodium metal, the products are sodium hydroxide and hydrogen gas.

As you saw in Chapter 8, metals vary in their reactivity. Platinum and gold are unreactive and widely used for jewellery. Other metals are very reactive. For example, sodium reacts so readily with oxygen and water (Figure 9.2.1) 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 9.2.2 shows a diagram of a cell constructed from $H^+(aq)/H_2(g)$ and $Zn^{2+}(aq)/Zn(s)$ half-cells.

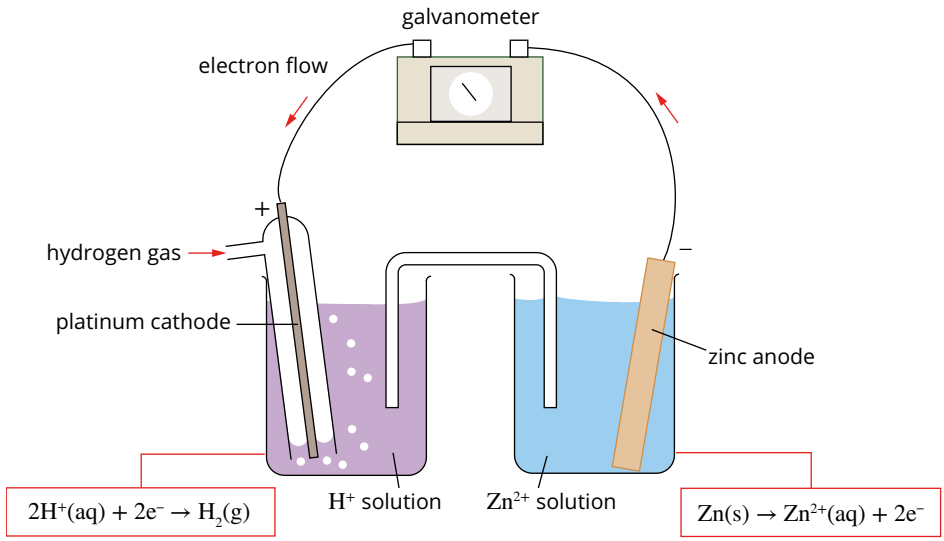


FIGURE 9.2.2 A diagram of a cell constructed from $H^+(aq)/H_2(g)$ and $Zn^{2+}(aq)/Zn(s)$ half-cells

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^+. 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, you 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 9.2.4 for the $Fe^{2+}(aq)/Fe(s)$ half-cell.

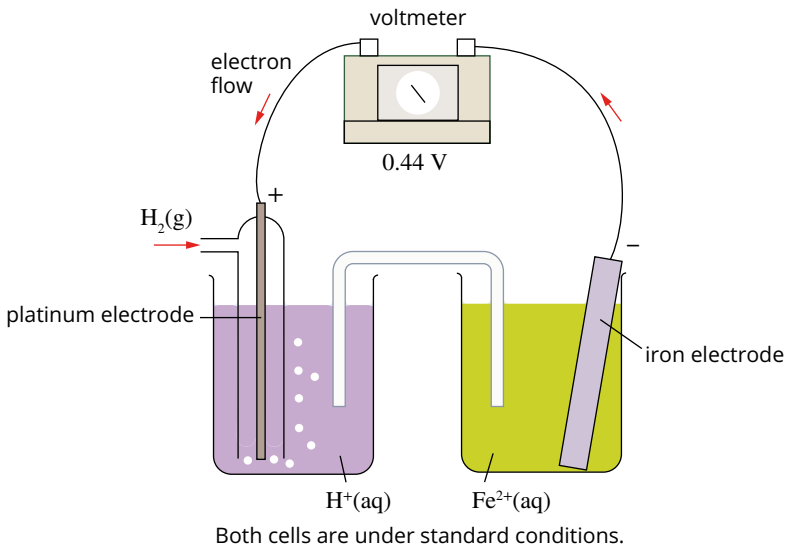


FIGURE 9.2.4 Measuring the standard half-cell potential of a $Fe^{2+}(aq)/Fe(s)$ half-cell. From the voltmeter reading and negative polarity of the iron electrode, the $E°$ of this half-cell is –0.44 V.

The information obtained from this measurement shown in Figure 9.2.4 can be summarised as follows:

$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \quad E° = -0.44\,V$$

CHEMFILE

Electrical energy from a lemon

You can generate electrical energy from a lemon or other fruit. As well as the lemon, you need a galvanised iron nail, a copper nail and two wires with crocodile clips at each end.

To make a galvanic cell, squeeze the lemon, without breaking its skin, to release its juices. Then push both nails half their length into the lemon, with the nails about 5 cm apart. Connect the nails to separate wires.

The free ends of the wires of this cell can then be connected to low current electronic devices, such as a battery-operated digital clock, an LED light or cheap calculator (Figure 9.2.3). A stronger source of electricity can be created by making several of these lemon cells and using wires to connect them in series to make a battery. (Use a wire to connect the zinc metal in one lemon directly to the copper metal in another lemon.)

FIGURE 9.2.3 An electrical cell made from a lemon

The zinc metal on the surface of the iron nail is oxidised to Zn^{2+} and H^+ in the acidic lemon juice is reduced to H_2. The cell is similar to the one shown earlier in Figure 9.2.2.

The negative sign indicates that the electrode in the half-cell was negative when connected to the hydrogen half-cell. 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.

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** (Figure 9.2.5).

strongest oxidising agent

increasing oxidising agent strength

Half-reaction	$E°$ (volts)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.89
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.76
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.69
$2HClO(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l)$	+1.63
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$HClO(aq) + H^+(aq) + 2e^- \rightleftharpoons Cl^-(aq) + H_2O(l)$	+1.49
$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$	+1.46
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.08
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.70
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(aq)$	+0.17
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0 exactly
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	–0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	–0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	–0.24
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	–0.28
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$	–0.36
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	–0.40
$2CO_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2C_2O_4(aq)$	–0.43
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	–0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	–0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	–0.83
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	–1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	–1.68
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	–2.36
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	–2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	–2.87
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	–2.90
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	–2.91
$K^+(aq) + e^- \rightleftharpoons K(s)$	–2.94

weakest reducing agent

increasing reducing agent strength

weakest oxidising agent

strongest reducing agent

FIGURE 9.2.5 The electrochemical series. The strongest oxidising agents are at the top left of the table and the strongest reducing agents are at the bottom right of the table.

Under non-standard conditions, the order of the half-cells 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 top left of the table and the strongest reducing agent, Li, is at the bottom 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

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 higher in the electrochemical series goes forward and the lower one is reversed. (This is sometimes called the 'clockwise rule'.) 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.

The equation for the overall cell reaction is found by adding the two half-equations. Worked Example 9.2.1 shows you how to use the electrochemical series to predict a cell reaction.

Worked example 9.2.1

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 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.

Thinking	Working
Identify the two relevant half-equations in the electrochemical series.	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $\quad E^\circ = +0.80$ V $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ $\quad E^\circ = -0.44$ 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 (bottom right).	Because Ag^+ is higher on the left side of the table than Fe^{2+}, it is the strongest oxidising agent. Fe, being lower on the right side of the table than Ag, is the strongest reducing agent.
Write 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 half-equation should be written in reverse.
Write 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 half-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 9.2.6.

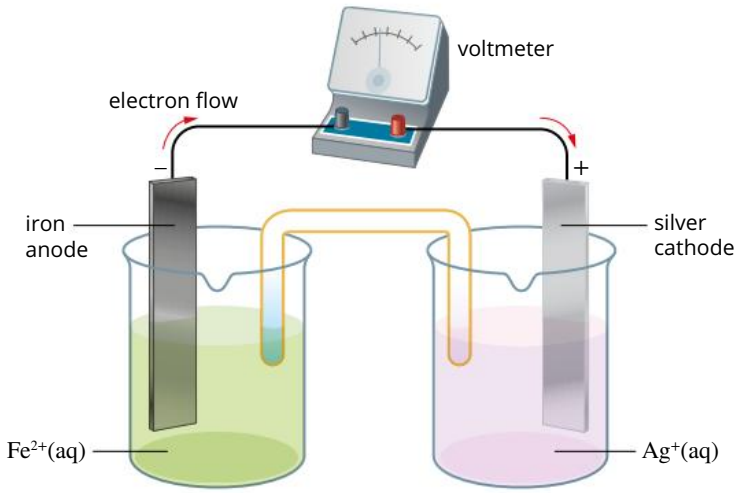


FIGURE 9.2.6 A cell containing Fe^{2+}/Fe and Ag^{+}/Ag half-cells

Worked example: Try yourself 9.2.1

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
$- E^\circ$ of half-cell containing the reducing agent

An easy way to remember this for galvanic cells is:

cell potential difference = higher half-cell E° – lower 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 = higher half-cell E° – lower half-cell E°
$= E^\circ(Ag^{+}(aq)/Ag(s)) - E^\circ(Fe^{2+}(aq)/Fe(s))$
$= 0.80 - (-0.44)$
$= 1.24\,V$

Note that because the standard electrode potentials are all determined under standard conditions, different values for the cell voltage are obtained under non-standard conditions.

As a galvanic cell discharges, the cell voltage eventually drops to zero as the reactants are consumed. A point will come when the forward reaction is going no faster than the reverse reaction, and a state of equilibrium is achieved. Electrons will stop flowing from the anode to the cathode and the cell is referred to as 'flat'.

The easiest way to calculate the cell potential difference is to remember:

cell potential difference = higher half-cell E° – lower half-cell E°

9.2 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 top left of the series (with the most positive $E°$ value) and the strongest reducing agent is at the bottom right (with the most negative $E°$ value).
- The electrochemical series is valid for standard conditions; that is, gas pressures of 100 kPa and solution concentrations of 1.00 mol L^{-1}. Standard electrode potentials are 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 = $E°$ of half-cell containing the oxidising agent – $E°$ of half-cell containing the reducing agent or, more simply: cell potential difference = higher half-cell $E°$ – lower 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 lower in the series.

KEY QUESTIONS

1 A galvanic cell was constructed from $Al^{3+}(aq)/Al(s)$ and $Pb^{2+}(aq)/Pb(s)$ half-cells. Use the electrochemical series to predict the:
- **a** oxidation and reduction half-equations
- **b** overall cell reaction
- **c** identity of the anode and cathode.

2 Draw a labelled diagram of a cell formed from $Cl_2(g)/Cl^-(aq)$ and $Sn^{2+}(aq)/Sn(s)$ half-cells. Use the electrochemical series to indicate the:
- half-cell reactions
- anode and cathode
- direction of electron flow
- electrode polarities (which electrode is positive and which is negative)
- directions of flow of the anions and cations in the salt bridge
- overall reaction.

3 Repeat Question **2** for the cells formed from the following half-cells.
- **a** $Fe^{3+}(aq)/Fe^{2+}(aq)$ and $H^+(aq)/H_2(g)$
- **b** $Cl_2(g)/Cl^-(aq)$ and $Pb^{2+}(aq)/Pb(s)$

4 Calculate the cell potential difference for each of the cells in Questions **1–3**.

9.3 Predicting direct redox reactions

The electrochemical series provides a ranking of the relative strengths of oxidising and reducing agents.

In this section, 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.

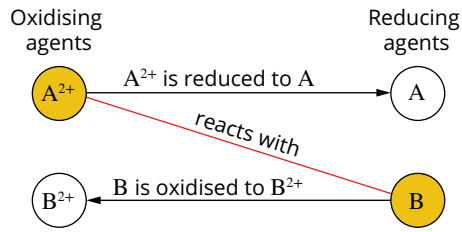
PREDICTING REACTIONS

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 section, you saw that in a galvanic cell the strongest oxidising agent in the cell reacts with the strongest reducing agent. In other words, the higher half-reaction (the one with the most positive E° value) in the electrochemical series occurs in the forward direction (as reduction), and the lower reaction (the one with the most 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 9.3.1, 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 is lower in the electrochemical series.



A^{2+} reacts with B.
No reaction occurs for the other combinations:
A and B, A^{2+} and B^{2+}, A^{2+} and A, A and A^{2+}, A^{2+} and B.

FIGURE 9.3.1 Oxidising agents only react significantly with reducing agents that are lower in the electrochemical series.

With half-equations arranged in order of increasing reducing agent strength, you can predict that a spontaneous reaction will occur by looking for substances that are arranged in a top-left/bottom-right position.

Worked example 9.3.1

PREDICTING DIRECT REDOX REACTIONS

Consider the following equations that appear in the order shown in the electrochemical series.

$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$ $\quad E^\circ = +1.09$ V

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

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

Use the electrochemical series to predict the effect of mixing:

a $Br_2(aq)$ 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 (an oxidising agent) of the electrochemical series reacts with a chemical species on the right (a reducing agent) that is lower in the series. Write the overall equation.	**a** $Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$ $E° = +1.08$ V $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $E° = -2.36$ V No reaction occurs because both $Br_2(aq)$ and $Mg^{2+}(aq)$ are oxidising agents. **b** $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E° = -0.24$ V $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $E° = -2.36$ V No reaction occurs because the oxidising agent, Mg^{2+}, is below the reducing agent, Ni, in the electrochemical series. **c** $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E° = -0.24$ V $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $E° = -2.36$ V A reaction occurs because the oxidising agent, Ni^{2+}, is above the reducing agent, Mg, in the electrochemical series. The higher half-equation occurs in the forward direction: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ The lower 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: $Ni^{2+}(aq) + Mg(s) \rightarrow Ni(s) + Mg^{2+}(aq)$

Worked example: Try yourself 9.3.1

PREDICTING DIRECT REDOX REACTIONS

Consider the following equations, which appear in the order shown in the electrochemical series:

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E° = +1.36$ V

$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$ $E° = +0.54$ V

$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$ $E° = -0.13$ 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 $Cl^-(aq)$ and Pb(s).

Predicting cell reactions can also be considered from cell potential differences calculated as shown in section 9.2. If the cell potential for an overall reaction is a positive value, that reaction should occur spontaneously. If the cell potential of a proposed reaction is a negative value, that reaction will not occur spontaneously.

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.

CHEMFILE

The thermite reaction

The thermite reaction is a highly exothermic reaction between powdered aluminium and iron(III) oxide.

The two relevant half-equations for this reaction, listed in their order in the electrochemical series are:

$Fe^{3+} + 3e^- \rightleftharpoons Fe$ $E° = -0.04$ V

$Al^{3+} + 3e^- \rightleftharpoons Al$ $E° = -1.67$ V

A spontaneous reaction is predicted to occur because the oxidising agent, Fe^{3+}, is above the reducing agent, Al, in the series. (Even though the actual reaction here does not occur in aqueous solution, and under standard conditions, you can still compare the electrode potentials to determine the stronger reducing agent.)

The thermite reaction releases so much heat that it is enough to melt the iron that is produced. One use for the thermite reaction is for welding together railway tracks (Figure 9.3.2).

FIGURE 9.3.2 Thermite welding of railway tracks

9.3 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 is lower in the series.
- 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

1 Which one of the following metals would you expect to be coated with lead when immersed in a solution of lead(II) nitrate?

A copper
B cobalt
C silver
D gold

2 Which one of the following species would react with $H_2S(g)$ but not with $H_2O(l)$ under standard conditions?

A $Cl_2(g)$
B $Mg(s)$
C $Ag^+(aq)$
D $Cu(s)$

3 Using the electrochemical series, predict whether a reaction will occur in the following situations. If a reaction does occur, write 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.

4 A reaction occurs when a strip of zinc metal is placed in a silver nitrate solution.

a Write the overall equation for the reaction.
b Describe the energy change that takes place in this reaction.

5 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 to identify in which solution(s) you would expect a coating of a metal other than iron to appear on the nail.

9.4 Everyday sources of power

The battery was invented by Alessandro Volta in 1800. More than two centuries later, 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 section, you will look at the three main types of cells in use and how chemical reactions in these cells are used to produce electricity for everyday applications.

The three 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
- **fuel cells**, which continuously produce electricity for as long as fuel is fed into the cells.

Primary cells, secondary cells and fuel cells are all 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** (Figure 9.4.1). They 'go flat' when most of the reactants are used up, the cell reaction reaches equilibrium, and you have to buy a replacement.

FIGURE 9.4.1 Non-rechargeable alkaline cells are used to power many devices, including torches, smoke detectors and calculators. They are discarded once they go flat.

EXTENSION

Primary cells—alkaline cells

Following World War II, an expanding range of electrical appliances became available that required small, high-capacity power sources. The earlier types of cells were unable to meet these demands, so the alkaline cell was developed in the late 1960s.

Figure 9.4.2 shows the construction of an alkaline cell. This cell is similar to the simple galvanic cells discussed 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.

An alkaline cell needs less electrolyte than a dry cell, which it has largely replaced for household use. The smaller quantity of electrolyte allows more reactant to be included. A typical D size alkaline cell contains about 40 g of manganese dioxide, compared with 25 g in a dry cell of equivalent size.

The following reactions occur in an alkaline cell.

- At the anode (–), zinc powder around the central metal rod is oxidised and reacts with hydroxide ions, forming zinc hydroxide:

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

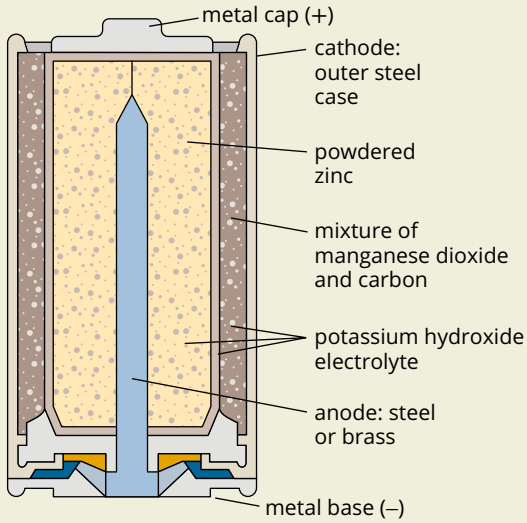


FIGURE 9.4.2 Construction of an alkaline cell

- At the cathode (+), manganese dioxide is reduced:

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

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.

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.

CHEMFILE

Powering the Overland Telegraph

One of the first primary cells in widespread use in the 19th century was called the Leclanché cell. It had a similar overall cell reaction to the reaction in alkaline cells.

Leclanché cells were one of the sources of power for the Australian Overland Telegraph Line, one of the great engineering feats of 19th-century Australia. The 3200 km telegraph line was completed in 1872 and connected Darwin in the Northern Territory with Port Augusta in South Australia, allowing fast communication between Australia and the rest of the world (Figure 9.4.3). An additional section to Western Australia was added in 1877.

FIGURE 9.4.3 The Alice Springs telegraph station, built in 1872

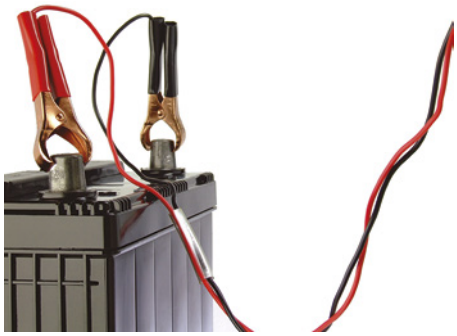


FIGURE 9.4.4 Charging a secondary battery involves connecting the positive terminal of a charger to the battery's positive electrode and the negative electrode of the charger to the battery's negative electrode.

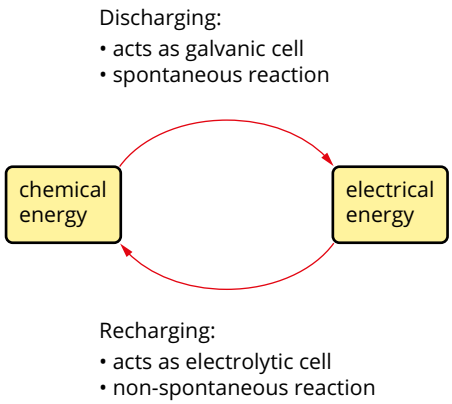


FIGURE 9.4.5 Energy transformations in secondary cells

SECONDARY CELLS

Rechargeable cells, such as **lithium-ion cells** 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 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 to the cell's negative electrode (see Figure 9.4.4).

Primary cells cannot be recharged, whereas secondary cells can be recharged by connecting them to an external source of electricity.

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 10.

The energy transformations and redox processes that occur during the discharging and recharging of a secondary cell are summarised in Figure 9.4.5.

Secondary batteries—car batteries

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 (Figure 9.4.6). 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.

FIGURE 9.4.6 Lead–acid batteries are used to start cars, trucks and motorcycles.

Lead–acid batteries are also used for emergency light and power systems, for small-scale energy storage and to power some electric vehicles, such as golf buggies and small fork lifts.

As shown in the diagram in Figure 9.4.7, a modern lead–acid battery is actually six separate cells connected together in series. The positive electrodes consist of a lead grid packed with lead(IV) oxide (PbO_2), while the negative electrodes consist of a lead grid packed with powdered lead. A solution of sulfuric acid, of about $4\,mol\,L^{-1}$ concentration, acts as the electrolyte.

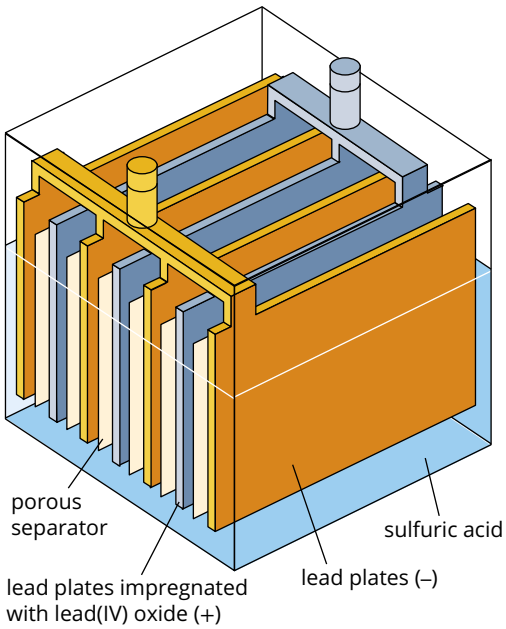


FIGURE 9.4.7 Construction of a lead–acid battery

Each cell has a potential difference of just over 2 V. A car battery has six of these cells connected in series, giving a total potential difference of about 12 V.

The following reactions occur in a lead–acid battery as it produces electricity.

- At the anodes (–), lead is oxidised to Pb^{2+} ions:

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

- At the cathodes (+), lead(IV) oxide is reduced to Pb^{2+} ions:

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$

The two half-equations can be combined as an overall equation:

$$Pb(s) + PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

The product of both electrode reactions, lead(II) sulfate, forms as a solid on the surface of the electrodes. This enables the battery to be recharged.

To recharge the battery, the electrode reactions are reversed. The alternator, with a potential difference of about 14 V, is used to force electrons into the battery's negative terminal and draw them out at the positive terminal, in effect driving the spontaneous reaction backwards. The recharging process converts electrical energy into chemical energy.

The overall equation for the reaction as the battery recharges is:

$$2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq)$$

CHEMISTRY IN ACTION

Lithium-ion batteries

Some car manufacturers are beginning to equip cars with lithium-ion batteries instead of traditional lead–acid batteries. Lithium-ion batteries are much lighter, lowering the overall weight of a car and offering a slight improvement in fuel efficiency. Although more costly, lithium-ion batteries also last longer than lead–acid batteries, which means they need replacing less often.

Lithium-ion cells and batteries are also the power source of choice for many portable electronic products, including phones, notebook computers, digital cameras and drones (Figure 9.4.8). They are light and powerful, and unlike ordinary alkaline cells, lithium-ion cells and batteries are not discarded when flat. Instead, they are secondary cells and can be recharged and reused.

Sony released the first commercial lithium-ion cells in 1991. Lithium's low weight and high reactivity had long been recognised as potentially useful in cells and batteries. However, while lithium's reactivity might be ideal, it also makes practical applications difficult. Lithium reacts with many everyday materials and can react explosively with water. As a consequence, the development of a lithium-based cell using a non-aqueous electrolyte has been a significant scientific as well as technological achievement.

Lithium-ion cells are designed principally to overcome the safety concerns surrounding the use of a strong reactant such as metallic lithium. Lithium-ion cells do not contain lithium in the metallic state; rather, the lithium is adsorbed into the lattice structure of a graphite electrode.

When a lithium-ion cell generates electricity, the following half-reactions occur.

- At the anode (–), oxidation of lithium generates electrons:

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

  Once formed, Li^+ ions migrate into the electrolyte.
- At the cathode (+), the electrode material, which is usually a metal oxide such as cobalt oxide, accepts electrons. The product combines with Li^+ ions from the electrolyte and precipitates. For example:

  $CoO_2(s) + Li^+ + e^- \rightarrow LiCoO_2(s)$

The equation for the overall cell reaction is formed by adding the two half-equations:

$$Li(s) + CoO_2(s) \rightarrow LiCoO_2(s)$$

A lithium-ion cell delivers a steady 3.6 V as it discharges. When a lithium-ion cell is discharging, the products of the reaction remain available within the cell. By supplying the discharged cell with electrical energy, the electrode reactions can be reversed and the reactants regenerated.

Although their complex internal structure makes them more expensive to manufacture, lithium ion cells are becoming increasingly popular because of their high energy density and low weight.

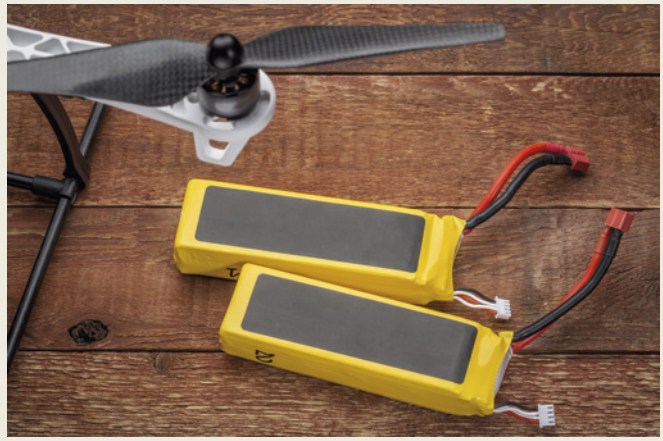


FIGURE 9.4.8 Lithium-ion power supplies are used in drones and radio-controlled models.

FUEL CELLS

The major limitation of the cells that have been examined so far is that they contain relatively small amounts of reactants. Furthermore, when the reaction reaches equilibrium the cell must be discarded or recharged.

Cells can be constructed in which the reactants are supplied continuously, allowing constant production of electrical energy. These devices are called fuel cells.

> **i** A key difference between a fuel cell and a primary or secondary cell is that the reactants are not stored in the fuel cell. They must be continuously supplied from an external source.

Fuel cells use the chemical energy of hydrogen or other fuels to cleanly and efficiently generate electricity. Even though fuel cell technology is still being developed, fuel cells can be used in numerous applications. These uses include as a source of power for transport (Figure 9.4.9) and for emergency back-up power applications.

A fuel cell is a type of galvanic cell, but, unlike the cells you studied previously in this chapter, fuel cells do not run down or need recharging. Electricity is produced for as long as fuel is supplied to them.

FIGURE 9.4.9 A hydrogen fuel cell for an electric bicycle. The hydrogen bicycle operates like a standard electric bicycle, but the battery lasts three times longer.

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, some 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 to up to 85%.

> **i** Fuel cells have a much higher efficiency than thermal power stations because chemical energy is directly converted into electrical energy.

A fuel cell using hydrogen as a fuel produces electricity, water, heat and very small amounts of nitrogen dioxide and other emissions.

Although the basic principles behind the operation of a fuel cell were discovered in 1838, it was not until the 1950s that fuel cells were used for small-scale power production. Fuel cells, such as the one shown in Figure 9.4.10, were the main on-board power supply units and source of water during the Apollo space program that put humans on the Moon. An explosion in a fuel cell was responsible for the failure of the Apollo 13 mission.

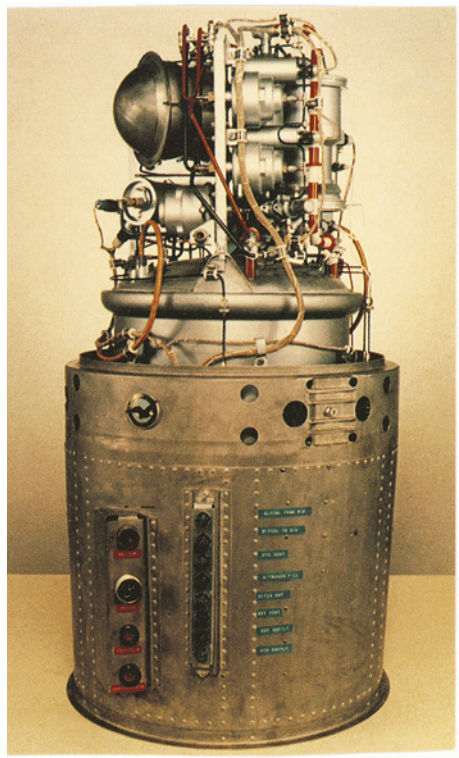


FIGURE 9.4.10 Fuel cells like this were used to supply electricity for the Apollo space program (1969–72). Fuel cells were also used in the later space shuttles.

Fuel cell design

Figure 9.4.11, on page 234, 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.

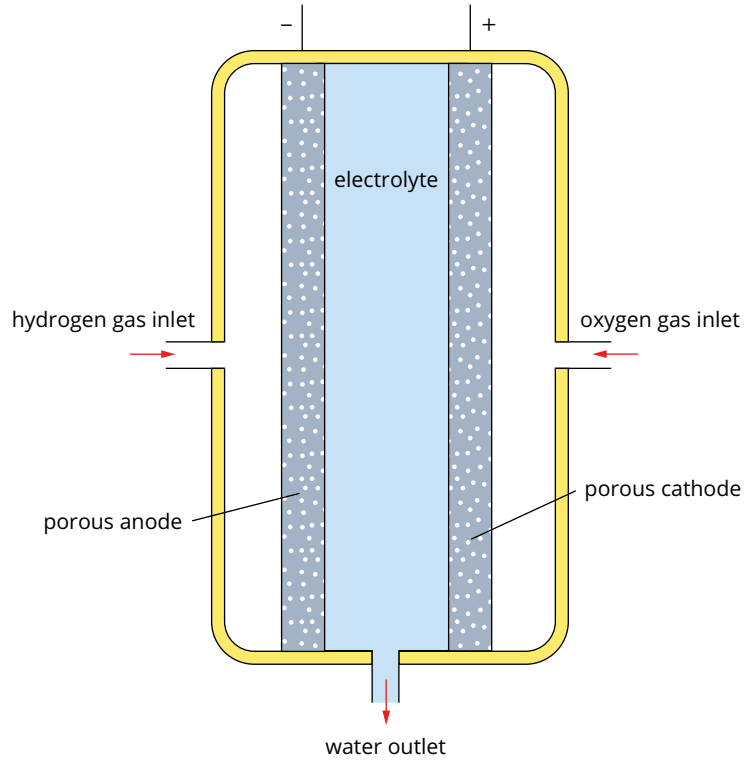


FIGURE 9.4.11 A simplified diagram showing the key parts of a hydrogen–oxygen fuel cell

The type of fuel cell used in the 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 (–), hydrogen gas (the 'fuel') is oxidised by reacting with hydroxide ions from the electrolyte:

  $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

- At the cathode (+), oxygen gas is reduced:

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

The overall equation for the reaction is:

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

Each cell produces about 1 V. Higher voltages are obtained by connecting a number of fuel cells in series to form a battery or fuel cell stack. The only by-product is water, and heat is also given off.

A range of different fuel cells has been developed, using different electrolytes, electrodes and operating temperatures.

The nature of the electrodes is crucial to the efficiency of a fuel cell. The electrodes must be both conducting and porous to allow the hydrogen and oxygen to come into contact with the ions in the electrolyte and to allow the redox half-reactions to 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.

Catalysts are used to enhance the rate of reaction and the current that can be produced from a cell. The catalyst incorporated in the anode increases the rate of oxidation of the fuel gas. Platinum metal is commonly used as a catalyst at this electrode. 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.

i Fuels cells contain porous electrodes that allow reactants to diffuse through them to react with ions in the electrolyte. They often contain catalysts to increase the rate of reaction.

THE HYDROGEN ECONOMY

Some scientists predict that, in the future, hydrocarbons will be replaced by hydrogen as the principal source of energy for transport and other purposes (the **hydrogen economy**). This would mean a drastic reduction in the production of greenhouse gases and other pollutants without affecting your quality of life. In the hydrogen economy, fuel cells are seen as a replacement for the 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 production and storage

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.

Alternative ways of producing hydrogen are being explored. At present, there are only two practical methods of generating hydrogen without producing carbon dioxide:

- using electrical energy to convert water to hydrogen. Electricity can be generated from renewable sources such as solar-power farms and wind farms (You will look at the chemical principles involved in the process of converting electrical energy to chemical energy in Chapter 10.)
- collecting **biogas** from landfill sites and converting the methane in the gas to hydrogen.

Widespread adoption of hydrogen as the primary fuel for powering vehicles and providing electricity for industrial and domestic applications would also require massive expenditure on infrastructure. Changes to pipelines and filling stations, as well as improvements in hydrogen storage methods, would be required.

The established methods of hydrogen storage in cars, trucks and buses are as liquid hydrogen or compressed hydrogen. Both storage methods provide substantially less energy per litre than the equivalent volume of a liquid hydrocarbon fuel such as petrol. Scientists are investigating alternative methods of storing hydrogen, including adsorption to the surface of materials such as metal hydrides. These storage methods offer considerable promise, but require further development.

Figure 9.4.14 (page 236) shows a vision for the future use of hydrogen.

Australia is a member of the International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE). This organisation was established in 2003 to accelerate the transition to a hydrogen economy. IPHE provides a mechanism for member countries to organise, coordinate and implement research and activities related to hydrogen and fuel cell technologies. Each country has committed to collaborating to advance hydrogen and fuel cell technologies in the marketplace in an effort to improve energy supply and the environment.

CHEMFILE

Fuel cells around us

Some types of breathalysers use fuel cell technology to measure blood alcohol levels. In this fuel cell, ethanol is oxidised and the electricity generated indicates the blood alcohol level (Figure 9.4.12).

FIGURE 9.4.12 Hand-held breathalysers are a type of fuel cell.

Fuel cells are also found in nature. The electric eel, which grows to more than 1 metre in length, has a natural battery made of specialised fuel cells within its body (Figure 9.4.13). The fuel for each cell is the food consumed by the eel and the oxidising agent is oxygen. Each cell generates about 1.5 V, yielding a total voltage from the head of the eel to its tail of more than 300 V.

FIGURE 9.4.13 Electric eels use electricity for several reasons. Low pulses of electrical discharge are emitted by the eel and then bounce back from passing objects to be detected by special electroreceptors on the skin. In this way, the eel navigates and locates its prey. High-intensity electrical discharges can also be used to stun or kill prey or as a form of defence.

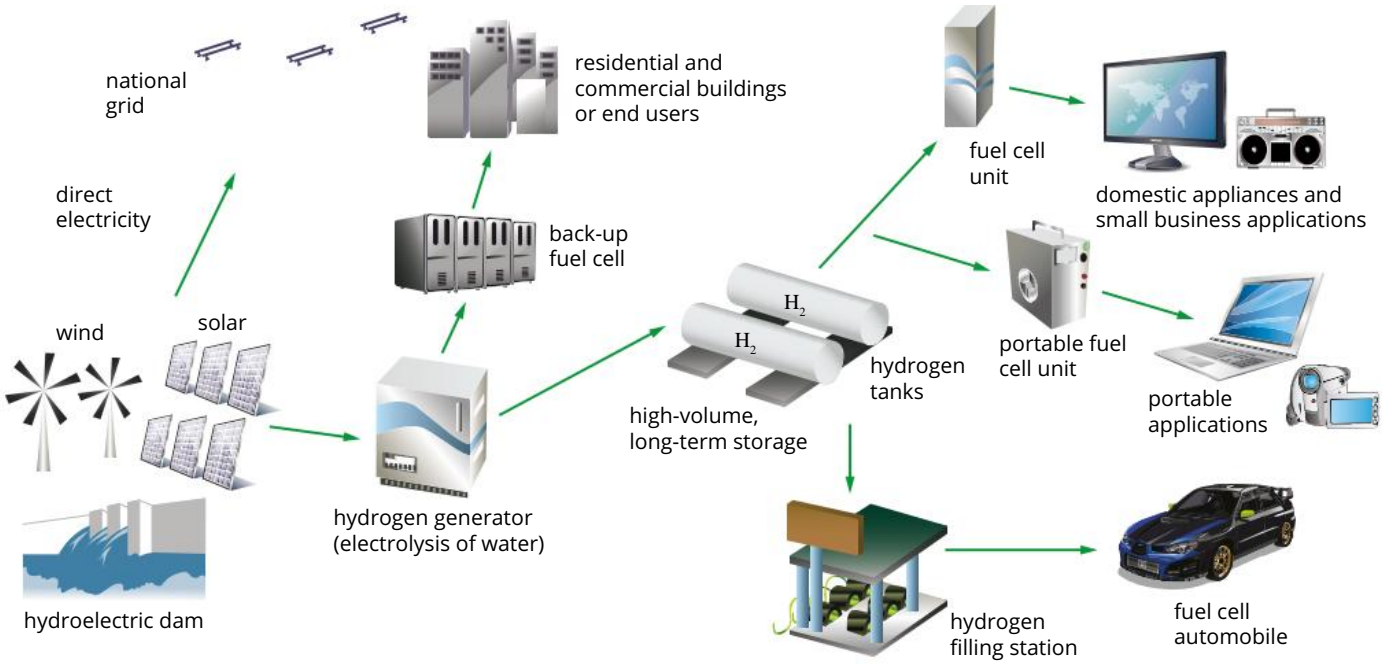


FIGURE 9.4.14 A view of future energy production based on the use of hydrogen

ADVANTAGES AND DISADVANTAGES OF FUEL CELLS

Scientists are striving to reduce the overall costs of fuel cells and to improve the electric current that can be drawn from them by increasing the rate of reaction at the electrodes. As described above, various types of fuel cells have been developed and tested, using a number of different fuels, electrolytes and catalysts.

Table 9.4.1 lists some of the advantages and disadvantages of fuel cells.

TABLE 9.4.1 Advantages and disadvantages of fuel cells

Advantages	Disadvantages
• Fuel cells convert chemical energy directly to electrical energy. This is more efficient than the series of energy conversions that takes place in power stations that burn fossil fuels: chemical energy → heat energy → mechanical energy → electrical energy. • Hydrogen fuel cells produce water and heat as by-products. No greenhouse gases, such as carbon dioxide, are released. • Fuel cells will generate electricity for as long as the fuel is supplied. Conventional batteries need to be recharged or replaced. • Fuel cells can use a variety of fuels. • Electricity can be generated on-site and users are not reliant on connection to an electricity grid. Waste heat can be used to heat water for a hot water system or provide heating for a home during winter.	• Fuel cells require a constant fuel supply. • Fuel cells are expensive. They are still a developing technology, and are not being made in large numbers, so there are no economies of scale as there are in other industries. • Some types of fuel cell use expensive electrolytes and catalysts. • The use of fuel cells in transport will require an extensive network of hydrogen filling stations before it can become widespread. • At present, the hydrogen used in many fuel cells is mainly sourced from fossil fuels. This process involves energy losses and generates greenhouse gases. • There are significant issues associated with the storage of hydrogen fuel.

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, lower emissions of greenhouse gases and other pollutants, and do not rely on oil (Figure 9.4.15).

FIGURE 9.4.15 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

Apart 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 uses phosphoric acid fuel cells that are powered by hydrogen from steam re-forming of natural gas (Figure 9.4.16).
- 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 forklift vehicles.
- Silicon Valley technology companies in California, USA, are installing fuel cells as a stable, sustainable source of power.

FIGURE 9.4.16 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.

9.4 Review

SUMMARY

- Primary, secondary and fuel cells are examples of galvanic cells, converting chemical energy directly into electrical energy.
- Primary cells cannot be recharged whereas 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 equation for the reaction that occurs during the recharging of a secondary cell is the reverse of the equation for the cell discharging.
- When a secondary cell discharges it acts as a galvanic cell, releasing electrical energy; when it is recharged, it acts as an electrolytic cell, converting electrical energy to chemical energy
- Fuel cells are devices in which the reactants are supplied continuously, allowing constant production of electrical energy.
- Electricity generation using fuel cells is more efficient than if the electricity were generated by the combustion of the same fuel.
- The emissions of greenhouse gases from a fuel cell are much less than if the fuel were burnt in a power station or vehicle.
- Some scientists predict that fuel cells will play a key role in the transition from a dependence on fossil fuels for energy to a hydrogen economy.

KEY QUESTIONS

1 Describe the key difference between a primary cell and a secondary cell.

2 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 non-spontaneous reaction occurs and the lithium-ion cell acts as an electrolytic cell.
B A non-spontaneous reaction occurs and the lithium-ion cell acts as a galvanic cell.
C A spontaneous reaction occurs and the lithium-ion cell acts as an electrolytic cell.
D A spontaneous reaction occurs and the lithium-ion cell acts as a galvanic cell.

3 Which one or more of the following features do secondary cells and fuel cells have in common as they produce electricity?

A A catalyst is used to increase reaction rate.
B Cations in the electrolyte move towards the cathode.
C The anode is negative.
D The cathode is constructed from a porous material.
E Oxidation occurs at the cathode.
F The oxidising agent is a gas.
G Chemical energy is converted into electrical energy.

4 Which one of the following is a correct statement about what happens in a hydrogen–oxygen fuel cell?

A Hydrogen gas is oxidised at the anode.
B Electrons flow through the external circuit from cathode to anode.
C Solid, impermeable electrodes are required to prevent contact between reactants and the electrolyte.
D Oxygen gas is oxidised at the anode.

5 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. Write a half-equation for the reaction occurring at the:

a anode
b cathode.

9.5 Corrosion

The reactions that occur when metals corrode are redox reactions. The costs associated with corroding metals are substantial, especially because 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 9.5.1.

FIGURE 9.5.1 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.

In this section, you will use your knowledge of redox chemistry and galvanic cells to consider the chemistry of corrosion. 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 9.5.2 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; 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 9.5.2 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 9.5.3.

Each of these observations gives you 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.

In order to understand the process of wet corrosion of iron, and how it can be prevented, it is useful to consider the reactions occurring as a form of galvanic cell, with an anode (oxidation) and a cathode (reduction). The conducting iron allows for electrons to travel between the anode (anodic site) and the cathode (cathodic site).

FIGURE 9.5.3 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.

Wet corrosion process

Rust is a hydrated oxide of iron with the formula $Fe_2O_3 \cdot xH_2O$. There can be 1–3 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 9.5.4.

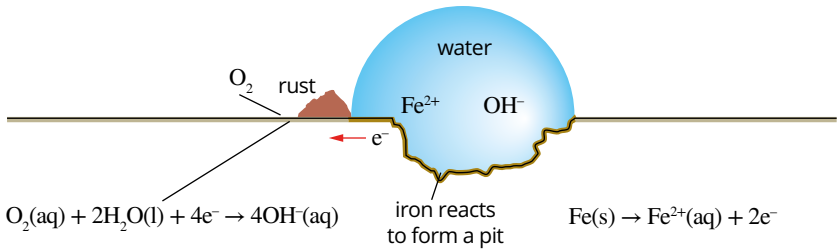


FIGURE 9.5.4 During wet corrosion, electrons are transferred through the iron from the area where oxidation occurs to the area where reduction occurs. Ions flow through the water droplets.

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. All methods will prevent one of the processes described above from happening. If you stop one process, then you will stop the overall rusting process.

The simplest way 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 both reduce friction and prevent contact with oxygen and moisture.

FIGURE 9.5.5 These food cans are made from steel that has been plated with tin to prevent them corroding.

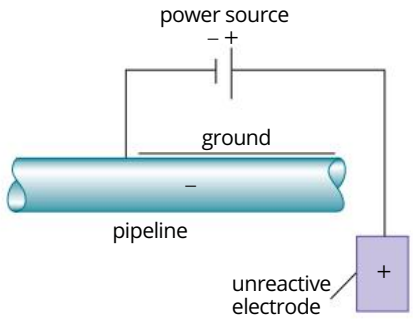


FIGURE 9.5.6 A pipeline carrying natural gas can be protected from corrosion if a direct current source is connected at intervals to give the pipe a negative charge.

Iron can also be protected by alloying it 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** (see Chapter 10). 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 9.5.5, have a plastic liner to prevent contact between the food and any metal oxides that may be present.

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. For corrosion to occur, the iron normally loses electrons (is oxidised). The act of making the iron negative pushes electrons towards the iron, thus reducing the chance of oxidation occurring. Instead, the iron becomes the site of the reduction reaction, and forms the cathode. This method, represented in Figure 9.5.6, is used to protect large-scale steel structures such as wharves and pipelines. A single DC source operating at 4.2 V and 2.5 A will protect many kilometres of pipeline.

Sacrificial protection also involves the iron acting as the cathode. A more easily oxidised metal, such as zinc, forms 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 9.5.7a. 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 9.5.7b depicts this process. The zinc slowly corrodes, but the iron is protected for years.

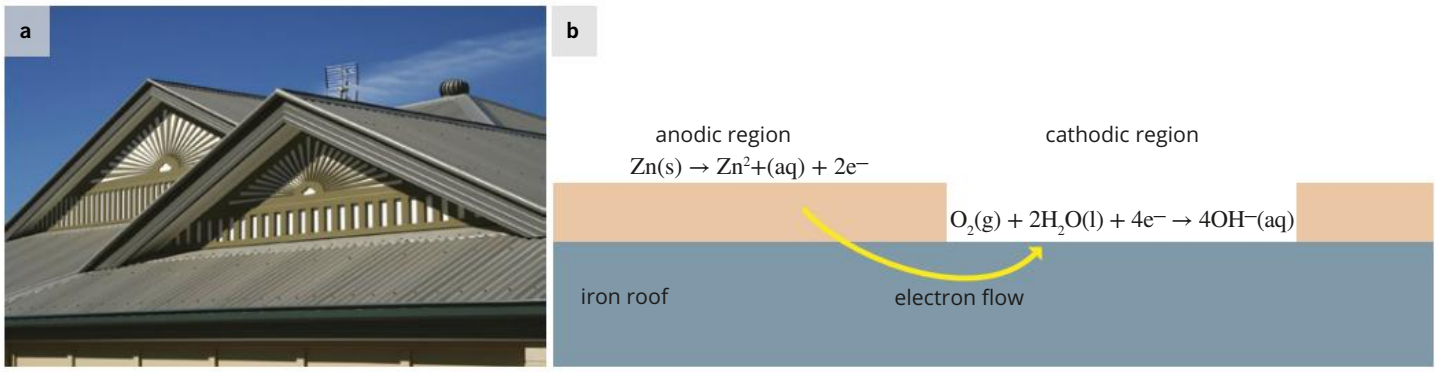


FIGURE 9.5.7 A galvanised iron roof is a common sight in Australia. The zinc coating is oxidised in preference to the iron, protecting the structural role of the iron.

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. 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 9.5.8).

FIGURE 9.5.8 These aluminium sacrificial anodes are attached to the underwater steel structures of offshore gas platforms to protect them against corrosion.

9.5 Review

SUMMARY

- Dry corrosion refers to the oxidation of a metal by oxygen gas.
- Wet corrosion involves both oxygen gas and water and can be considered as an electrochemical process.
- During the wet corrosion of iron, iron is oxidised to $Fe^{2+}(aq)$ and oxygen gas is reduced to $OH^-(aq)$. These form a precipitate of $Fe(OH)_2(s)$, which is converted to rust ($Fe_2O_3 \cdot xH_2O$).
- Protection measures against corrosion include surface coating, alloying, cathodic protection and the use of a more reactive metal as a sacrificial anode.

KEY QUESTIONS

1 Use equations to explain why the corrosion of iron is a redox process.

2 Explain why iron corrosion occurs more rapidly in coastal environments.

3 **a** Which one or more of the following metals could be used as a sacrificial anode to prevent the corrosion of iron: magnesium, zinc, lead, copper?

b Explain your answer to part **a** in terms of the reactivity series of metals.

4 Underwater steel pillars often corrode more rapidly just beneath the surface of the water than above. Suggest a reason for this.

5 Explain why it is common for steel nails to be coated with zinc rather than copper or tin.

Chapter review

09

KEY TERMS

accumulator
alkaline cell
alloy
anode
battery
biogas
cathode
cathodic protection
conjugate redox pair
direct corrosion
dry corrosion
electrochemical cell
electrochemical series
electrode
electrolyte
electrolytic cell
electromotive force
electroplating
external circuit
fuel cell
galvanic cell
galvanometer
half-cell
hydrogen economy
inert electrode
internal circuit
lead–acid battery
lithium-ion cell
nickel–metal hydride cell
non-rechargeable cell
oxidant
oxidising agent
potential difference
primary cell
rechargeable cell
redox reaction
reducing agent
reductant
sacrificial anode
sacrificial protection
salt bridge
secondary cell
spontaneous reaction
standard conditions
standard electrode potential
standard hydrogen half-cell
standard reduction potential
volt
voltaic cell
voltmeter
wet corrosion

Galvanic cells

1 Which one of the following statements best describes the role of the salt bridge in a galvanic cell?

A It allows positive charges to accumulate in one half-cell and negative charges to accumulate in the other.
B It provides a pathway for electrons to move between the half-cells.
C It allows reactants from one half-cell to mix with reactants from the other half-cell.
D It allows movement of ions to balance charges formed at the electrodes.

2 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 platinum
C graphite
D gold

3 Explain the difference between:

a oxidising agent and reducing agent
b anode and cathode
c conjugate redox pair and conjugate acid–base pair
d external circuit and internal circuit.

4 The overall reaction for a galvanic cell constructed from the $Cl_2(g)/Cl^-(aq)$ and $Pb^{2+}(aq)/Pb(s)$ half-cells is:

$$Cl_2(g) + Pb(s) \rightarrow 2Cl^-(g) + Pb^{2+}(aq)$$

A platinum electrode is used in the $Cl_2(g)/Cl^-(aq)$ half-cell.

a Draw a diagram of the galvanic cell. On your diagram, show:
- the direction of electron flow in the external circuit
- a half-equation for the reaction at each electrode
- which electrode is the anode
- which electrode is positive
- which way cations flow in the salt bridge.

b Write the galvanic cell in shorthand cell notation.

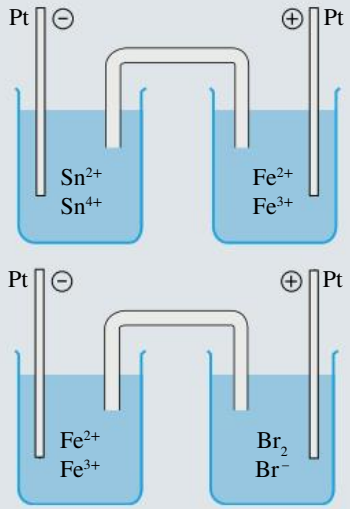
5 Two half-cells are set up. One contains a solution of magnesium nitrate with a strip of magnesium as the electrode. The other contains lead nitrate with a strip of lead as the electrode. The solutions in the two half-cells are connected by a piece of filter paper soaked in potassium nitrate solution. 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 Write 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.

The electrochemical series

6 Show that under standard conditions, according to the electrochemical series, the Daniell cell (Figure 9.1.4, page 213) should have a cell potential difference of 1.10 V.

7 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.

8 Consider the four galvanic cells made from half-cells as listed below. Use the electrochemical series 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 $Fe^{3+}(aq)/Fe^{2+}(aq)$

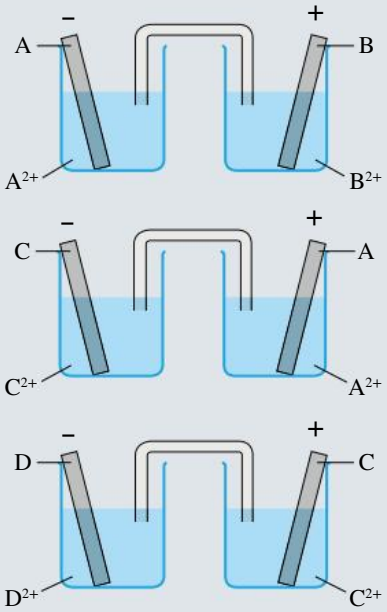
9 Each of these pairs of half-cells combines to form a galvanic cell.

a $Ag^+(aq)/Ag(s)$ and $Zn^{2+}(aq)/Zn(s)$
b $Fe^{2+}(aq)/Fe(s)$ and $Pb^{2+}(aq)/Pb(s)$
c $Ni^{2+}(aq)/Ni(s)$ and $Cu^{2+}(aq)/Cu(s)$

Draw a diagram of each galvanic cell and on your diagrams show:

- the direction of electron flow in the external circuit
- a half-equation for the reaction at each electrode
- an equation for the overall reaction in the galvanic cell
- which electrode is the anode
- which electrode is positive
- which way negative ions flow in the salt bridge.

10 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 order of their reduction half-cell potentials, from highest to lowest.

Predicting direct redox reactions

11 The following equations appear in the order shown in the electrochemical series:

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$

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

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, write:

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 $Cl^-(aq)$

12 Use the electrochemical series to predict whether a reaction will occur in each of the following situations. Write 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.

13 The following equations form part of the electrochemical series. They are ranked in the order shown.

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$

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

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

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

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

- **a** Which species is the strongest oxidising agent and which species is the weakest oxidising agent?
- **b** 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. In which solutions would you expect to see a coating of another metal form on the lead rod? Explain.
- **d** Which of the metals silver, zinc or magnesium might be coated with lead when immersed in a solution of lead(II) nitrate?

14 Use the electrochemical series 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.

15 **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** Write an equation for the predicted reaction.
- **c** When the reactants were mixed in an experiment, no reaction was observed. Suggest possible reasons for this.

Everyday sources of power

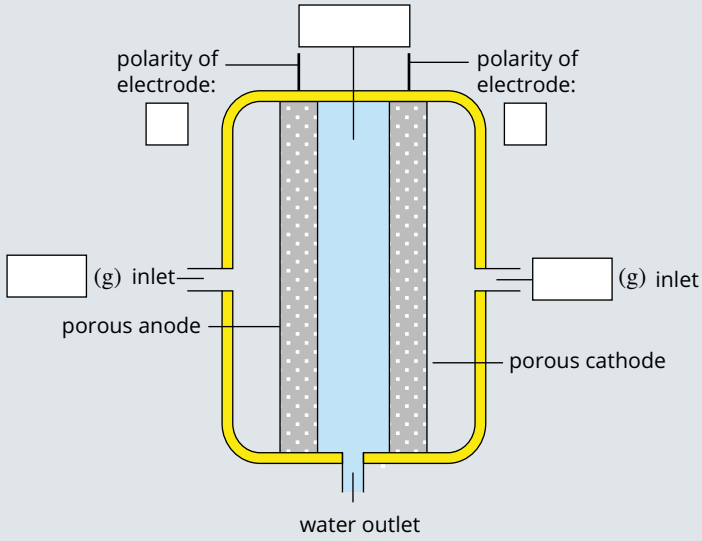
16 Match the following terms with their correct definition.

Term	Definition
Galvanic cell	A cell in which reactants are supplied continuously
Primary cell	A device that converts chemical energy into electrical energy
Secondary cell	A non-rechargeable galvanic cell
Fuel cell	A rechargeable galvanic cell

17 Explain the difference between:

- **a** anode and cathode
- **b** cell and battery
- **c** discharge and recharge.

18 Label the following diagram of a hydrogen–oxygen fuel cell.



19 Which one of the following reactions might be used as the basis for an experimental fuel cell?

- **A** $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
- **B** $2NO_2(g) \rightarrow N_2O_4(g)$
- **C** $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
- **D** $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$

20 Decide whether the following statements apply to fuel cells, primary cells or secondary cells. Some statements apply to all types of cells.

- **a** They convert chemical to electrical energy.
- **b** Oxidation occurs at the anode and reduction occurs at the cathode.
- **c** The anode is the negative electrode as the cell generates electricity.
- **d** They are recharged by connecting to a power supply.
- **e** Electrode reactions occur in separate compartments.
- **f** Chemical energy is stored within the cell.
- **g** The reactant is supplied constantly.

21 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. Why are people prepared to use cells and pay such relatively high prices for electricity?

Corrosion

22 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 impurities, such as salt, dissolved in water
- **C** the presence of acidic pollutants dissolved in water
- **D** the presence of a coating of paint over the surface of the metal object

23 Consider the following products that are made during the wet corrosion of iron. List them in the correct order in which they are made: $Fe(OH)_3(s)$, $Fe_2O_3{\cdot}xH_2O(s)$, $Fe(OH)_2(s)$, $Fe^{2+}(aq)$ and $OH^-(aq)$.

24 Why is it usually not necessary to protect structures made of copper from corrosion?

25 Steel garden furniture rusts much more readily near the seaside than inland. Explain why.

Connecting the main ideas

26 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.

27 A student was told that the redox pair $Mn^{2+}(aq)/Mn(s)$ is lower in the electrochemical series than the $Fe^{2+}(aq)/Fe(s)$ pair and higher than $Al^{3+}(aq)/Al(s)$. Explain how the student could experimentally determine the relative positions of the three pairs in the series.

28 Account for 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.

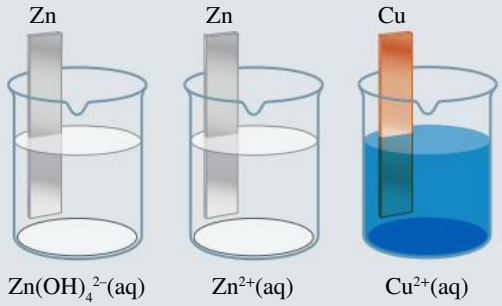
29 A student working in the laboratory spilled an iodine solution over the bench, causing a dark brown stain to form. Suggest how the student could remove the iodine stain.

30 What are the limitations that need to be considered when using the electrochemical series to predict whether or not a certain reaction will occur?

31 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** Write 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.

32 Consider the similarities and differences between a primary cell and a fuel cell.

- **a** List the design features that the two types of cells have in common.
- **b** List the design features that are different in the two types of cells.

33 'Hydrogen–oxygen fuel cells are the energy source of the future.' Discuss the advantages and disadvantages of an energy supply based on these fuel cells.

CHAPTER

10 Electrolysis

A large number of chemicals are produced through electrolysis. Some of these chemicals are often difficult to obtain by other means. This makes electrolysis an important process. Electrolysis is used in a number of industrial applications. These include 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 purifying metals such as copper.

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

Science understanding

- electrochemical cells, including galvanic and electrolytic cells, consist of oxidation and reduction half-reactions connected via an external circuit through which electrons move from the anode (oxidation reaction) to the cathode (reduction reaction)
- electrochemical cells can be described in terms of the reactions occurring at the anode and cathode, the role of the electrolyte, salt bridge (galvanic cell), ion migration, and electron flow in the external circuit
- cell diagrams can be used to represent electrochemical cells
- electrolytic cells use an external electrical potential difference to provide the energy to allow a non-spontaneous redox reaction to occur; electrolytic cells are used in a range of industrial situations, including metal plating and the purification of copper

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10.1 Electrolytic cells

FIGURE 10.1.1 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.

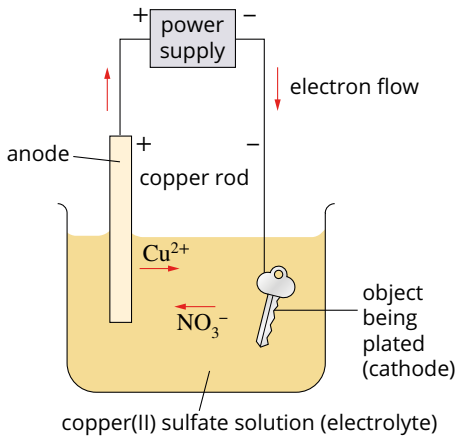
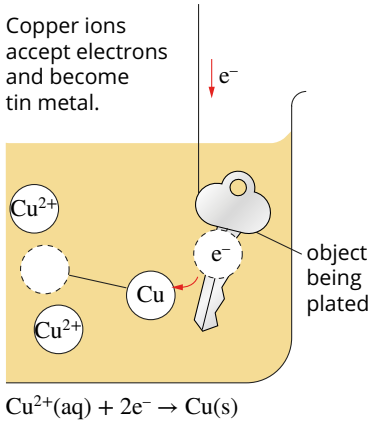


FIGURE 10.1.2 A cell used for electroplating copper



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

FIGURE 10.1.3 A representation of the reaction at the cathode in the process of copper plating

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 normally non-spontaneous to occur. An example of this is shown in Figure 10.1.1, where an electric current is being passed through a dilute sodium chloride solution, causing water to decompose into hydrogen gas and oxygen gas.

In this section, you will learn about the principles of electrolysis by examining the operation of a simple electrolytic cell for electroplating copper. You will also look at cells for the electrolysis of molten sodium chloride and aqueous sodium chloride. In the next section, you will learn how these principles are applied to industrial situations, such as metal plating and the electrorefining of copper.

ELECTROPLATING OF COPPER

One commercially important application of electrolysis is **electroplating**. During this process, a thin surface coating of metal, only a fraction of a millimetre thick, is applied over another metal surface.

Electroplating is performed in **electrolytic cells**, such as the simplified one shown in Figure 10.1.2 for copper plating. The object to be plated, such as the key shown in the figure, is connected by a wire to the negative terminal of a power supply. This object becomes the negative electrode in the cell.

A rod or sheet of copper metal is connected to the positive terminal of the power supply. This metal becomes the positive electrode in the cell.

The two electrodes are immersed in an aqueous solution, such as copper(II) sulfate solution, which contains ions of the metal to be plated. Copper(II) sulfate is an ionic solid, composed of Cu^{2+} and SO_4^{2-} ions, which dissociates when it dissolves in water. The solution is described as an **electrolyte** because it is a conducting liquid.

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', pushing electrons onto one electrode and withdrawing them from the other. The electrode that negative electrons are pushed to (by the external power source) is the negative electrode.

The Cu^{2+} ions in the solution move towards the negative electrode (the object to be plated) and SO_4^{2-} ions move towards the positive electrode, allowing current to pass through the cell.

At the negative electrode

As shown in Figure 10.1.3, copper ions are attracted to the negative electrode, where they accept electrons and are converted to copper metal:

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

A coating of copper is formed on the object. Because reduction of the copper ions (Cu^{2+}) occurs, by definition the negative electrode is known as the **cathode**.

At the positive electrode

As shown in Figure 10.1.4, the positive terminal of the power supply withdraws electrons from the copper electrode, causing an oxidation reaction to occur. Copper metal slowly dissolves as Cu^{2+} ions are formed:

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

This reaction replaces Cu^{2+} ions in solution that were consumed by the reaction at the negative electrode. The overall concentration of copper ions in the electrolyte remains constant.

Because an oxidation reaction is involved, by definition the positive electrode is acting as an **anode**.

> **In an electrolytic cell:**
>
> - oxidation occurs at the anode, which is the positive electrode
> - reduction occurs at the cathode, which is the negative electrode.

You will learn about the industrial applications of electroplating using different metals in the next section.

ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE

Sodium and chlorine are produced in commercial quantities by the electrolysis of molten sodium chloride. A diagram showing the process of electrolysis of molten sodium chloride in a simple electrolytic cell is shown in Figure 10.1.5.

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.

Sodium chloride is an ionic solid, so the forces between particles are strong and NaCl melts at a relatively high temperature (801°C). Therefore, this electrolysis reaction occurs at an elevated temperature. The molten sodium chloride acts as the electrolyte. The species present in the electrolyte in the cell are Na^+ ions and Cl^- ions. No water is present.

At the negative electrode (cathode)

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 the cathode.

Sodium is solid at normal temperatures but liquid at the temperatures required to melt sodium chloride. Sodium is less dense than molten sodium chloride and floats to the top of the cell.

At the positive electrode (anode)

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 the anode.

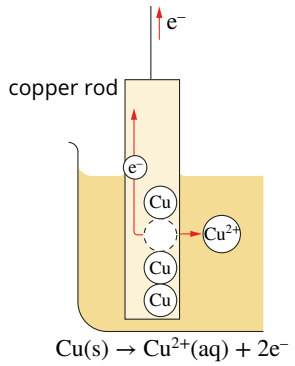
The overall redox reaction that takes place in the cell is:

$$2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$$

This is a **non-spontaneous reaction**—a reaction that would not occur naturally. In such reactions, the supply of electrical energy from a power supply is converted into chemical energy in the products of electrolysis. The reverse reaction, between sodium and chlorine, is a **spontaneous reaction**.

In **galvanic cells**, the chemical energy in the cells is converted to electrical energy. The opposite occurs in electrolytic cells, where electrical energy supplied from an external power source is converted to chemical energy.

The electrolytic process usually takes place in a single container. Unlike with 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. Otherwise, they would spontaneously react with each other to re-form the original reactants.



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

FIGURE 10.1.4 A representation of the reaction at the anode in the process of copper plating.

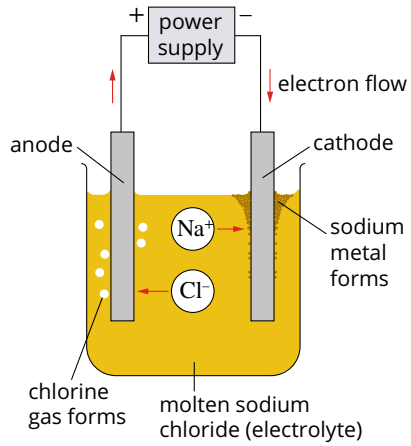


FIGURE 10.1.5 Electrolysis of molten sodium chloride.

> Galvanic cells involve spontaneous redox reactions in which chemical energy is converted to electrical energy.
>
> Electrolytic cells involve non-spontaneous redox reactions in which electrical energy is converted to chemical energy.

CHEMFILE

Sodium first isolated by electrolysis

Sodium is one of the most reactive metals. Few substances are capable of reducing Na^+ ions to the metal, Na. Because of this, sodium was not isolated until 1807 when Humphry Davy (Figure 10.1.6) electrolysed molten sodium hydroxide.

The following year, Davy discovered five elements—barium, magnesium, strontium, boron and calcium—and reported news of his discoveries in two entertaining public lectures in London. Davy was renowned for the flair of his lectures and demonstrations.

FIGURE 10.1.6 Humphry Davy (1778–1829) used electrolysis to be the first person to isolate potassium, calcium, barium, magnesium, sodium and strontium.

EXTENSION

Competition at electrodes

In some electrolytic cells, there may be several chemicals present at each electrode that could react. Water is often a potential reactant. Even the material used for the electrodes may participate in the reaction.

In these cases, you can use the **electrochemical series** (Figure 9.2.5, page 222) 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 reaction highest 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 reaction lowest in the series that can occur in reverse is likely to occur at the anode).

It is important to also be aware that in many electrolytic cells the electrodes are consumed in the cell reaction. Such electrodes are called **reactive electrodes**.

Electrolysis of nickel sulfate

As an example, consider the electrolysis of 1 M nickel(II) sulfate solution with copper electrodes at 25°C. A diagram of this electrolytic process is shown in Figure 10.1.7.

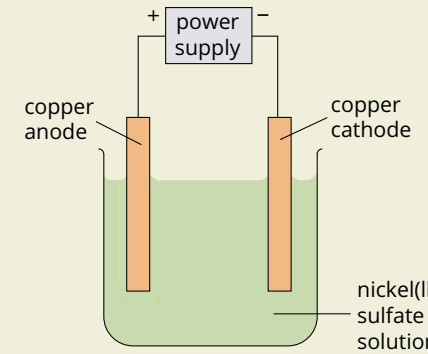


FIGURE 10.1.7 Electrolysis of nickel(II) sulfate solution using copper electrodes.

At the negative electrode (cathode)

The strongest oxidising agent present at the cathode will undergo reduction. Oxidising agents are found on the left side of the electrochemical series. By referring to the series, you can see that there are two oxidising agents at the cathode, $Ni^{2+}(aq)$ and $H_2O(l)$, and $Ni^{2+}(aq)$ is the stronger of the two. The likely cathode reaction is therefore:

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

At the positive electrode (anode)

The strongest reducing agent present at the anode will undergo oxidation. Reducing agents are found on the right side of the electrochemical series. By referring to the series,

you can see that there are two oxidising agents at the anode, Cu(s) and $H_2O(l)$, and Cu(s) is the stronger of the two. The likely anode reaction is therefore:

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

The overall equation for the cell reaction is:

$$Ni^{2+}(aq) + Cu(s) \rightarrow Ni(s) + Cu^{2+}(aq)$$

Electrolysis of aqueous sodium chloride

Electrolysis is one option being explored for the production of hydrogen fuel from renewable resources. A simple electrolytic cell for the production of hydrogen from a dilute solution of sodium chloride is shown in Figure 10.1.8. The cell uses **inert electrodes**, such as platinum.

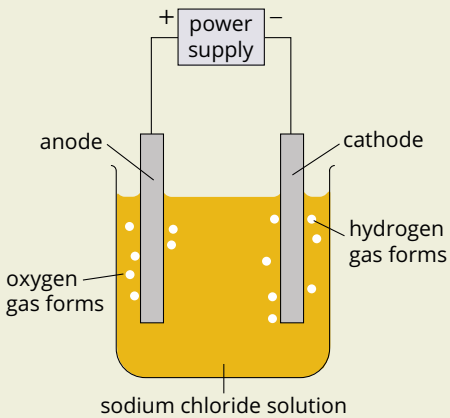


FIGURE 10.1.8 Electrolysis of aqueous sodium chloride solution

At the negative electrode (cathode)

The power supply pushes electrons towards the negative electrode and Na^+ ions are attracted to this electrode. Water is the strongest oxidising agent present in the cell and undergoes reduction:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

The sodium ions do not react and they remain in solution as spectator ions.

At the positive electrode (anode)

Electrons are withdrawn from this electrode by the power supply. Water is the strongest reducing agent present in the cell and undergoes oxidation:

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

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.

In practice, the anode reaction that occurs when sodium chloride solution is electrolysed depends on conditions such as the concentration of the solution. In some cases, O_2 and H^+ are formed as described above, whereas in others Cl_2 is produced.

CHEMISTRY IN ACTION

Producing hydrogen for the hydrogen economy

As seen in Chapter 9 (page 235), some scientists predict that one day our society will transition to a hydrogen economy, where the main source of energy for transport and other sources will be hydrogen.

Currently, the major source of hydrogen is fossil fuels. Ideally, in the future, this source will be replaced by a greener process that does not rely on fossil fuels or produce greenhouse gases.

As discussed in this section, hydrogen is produced through the electrolysis of water with the addition of an electrolyte such as NaCl. The electrolytic process can be made greener by using renewable electricity sources. However, the efficiency of the process ranges from 50 to 70%. Efficiency can be increased by the use of electrodes with catalytic abilities, such as platinum, but this is prohibitively expensive. Scientists are currently working on developing cheap and effective catalytic electrodes from materials such as molybdenum sulfide, carbon nanotubes and nickel/nickel oxide.

Electrolysis is still an energy-intensive way of producing hydrogen. Another area of scientific research is artificial photosynthesis, which aims to replicate the process of splitting water molecules using light, just as green plants do. Titanium dioxide and other titanium-based compounds form a group of materials that can split water in the presence of light to produce hydrogen.

With these scientific developments, the prospect of a future hydrogen economy is looking much brighter.

COMPARISON OF ELECTROLYTIC AND GALVANIC CELLS

Galvanic cells and electrolytic cells are types of **electrochemical cells**. Although both cells involve the conversion between electrical energy and chemical energy, there are important differences between them.

Table 10.1.1 and Figure 10.1.9 summarise the similarities and differences between galvanic and electrolytic cells.

TABLE 10.1.1 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
Anions flow towards the anode and cations flow towards the cathode.	Anions flow towards the anode and cations flow towards the cathode.

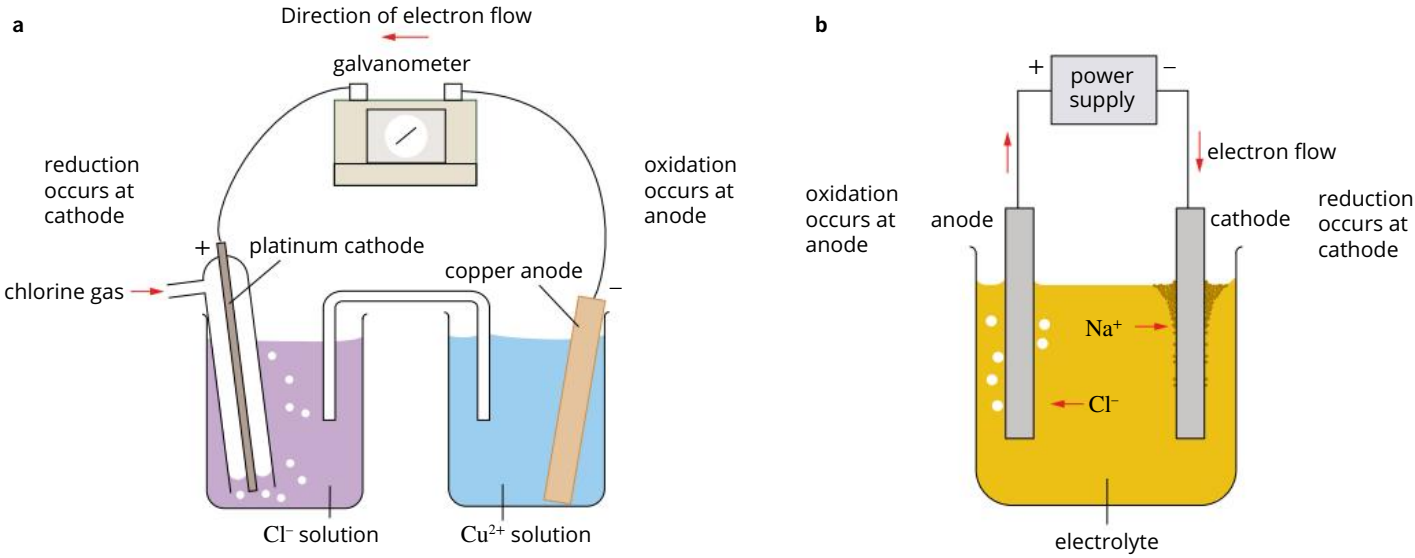


FIGURE 10.1.9 General construction of (a) a galvanic cell and (b) an electrolytic cell

10.1 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.
- The electrodes used in electrolysis can be either inert or reactive.
- Both molten and aqueous electrolytes can be used in electrolysis.

KEY QUESTIONS

1 Which one of the following applies to both galvanic and electrolytic cells?

A Oxidation occurs at the anode and reduction occurs at the cathode.

B The anode is negative and cathode is positive.

C Both cells convert chemical energy to electrical energy.

D Both cells have non-spontaneous reactions.

2 What are the products of electrolysis of molten potassium iodide using inert electrodes?

A potassium at the anode and iodine at the cathode

B potassium at the cathode and iodine at the anode

C iodine at the negative electrode and potassium at the positive electrode

D iodine at the anode and hydrogen at the cathode

3 Select the correct words to complete the following statements.

In electrolytic cells:

- the reactions are spontaneous/non-spontaneous
- chemical/electrical energy is converted into chemical/electrical energy
- the anode is negative/positive and the cathode is negative/positive
- oxidation/reduction occurs at the anode and oxidation/reduction occurs at the cathode.

4 Write the electrode reactions and overall reaction if molten $ZnCl_2$ is the electrolyte in an electrolytic cell with inert electrodes.

5 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 During operation of the cell, a nickel coating will appear on which rod?

b If water undergoes oxidation at the anode of the cell, write the half-equations for the reactions that occur at each electrode.

c Write an equation for the overall reaction.

10.2 Industrial applications of electrolysis

FIGURE 10.2.1 Tin cans are used as packaging for a wide range of products. The tin coating on the can prevents it from corroding.

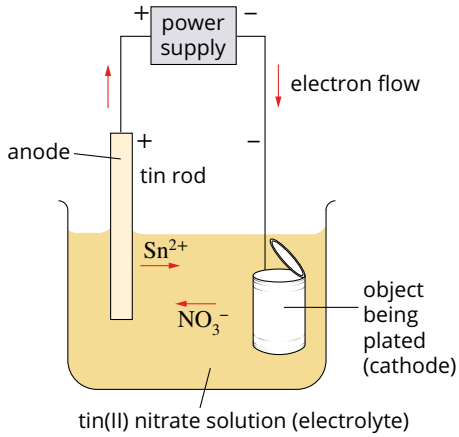


FIGURE 10.2.2 A cell used for electroplating tin

Although chemical industries tend to avoid using electrolysis for the manufacture of chemicals because of the relatively high cost of electrical energy, this process enables some chemicals to be produced that could not be readily produced any other way.

In an electrolytic cell, the transformation of electrical energy into chemical energy results in non-spontaneous reactions in which reactive chemicals are products, rather than reactants.

In this section, you will look at two useful applications of electrolysis:

- electroplating
- electrorefining of copper.

ELECTROPLATING

As you learnt in the previous section, electrolytic cells can be used to electroplate thin surface coatings of one metal over the surface of another metal.

A common application of electroplating is the coating applied to 'tin' cans (Figure 10.2.1). Tin cans are used extensively for packaging food items as varied as soups, fruit and fish. 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.

An electrolytic cell for tin plating is shown in Figure 10.2.2. The object to be plated is connected to the negative terminal of a power supply. An electrode of tin metal is connected to the positive terminal of the power supply. The object is immersed in an electrolyte solution, such as tin(II) nitrate solution, which contains ions of the metal to be plated.

At the negative electrode (cathode)

Tin ions are attracted to the cathode, where they undergo reduction and are converted to tin metal:

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

A coating of tin is formed on the object.

At the positive electrode (anode)

The tin at the anode undergoes oxidation. Tin metal dissolves as Sn^{2+} ions are formed:

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

Because Sn^{2+} ions are consumed by the reaction at the cathode and produced by the reaction at the anode, the overall concentration of tin ions in the electrolyte remains constant.

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).**

Electroplating in practice

The cell described for electroplating tin is simpler than the cell used in practice. Such a simple cell would produce a metal coating that would adhere poorly and would be unattractive because of irregularities in its thickness.

The factors that are critical for achieving a smooth, tightly bonded metal coating that prevents oxygen and water from reaching the base metal are the:

- voltage
- current
- temperature
- electrode positions
- concentration
- identity of the electrolyte.

The conditions that are most suitable for industrial electroplating are largely determined by trial and error. An electrolyte containing a strong acid is often used to ensure high currents and rapid deposition of metal.

In practice, during the manufacture of tin cans the tin coating is applied to the steel sheet before the can is made, using a series of large cells. Before entering the cell, the steel sheet is cleaned to remove grease and surface deposits of iron oxide. The tin plate produced from the cell is then coiled into large rolls before being transported to the can manufacturers.

Other examples of electroplating

Silver

Apart from using electroplating to improve the resistance to corrosion, it can also be used to make an object more attractive. If you browse through a jeweller's shop you will see many shiny 'silver' items, such as bracelets, necklaces, cutlery, watches and pens (Figure 10.2.3). The main metals present in many of these articles will be less expensive metals, such as copper, zinc and nickel; the silver is a surface coating that has been applied by electrolysis.

The cell used for silver plating is similar to the one used for tin plating. Silver is used instead of tin as the anode and the electrolyte contains silver ions.

Chromium

Chromium is another metal used for electroplating because it is decorative, non-tarnishing and hard-wearing. Chromium plating is used extensively on items such as bicycle handlebars, wheel rims, taps, and even on engines (Figure 10.2.4).

Electroplating cells in common use

Table 10.2.1 gives information about the electrolytic cells used for plating different metals. Note the different combinations of compounds used as electrolytes to ensure a uniform coating of the metals.

FIGURE 10.2.3 Silver electroplated cutlery. The letters EPNS stand for Electroplated Nickel Silver. Nickel silver is a copper alloy with nickel and often zinc that is used as the base metal for the cutlery.

FIGURE 10.2.4 A chrome-plated motorcycle exhaust pipe

TABLE 10.2.1 Electroplating cells in common use

Metal being plated	Anode	Electrolyte	Application
Ag	Ag	AgCN, KCN, K_2CO_3	Jewellery and cutlery
Au	Au, C or Ni–Cr	AuCN, KCN	Jewellery
Cr	Pb–Sn	CrO_3	Taps, engines, car parts, bicycles
Ni	Ni	$NiSO_4$, $NiCl_2$, H_3BO_3	Bases for Cr plated objects
Zn	Zn	$Zn(CN)_2$, NaCN, NaOH, Na_2CO_3, $Al_2(SO)_4)_3$	Galvanised steel

FIGURE 10.2.5 This molten copper metal is being poured into moulds.

CHEMFILE

Electroplating plastics

Non-metallic objects also can undergo an electroplating process. Plastic objects can be plated with metal to produce an attractive and protective coating. When the object being electroplated is not metallic, the electroplating process is called metallising.

The plastic surface has to be made conductive before the electroplating process can begin. There are various methods to make the surface conductive. One method is to place the object into a bath that contains chromic and sulfuric acids to etch the surface. The object can then be dipped into a solution of tin(II) chloride and palladium chloride. The electroplating process then continues in the same manner as with other metal objects.

FIGURE 10.2.6 These plastic car parts have been chrome electroplated.

ELECTROREFINING OF COPPER

Copper is usually found in minerals on Earth as a mixture of other metals. These minerals are called copper ore. Australia has the third largest reserve of copper ore in the world and each year it extracts about 900 000 tonnes of copper metal (10% of world production). In Western Australia, copper deposits are located at the Golden Grove mine near Yalgoo, at the Nifty mine in East Pilbara and at the DeGrussa mine about 900 km north-east of Perth.

Copper metal is extracted from its ores by **smelting**. Australia's largest mining and copper smelters are at Olympic Dam in South Australia and Mount Isa in Queensland. Copper produced in the smelter at Mount Isa is shipped to Townsville for refining. Copper refining occurs at Olympic Dam and at Port Pirie in South Australia.

The smelting process involves several stages in which the copper ore is heated strongly in air to produce impure molten copper metal (Figure 10.2.5). As the metal solidifies and 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, in a process called **electrorefining**. Electrorefining uses a large amount of electrical energy, so a refinery must be located close to a source of abundant cheap power.

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 10.2.7.

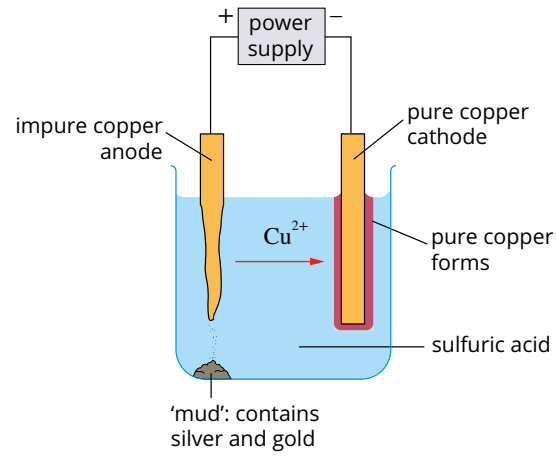


FIGURE 10.2.7 Electrorefining of copper metal by electrolysis

At the positive electrode (anode)

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 negative electrode (cathode)

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, which is suitable for use in electrical applications, is obtained in this way (Figure 10.2.8).

In a copper electrorefining cell, copper metal undergoes oxidation at the anode and copper ions undergo reduction at the cathode. The process yields copper metal of high purity.

FIGURE 10.2.8 Plates of freshly deposited copper are removed from a copper electrorefining cell.

CHEMISTRY IN ACTION

Production of sodium

In the previous section, you looked at the electrolysis of molten sodium chloride. Sodium and chlorine are the products from this electrolytic cell.

In order to produce sodium and chlorine commercially, a modified cell, known as the Downs cell, is required (Figure 10.2.9).

Because sodium is a strong reducing agent and chlorine is a strong oxidising agent, there must be no contact between these chemicals, otherwise a spontaneous reaction will occur and the products of the cell will react to re-form as sodium chloride. The Downs cell uses a screen to ensure the products formed at the electrodes are kept apart.

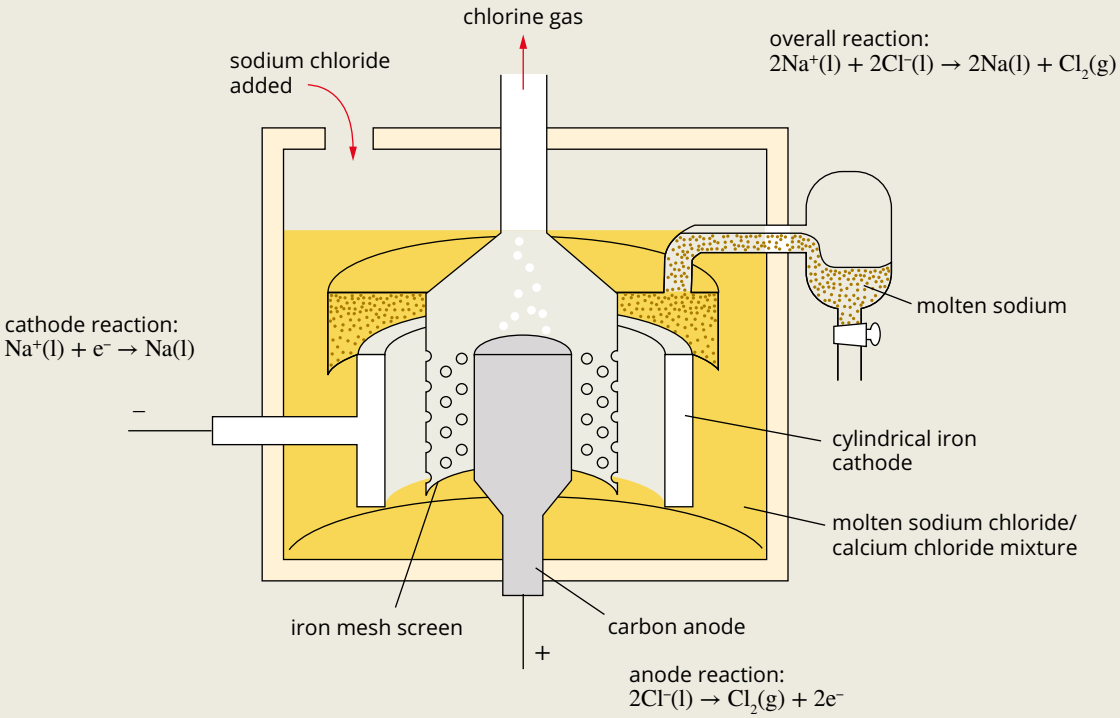


FIGURE 10.2.9 Diagram of a Downs cell, which produces sodium and chlorine gas

CHEMISTRY IN ACTION

Production of aluminium

The low density and high strength of aluminium makes it a particularly useful metal for many applications, including cooking foil, drink cans, car engines, gutters, caravans, aeroplanes, window frames and boats (Figure 10.2.10).

Aluminium is much more reactive than you might imagine, considering how widely it is used. By referring to the electrochemical series, you can see that it is only slightly less reactive than magnesium.

FIGURE 10.2.10 Boats made from aluminium are light, strong and resistant to corrosion.

However, aluminium reacts rapidly with oxygen in the air to form a thin, unbroken layer of aluminium oxide that prevents further reaction between the metal and oxygen. As a result of this oxide layer, aluminium resists further corrosion and other chemical attack.

Today, aluminium metal is obtained from aluminium oxide (also known as alumina, Al_2O_3) by electrolysis. Pure alumina is extracted from the mineral bauxite, which is found in large deposits in the Darling Ranges in Western Australia, Weipa in northern Queensland and Gove in the Northern Territory.

Alumina melts at 2050°C, which prohibits its use as the electrolyte. However, it is soluble in molten cryolite (Na_3AlF_6). By dissolving alumina in cryolite, electrolysis can be performed at 950–1000°C. The Hall–Heroult cell used to extract aluminium is shown in Figure 10.2.11.

The overall equation for the extraction of aluminium is:

$$2Al_2O_3(\text{in cryolite}) + 3C(s) \rightarrow 4Al(l) + 3CO_2(g)$$

Australia produces about 60 million tonnes of bauxite a year and has one of the largest identified reserves of the ore. Only a small fraction of ore is converted to aluminium in Australia. Most of the ore is converted to alumina and shipped overseas.

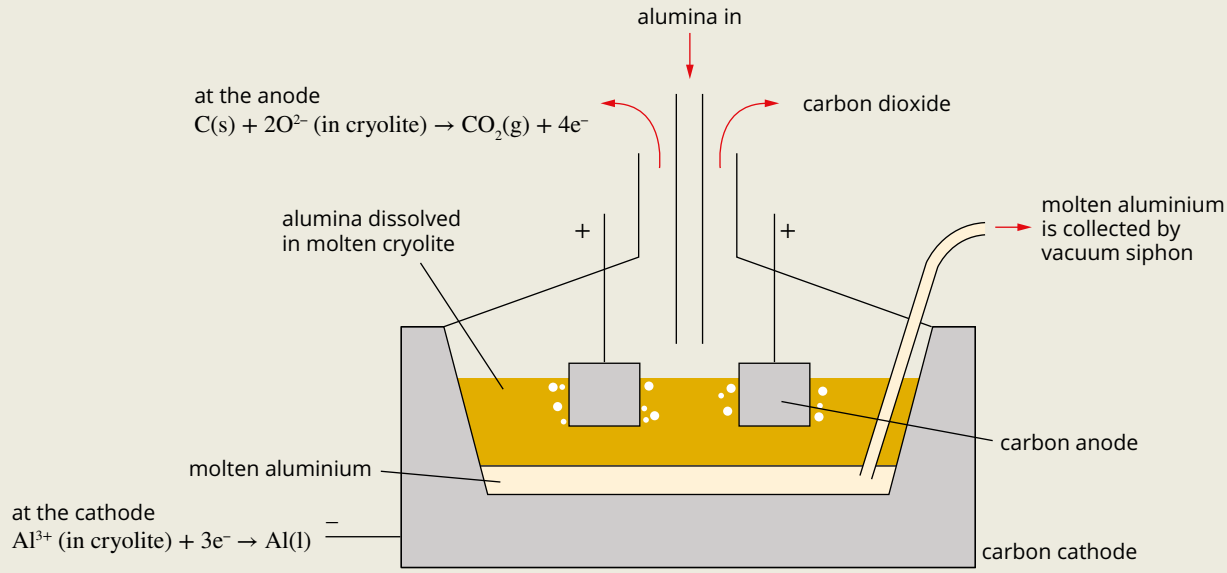


FIGURE 10.2.11 Diagram of a Hall–Héroult cell used to extract aluminium from alumina

10.2 Review

SUMMARY

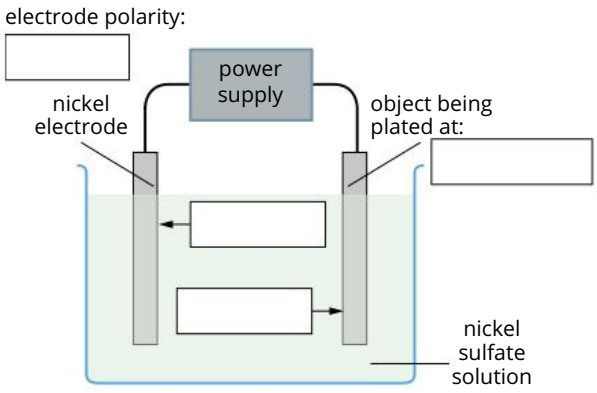
- Electrolytic cells are used in a range of industrial situations, including electroplating and copper refining.
- Electroplating involves the deposition of a thin surface coating of metal over another surface to improve the appearance of an object, its resistance to corrosion, or both.
- During electroplating, the object being plated is the cathode of the cell.
- Pure copper can be obtained from impure blister copper by electrorefining.
- During the electrorefining process to produce pure copper:
  - the blister copper is placed at the anode, and the equation for the reaction is:
    $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
  - pure copper is used as the cathode, and pure copper metal is deposited according to the equation:
    $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

KEY QUESTIONS

1 Which one of the following statements is true about an electrolytic cell that is being used to electroplate an iron object?

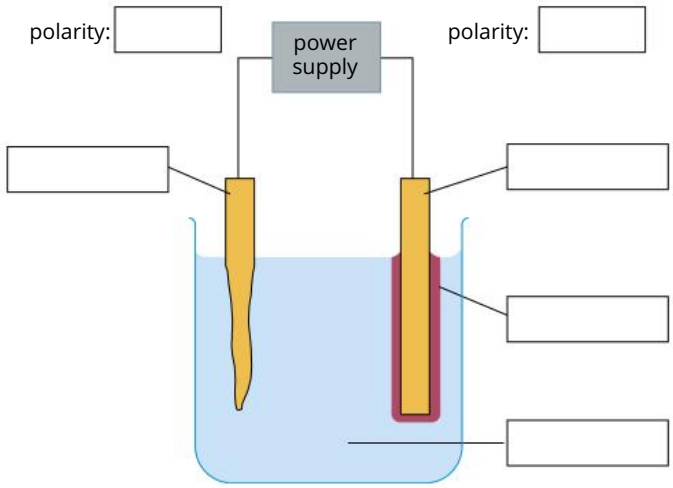
A The anode is the negative electrode.
B The movement of ions through connecting wires completes the circuit.
C Energy is produced by the cell.
D The reaction involves a non-spontaneous redox process.

2 The following diagram shows a nickel electroplating cell.



a Complete the missing labels for this cell to show the polarity of the nickel electrode, the direction of movement of ions in the electrolyte and whether the object being plated is at the anode or cathode.
b Write a half-equation for the reaction that occurs at the anode.
c Write a half-equation for the reaction that occurs at the cathode.
d Describe the direction of movement of Ni^{2+} and SO_4^{2-} ions in the cell.

3 Impure copper, called 'blister copper', is produced by the reduction of copper ore in a blast furnace. Blister copper can be purified by electrorefining. Label the parts of the electrorefining cell shown below for blister copper.



a Complete the missing labels for this cell to show:
i the polarity of the electrodes
ii the nature of the electrodes and the electrolyte.
iii whether the object being plated is at the anode or cathode.
b Write a half-equation for the reaction that occurs at the anode.
c Write a half-equation for the reaction that occurs at the cathode.

4 During the electrorefining of copper, explain why the concentration of Cu^{2+} ions in the electrolyte remains constant while the cell is in operation.

Chapter review

10

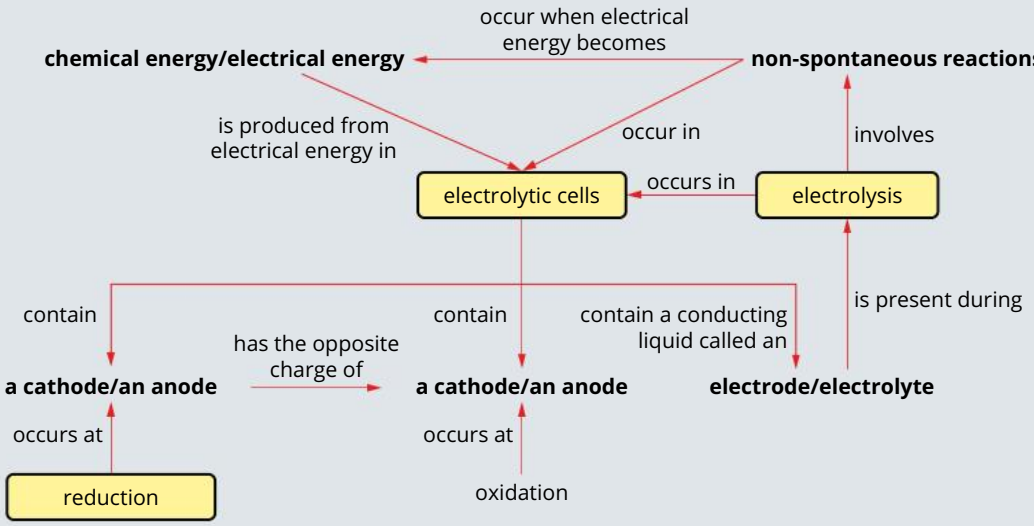
KEY TERMS

anode
cathode
electrochemical cell
electrochemical series
electrolysis
electrolyte
electrolytic cell
electroplating
electrorefining
galvanic cell
inert
inert electrode
non-spontaneous reaction
reactive electrode
smelting
spontaneous reaction

Electrolytic cells

1 For electrolytic and galvanic cells, compare 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.

2 Select the correct terms in bold in the concept map, which illustrates the basic concepts of electrolytic cells and energy conversion.

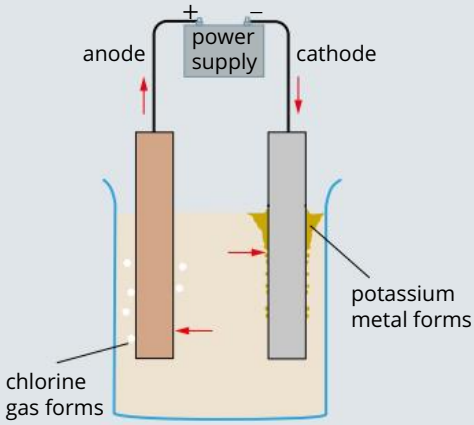


3 Which one of the following statements best describes the role of the electrolyte in an electrolytic cell?
- **A** It allows positive charges to accumulate at one electrode and negative charges to accumulate at the other electrode.
- **B** It provides a pathway for electrons to move in the cell.
- **C** It allows reactants to mix in the cell.
- **D** It allows movement of ions to balance charges formed at the electrodes.

4 For each one of the following statements, state whether it applies to galvanic cells, electrolytic cells, or both.
- **a** They have spontaneous reactions.
- **b** Electrical energy is converted into chemical energy.
- **c** Oxidation occurs at the anode.
- **d** The anode is negative.
- **e** Cations in electrolyte solution(s) move towards the cathode.

5 Write the electrode reactions and overall reaction that occur when molten $ZnCl_2$ is used as the electrolyte in an electrolytic cell with inert electrodes.

6 The following electrochemical cell is set up to produce potassium metal. Label the parts of the cell using the following options (options may be used more than once): Cl^-, molten potassium chloride, platinum, K^+.



7 An aqueous solution of potassium iodide was electrolysed using platinum electrodes. A brown colour solution appeared at one electrode and bubbles of gas were formed at the other electrode.

a Write the half-equation for the reaction at the:

i positive electrode

ii negative electrode.

b Write the overall equation for the cell reaction.

Industrial applications of electrolysis

8 Select the correct words in the following sentence about electroplating.

In the electroplating process, the object to be plated is placed at the cathode/anode where oxidation/reduction occurs and pure metal is at the negative/positive electrode where oxidation/reduction occurs.

9 The inside of a 'tin' can has a thin layer of metal coated onto another metal. Select the correct description of the metals involved.

A A thin layer of steel is coated on to a tin layer.

B A thin layer of tin is coated on to a steel layer.

C A thin layer of steel is coated on to an aluminium layer.

D A thin layer of aluminium is coated on to a tin layer.

10 Most bathroom taps are made of iron covered with a thin layer of nickel and another layer of chromium metal. What is the purpose of the nickel and chromium?

11 A metal object made of tin is to be plated with silver using an electrolytic cell. The tin metal acts as one electrode and the other electrode is made of silver. The electrolyte is silver nitrate, and a power source is connected to both electrodes. Which one of the following statements best describes the cell in operation?

A The negative terminal of the power source is connected to the metal where oxidation occurs.

B The positive terminal of the power source is connected to the cathode.

C The negative terminal of the power source is connected to the metal where reduction occurs.

D The positive terminal of the power source is connected to the metal where reduction occurs.

12 A student decided to construct an electroplating cell to silver plate a locker key.

a Draw a diagram of a simple cell suitable for this purpose. Label the following on your diagram:

- anode and cathode
- positive and negative electrodes
- composition of the electrodes and the electrolyte
- direction of electron flow in wires
- directions of movement of ions.

b Several minutes after electroplating commenced the student reversed the connections of the cell to the power supply. What would happen?

13 Select the correct statement about the electrorefining of copper.

A The cathode increases in mass during the process.

B Pure copper is placed at the anode.

C Pure copper forms at the positive electrode.

D Copper ions in the electrolyte flow towards the anode.

14 Select the correct words in the following sentences about the purification of copper by electrolysis.

In the purification process, the impure copper is placed at the cathode/anode of the electrolytic cell where oxidation/reduction occurs and pure metal is at the negative/positive electrode where oxidation/reduction occurs. Copper ions in the electrolyte flow towards the anode/cathode. Electrons flow in the wires attached to the cell from the anode/cathode to the anode/cathode.

Connecting the main ideas

15 Explain the difference between:

a spontaneous and non-spontaneous reactions

b anode and cathode

c electrochemical cell and electrolytic cell

d electrorefining and electroplating.

16 Construct a concept map that includes the terms electrolysis, electrolytic cell, chemical energy, electrical energy, anode, cathode, reducing agent, oxidising agent, reduction, oxidation, electrolyte and non-spontaneous reactions.

17 Explain why the anode is negative in a galvanic cell but positive in an electrolytic cell.

18 When constructing a galvanic cell in the laboratory, why are two half-cells usually used whereas the reactants of an electrolysis cell are often placed in a single container?

UNIT 3 • EQUILIBRIUM, ACIDS AND BASES, AND REDOX REACTIONS

REVIEW QUESTIONS

Section 1: Multiple choice

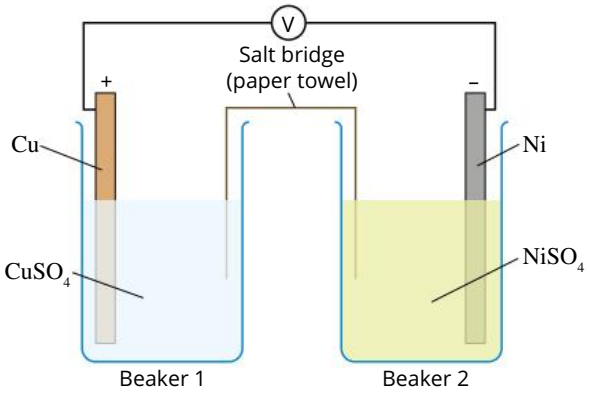
1 Which of the following lists species arranged with the nitrogen atoms in order of increasing oxidation number?

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 Use the electrochemical series to determine which one of the following would not be expected to occur to an appreciable extent.

A $2H^+(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + H_2(g)$
B $2Ag^+(aq) + Ni(s) \rightarrow 2Ag(s) + Ni^{2+}(aq)$
C $Br_2(aq) + 2Fe^{2+}(aq) \rightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$
D $2I^-(aq) + Pb^{2+}(aq) \rightarrow I_2(s) + Pb(s)$

3 An electrochemical cell was made by dipping a copper rod into a solution of 1 mol L^{-1} $CuSO_4$ in one beaker and dipping a nickel rod into a solution of 1 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. Which of the following changes might it be possible to detect after the galvanic cell has been discharging for a period of time?

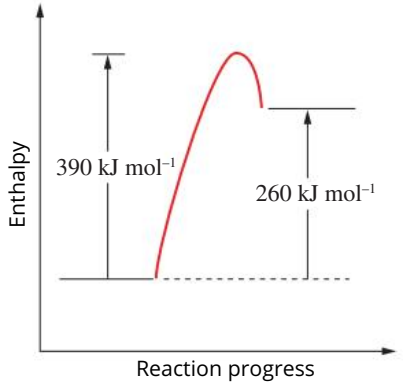
A The green colour in beaker 2 has faded and the mass of the copper electrode has increased.
B The blue colour in beaker 1 has faded and the mass of the nickel electrode has increased.
C The green colour in beaker 2 has faded and the mass of the copper electrode has decreased.
D The blue colour in beaker 1 has faded and the mass of the nickel electrode has decreased.

4 Which of the following requires involvement of a reversible chemical reaction?

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

5 The energy profile diagram shown below is for the reaction:

$$CO_2(g) + NO(g) \rightleftharpoons CO(g) + NO_2(g)$$



Which of the following shows the activation energy and ΔH of the reverse reaction?

	Activation energy of reverse reaction (kJ mol^{-1})	ΔH of reverse reaction (kJ mol^{-1})
A	–390	+260
B	+130	–260
C	+130	+260
D	–390	–260

6 A student conducted an acid–base volumetric analysis experiment. A 20.0 mL aliquot of a 0.10 mol L^{-1} solution of hydrochloric acid was pipetted into a flask. A 0.10 mol L^{-1} solution of potassium hydroxide was added from a burette. A titre of 19.5 mL was obtained, not the expected 20.0 mL value. Which of the following procedures could be a reason for the low titre?

A The student accidently used a 25.0 mL pipette.
B The 20.0 mL pipette was rinsed with water immediately prior to delivering the aliquot.
C The conical flask was rinsed with water prior to the titration.
D The burette was rinsed with water immediately prior to adding the potassium hydroxide solution.

7 Which of the following statements about a catalyst is not true?

A A catalyst is not consumed in the course of a reaction.
B A catalyst alters the reaction pathway between reactants and products.
C A catalyst reduces the energy released or absorbed by a reaction.
D The proportion of molecules with sufficient energy to react is increased by a catalyst.

8 In a sealed vessel, nitrogen monoxide, oxygen and nitrogen dioxide form the following equilibrium:

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

Which one of the following sets of conditions is likely to lead to the highest yield of nitrogen dioxide gas?

A 200°C and 100 kPa pressure
B 200°C and 200 kPa pressure
C 300°C and 100 kPa pressure
D 300°C and 200 kPa pressure

9 The reaction between nitrogen monoxide and ozone is:

$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g) \quad K = 6 \times 10^{34}$ at 25°C

Equal amounts of NO and O_3 are used. 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 equilibrium of the reaction lies to the right.
C The reaction has a low activation energy.
D Very little ozone will remain at equilibrium.

10 The endpoint of an acid–base titration is the point at which:

A the reactants have been mixed in the mole ratios given in the balanced equation for the reaction.
B the pH of the solution in the titration flask is 7.
C equal volumes of reactant solutions have been added.
D the indicator changes colour.

11 In an experiment, the following standard half cells were set up.

I Mn^{2+}/Mn
II Ni^{2+}/Ni
III Mg^{2+}/Mg
IV Fe^{2+}/Fe

Which combination of half-cells will produce the lowest cell voltage?

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

12 The following table shows the characteristics of the indicator methyl red.

Low pH colour	Transition pH range	High pH colour
red	4.4–6.2	yellow

During the titration of a 0.1 mol L^{-1} solution of the weak base ammonia using a standardised hydrochloric acid solution (from the burette), the most appropriate determination of the endpoint of the titration would be a colour change for methyl red from:

A red to yellow occurring at a pH of 7.
B yellow to red occurring at a pH of 7.
C yellow to red occurring at a pH above 7.
D yellow to red occurring at a pH below 7.

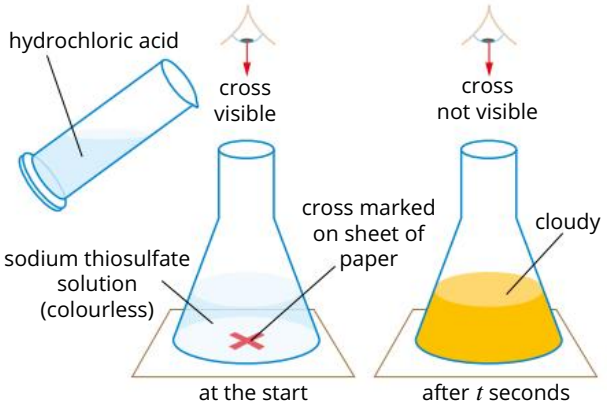
Section 2: Short answer

1 Two experiments were conducted to investigate the rate of reactions for both aqueous and gaseous reaction mixtures.

a A student investigated the factors affecting the rate of reaction between a solution of sodium thiosulfate and hydrochloric acid:

$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + SO_2(g) + S(s) + H_2O(l)$

The reaction was carried out in a conical flask placed on top of a piece of white paper with a dark cross marked on it. The rate of reaction was determined by measuring the time taken for the cross to be masked by the suspension of sulfur formed during the reaction, as shown.



The rate was determined for different concentrations of sodium thiosulfate and for different temperatures. The volume of each solution and the concentration of hydrochloric acid were kept constant. The results are summarised in the following table.

Experiment number	Concentration of $Na_2S_2O_3(aq)$ ($mol\,L^{-1}$)	Temperature (°C)	Time taken for the cross to be masked (s)
1	0.1	20	36
2	0.2	20	20
3	0.1	25	28

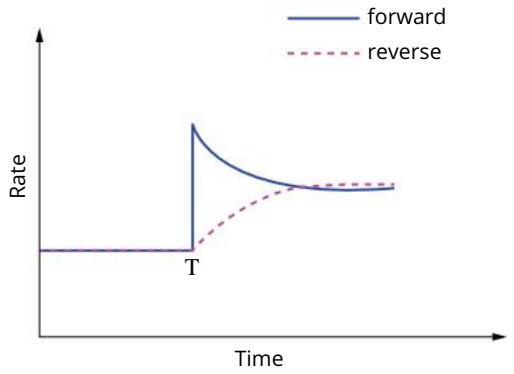
i Explain, in terms of collision theory, why the rate in experiment 2 is higher than the rate in experiment 1.

ii Explain, in terms of collision theory, why the rate in experiment 3 is higher than the rate in experiment 1.

b In the second investigation, a readily reversible gas-phase reaction was used:

$$W(g) + 2X(g) \rightleftharpoons Y(g) + Z(g)$$

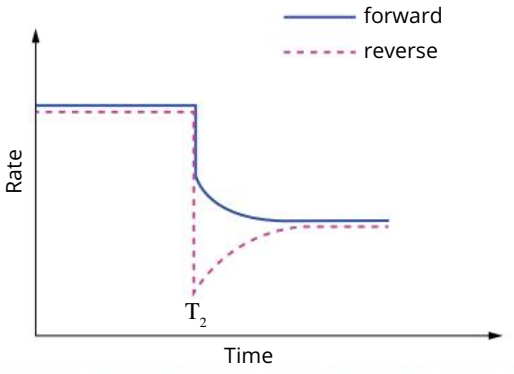
The following graph shows the changes to the rates of the forward and reverse reactions when some additional reactant, W, is added to an equilibrium mixture of these gases at time T.



i Explain how this graph shows that the mixture was at equilibrium before time T.

ii Use collision theory to account for the change in the rate of the reverse reaction from time T.

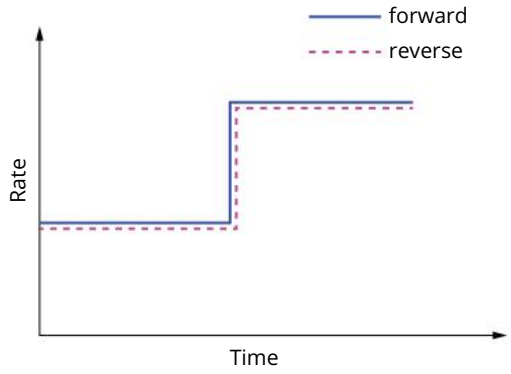
The following graph shows the rate changes after lowering the temperature at time T_2.



iii Considering the period during which the rates are unequal, in which direction does the equilibrium shift?

iv Is the reaction exothermic or endothermic? Explain.

The following graph shows the rate change when a change was made to the system at time T_3.

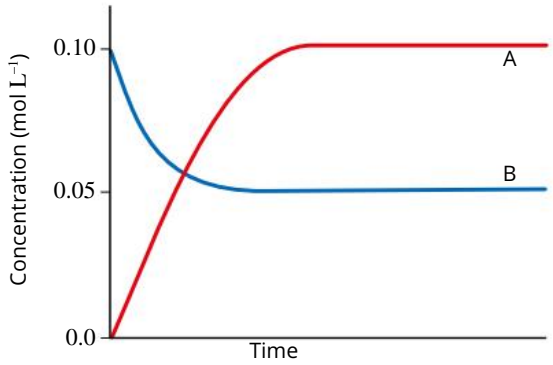


v Suggest what change was made to the system to produce the rate graph shown.

2 The gases dinitrogen tetroxide, N_2O_4, and nitrogen(IV) oxide, NO_2, coexist according to the following equilibrium reaction:

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

A concentration–time graph for the system establishing equilibrium is shown below.



a Identify A and B.

b Write an expression for the equilibrium constant of the decomposition of N_2O_4.

c On the graph, sketch the line showing the effect on A if a catalyst had been present in the mixture from the beginning.

d Use your knowledge of Le Châtelier's principle to predict the effect (decrease, increase or no change) of the change (column 1) on the designated quantity (column 2). Assume that the change listed is the only one taking place (e.g. if N_2O_4 is added, the volume and the temperature are kept constant).

Change	Quantity	Increase/decrease/no change
i Double the volume	Amount of NO_2	
ii Double the volume	Concentration of NO_2	
iii Add an inert gas at constant volume	Amount of N_2O_4	

3 **a** Lithium metal is produced commercially by electrolysis of a molten mixture of lithium chloride and potassium chloride.

i Write the half-equation for the electrode reaction occurring at the anode.

ii Write the half-equation for the electrode reaction occurring at the cathode.

iii Why is it not possible to produce lithium metal by the electrolysis of an aqueous solution of lithium chloride?

iv Suggest why a mixture of lithium chloride and potassium chloride is used, rather than pure lithium chloride, in this electrolytic process.

b Suggest three properties of graphite that account for its frequent use as an electrode material in commercial electrolytic cells.

c Steel cathodes are often used in commercial electrolytic cells, but never steel anodes. Account for this.

4 **a** List two structural features (components) that galvanic cells and electrolytic cells both 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.

5 Hydrogen sulfide (H_2S) can act as a weak acid and as a reducing agent in aqueous solution.

a **i** Write an equation for the first ionisation of hydrogen sulfide in water.

ii Write an expression for the equilibrium constant (K) for hydrogen sulfide ionisation in terms of the concentration of the chemical species present.

b 1.7 g of hydrogen sulfide will dissolve in 500.0 mL of water at room temperature to form a saturated solution. Calculate the concentration of this solution.

c Addition of solid sodium hydrogensulfide (NaHS) to this saturated solution will form a buffer solution.

i What is a buffer solution?

ii Using Le Châtelier's principle, predict what happens in this buffer solution when a small amount of HCl(aq) is added.

d Write a balanced ionic equation to show H_2S(aq) acting as a reducing agent in reaction with a silver nitrate solution.

6 **a** An old metal key composed mainly of iron, but showing some signs of forming an iron oxide (Fe_2O_3) coating, was placed into a dilute sulfuric acid solution. The key reacted slowly, removing the oxide layer, and then releasing hydrogen gas.

i Write a balanced equation for the reaction between the iron and sulfuric acid.

ii Show that this reaction is a redox reaction.

iii Write a balanced equation for the reaction between the iron oxide and sulfuric acid.

iv Show that this reaction is an acid–base reaction.

b A student wishes to electroplate copper metal onto the key, after first cleaning the surface of the metal.

i Draw a diagram of the cell needed to achieve this aim, using the key as one electrode and a strip of copper metal as the other.

ii Indicate on the diagram the polarity of the power source (positive or negative) to which the key should be attached.

iii Which electrode (the cathode or the anode) is the key?

iv Show why the concentration of Cu^{2+} ions in the electrolyte does not change.

v If the copper electrode was replaced with a graphite electrode, how would the pH near the electrode change as the electrolysis continued?

Section 3: Extended answer

1 Methanol may be used as a fuel for some racing cars, and can be used to generate energy in a direct methanol fuel cell (DMFC). The synthesis of methanol from methane involves two reversible reactions.

I A reaction of methane with steam to yield carbon monoxide and hydrogen.

II An exothermic reaction between carbon monoxide and hydrogen to produce methanol.

a Write equations for the two reactions (I and II) that are described.

b The reaction of carbon monoxide with hydrogen (reaction II) is performed in a reactor at about 250°C and 100 times atmospheric pressure. Copper, zinc oxide and alumina are also present.

i What is the likely function of the copper, zinc oxide and alumina in the reactor?

ii How would the yield of methanol be affected if the reaction were performed at a higher temperature?

iii State two advantages of using such a high pressure in the reactor.

c Any process involving carbon monoxide presents hazards because of its toxicity, which arises because of its ability to bind very strongly to haemoglobin (represented as Hb_4) in the blood, in competition with oxygen. The simplified equations are:

$Hb_4 + CO \rightleftharpoons Hb_4.CO$

$Hb_4 + O_2 \rightleftharpoons Hb_4.O_2$

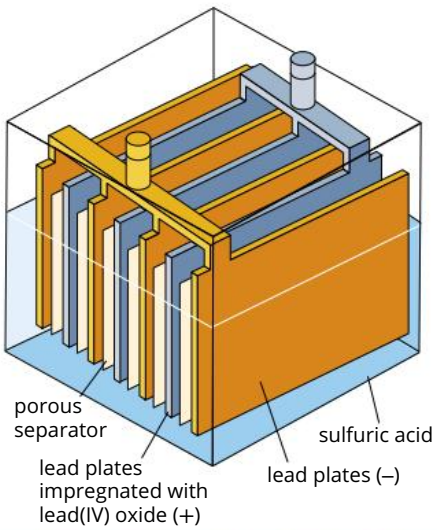
Referring to these competing equilibria, explain why exposure to carbon monoxide leads to decreased levels of oxyhaemoglobin ($Hb_4.O_2$) in the blood.

d Draw an energy profile for reaction of methanol as a fuel. Include the following labels on your profile: reactants, products, ΔH, activation energy

e The equation for the reaction in the DMFC is the same as that for the direct combustion of methanol with liquid water as a product. The fuel cell has an acidic electrolyte.

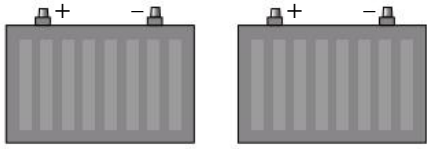
- **i** Write a balanced equation for the combustion of methanol to produce carbon dioxide and water.
- **ii** Write the half-equation for the reaction occurring at the anode.
- **iii** Write the half-equation for the reaction occurring at the cathode.
- **iv** Fuel cells provide an alternative method, often more efficient than direct combustion, of extracting energy from the reaction between a fuel and oxygen. Compare the energy transformation occurring in a fuel cell with that occurring in a direct combustion reaction.
- **v** Fuel cells share a number of similarities to galvanic cells, but have several differences. State one similarity and one difference between a fuel cell and a galvanic cell.

f Fuel cells may provide an energy source suitable for use in electric powered vehicles. Another possible energy source is the lead-acid battery, made up of six lead-acid cells connected in series. A simplified diagram of the lead-acid battery is shown below.



- **i** Write an equation for the overall cell reaction when electrical energy is being produced.
- **ii** Calculate the voltage of the cell using the E° values provided in the Chemistry Data Book.
- **iii** Suggest a reason why the actual voltage of the cell could be different to the voltage calculated from the E° values.
- **iv** What type of reaction (oxidation or reduction) occurs at the negative electrode when the cell is discharging?
- **v** To recharge the lead-acid battery, an external power supply must be attached to the electrodes.

  On the following diagram, draw lines to represent wires showing the correct connections to recharge the lead-acid battery.



2 **a** Ethanoic acid (CH_3COOH) is a monoprotic weak acid found in vinegar.

- **i** Explain the meaning of the term 'weak acid'.
- **ii** Write an expression for the equilibrium constant (K) for ethanoic acid ionising in water in terms of the concentration of the chemical species present.

b In a volumetric analysis to determine the concentration of an ethanoic acid solution, 10.0 mL of the acid was diluted to a total volume of 250.0 mL in a standard flask. 20.00 mL aliquots of this diluted acid solution were separately titrated with a standardised 0.100 mol L^{-1} solution of sodium hydroxide. The average volume to reach the endpoint was 18.5 mL.

- **i** Phenolphthalein indicator was used in the titration. What is the purpose of the indicator?
- **ii** Write a balanced equation for the titration reaction.
- **iii** Calculate the concentration of the undiluted ethanoic acid.
- **iv** Calculate the pH of the 0.100 mol L^{-1} sodium hydroxide solution.

c In a separate titration experiment the 0.100 mol L^{-1} sodium hydroxide solution was used to titrate 25.0 mL of a 0.10 mol L^{-1} hydrochloric acid solution.

- **i** State the volume of sodium hydroxide needed for complete reaction.
- **ii** State the pH value at the start of the titration.
- **iii** State the pH value at the equivalence point.
- **iv** The experiment in was repeated using a 25.0 mL sample of 0.10 mol L^{-1} ethanoic acid in the conical flask instead of the hydrochloric acid. For this titration, would the value of the pH at the equivalence point be equal to, greater than, or less

than the value for the titration using hydrochloric acid? Explain your choice.

d Like ethanoic acid, hydrogen peroxide (H_2O_2) is a weak acid. In addition to being an acid, hydrogen peroxide is both an oxidising agent and a reducing agent. Hydrogen peroxide reacts with itself according to the equation:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

- **i** Write an equation to show the first ionisation of hydrogen peroxide when it acts as an acid.
- **ii** While hydrogen peroxide does undergo this decomposition reaction, bottles of hydrogen peroxide can be kept in a dark bottle on the bathroom shelf for an extended period of time. Hydrogen peroxide solutions are also kept in the refrigerator. Explain why hydrogen peroxide solutions can be stored, and why they are often refrigerated.

e Like hydrogen peroxide, water can act as an acid, an oxidising agent and a reducing agent. Pure water has a very low, but measurable, electrical conductivity. At 25°C the pH of pure water is 7. The ionic product of water (K_w) varies with temperature as shown in the following table.

Temperature (°C)	5	15	35	55
K_w	1.85×10^{-15}	4.51×10^{-15}	2.09×10^{-14}	7.29×10^{-14}

- **i** Why does pure water conduct electricity, and why is this conductivity extremely low? Include a balanced chemical equation in your response.
- **ii** What is the pH of pure water at 5°C?
- **iii** Calculate the concentration of the hydroxide ion in water at 35°.
- **iv** How is water acting in the reaction represented by the equation shown below? Select your answer from the terms: acid, base, reducing agent, oxidising agent.

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

UNIT 4

Organic chemistry and chemical synthesis

This unit focuses on organic chemistry and the processes of chemical synthesis by which useful substances are produced for the benefit of society. Students investigate the relationship between the structure, properties and chemical reactions of different organic functional groups and the vast diversity of organic compounds. Students also develop their understanding of the process of chemical synthesis to form useful substances and products and the need to consider a range of factors in the design of these processes.

Learning outcomes

By the end of this unit, students:

- understand how the presence of functional groups and the molecular structure of organic compounds are related to their properties
- understand addition, condensation and oxidation reactions, and predict the products of these reactions
- understand how knowledge of chemical systems is used to design synthesis processes
- understand how models and theories have developed over time, and the ways in which chemical knowledge interacts with social and economic considerations in a range of contexts
- use science inquiry skills to design, conduct, evaluate and communicate investigations into reactions to identify organic compounds, including analysis of secondary data derived from chemical analysis
- evaluate, with reference to empirical evidence, claims about organic synthesis and chemical design, and justify evaluations
- communicate, predict and explain chemical phenomena using qualitative and quantitative representations in appropriate modes and genres.

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CHAPTER

11 Key products from the chemical industry

The chemical industry provides numerous chemicals, including luxuries, such as perfumes, and essentials, such as agricultural chemicals, fibres and fuels. Their production is an important part of Australia's industry. Chemical industries convert raw materials, such as plant material, minerals or atmospheric gases, into useful products. The production of two key chemicals—ammonia and sulfuric acid—will be studied in this chapter. You will learn that the concepts of rate and equilibrium that you studied in previous chapters are fundamental to the design of manufacturing processes so that production of useful chemicals is efficient and economically viable. You will perform calculations involving limiting reagents and percentage yields. As well, you will see that the synthesis of a final chemical often involves a sequence of individual reactions.

Science understanding

- the percentage yield of a chemical synthesis reaction can be calculated by comparing theoretical versus actual product quantities
- reagents and reaction conditions are chosen to optimise yield and rate for chemical synthesis processes, including in the production of ammonia (Haber process), sulfuric acid (Contact process) and biodiesel (base-catalysed and lipase-catalysed methods)
- quantities of products in a chemical synthesis reaction can be calculated by comparing stoichiometric quantities with actual quantities and by determining the limiting reagent
- chemical synthesis to form products with specific properties may require the construction of reaction sequences with more than one chemical reaction and involves the selection of particular reagents and reaction conditions in order to optimise the rate and yield of the product

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11.1 Yield and the chemical industry

FIGURE 11.1.1 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.

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. Industrial chemists must consider the efficiency of a reaction pathway and the wastes that are produced (Figure 11.1.1).

In this section, you will learn to perform calculations that can be used to determine the efficiency of processes that involve chemical reactions and help in the development of strategies to minimise waste.

YIELD

Theoretical and actual yields

If all reactants react to produce products according to the reaction equation, the mass of product formed is known as the **theoretical yield**. The theoretical yield is calculated using the mole ratios of the equation and assumes 100% conversion of the reactants. However, when reactants are mixed in the correct mole ratio, the amount of products will not always be exactly as predicted from stoichiometric calculations.

> Theoretical yield is the maximum amount of product that can be formed using stoichiometric ratios of the reactants and assumes 100% conversion.

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 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 all 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 from the formula:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

Worked example 11.1.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

30.0 g of solid calcium carbonate was mixed with excess hydrochloric acid solution. The calcium chloride recovered from the reaction mixture had a mass of 25.6 g. Calculate the percentage yield of this reaction.

Thinking	Working
Write a balanced equation for the reaction.	$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$
Use the appropriate formula, in this case $n = \frac{m}{M}$, to determine the amount, in moles, of reactant.	$n(CaCO_3) = \frac{m}{M}$ $= \frac{30.0}{100.09}$ $= 0.300\,\text{mol}$
Use the mole ratio for the reaction to determine the amount, in moles, of the product that would be made if all of the reactant reacted.	$\text{Mole ratio} = \frac{n(CaCl_2)}{n(CaCO_3)} = \frac{1}{1}$ $n(CaCl_2) = \frac{1}{1} \times n(CaCO_3)$ $= 0.300\,\text{mol}$
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.	$m(CaCl_2) = n \times M$ $= 0.300 \times 110.98$ $= 33.3\,\text{g}$
Calculate the percentage yield for this reaction from the formula: $\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$	$\text{Percentage yield} = \frac{25.6}{33.3} \times \frac{100}{1}$ $= 76.9\%$

Worked example: Try yourself 11.1.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

A 50.0 mL volume of 0.250 mol L^{-1} silver nitrate aqueous solution is mixed with excess sodium chloride solution. The precipitate is filtered and dried to give 1.37 g of silver chloride. Calculate the percentage yield of this reaction.

Percentage yields in multistep syntheses

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.

You can compare the overall percentage yields for different pathways to the same product to determine whether a particular synthetic pathway is the best way to produce a compound. Multistep synthesis is particularly common for making organic compounds (see Chapter 14). 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 11.1.2

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 → B followed by B → C

The yield of A → B is 80% and the yield of B → C is 70%.

Thinking	Working
Calculate the overall yield of C by multiplying the percentage yields together and expressing as a percentage (multiplying by 100).	The overall yield of C is: $\frac{80}{100} \times \frac{70}{100} \times \frac{100}{1}$ = 56%

Worked example: Try yourself 11.1.2

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 → B followed by B → C followed by C → D

The yield of A → B is 90%, the yield of B → C is 80% and the yield of C → D is 60%.

QUANTITIES OF GASES IN REACTIONS

Many reactions involve gases as reactants, products or both. The quantity of gas involved in a reaction is often measured or given as a volume. You will have learnt that the moles of a gas at standard temperature and pressure (STP), 0°C (273.15 K) and 100 kPa, respectively, can be calculated using $n = \frac{V}{22.71}$, where V is the volume of gas in litres.

However, it is unlikely that a reaction will be carried out at STP. Most industrial processes take place under different conditions of temperature and pressure. To find the number of moles of a gas under non-standard conditions, you can use the **ideal gas law**. The ideal gas law is normally stated as:

$$PV = nRT$$

where P is the gas pressure in kilopascals (kPa)

V is the gas volume in litres (L)

n is the amount in moles (mol)

R is 8.314 $JK^{-1}mol^{-1}$ (the universal gas constant)

T is the temperature in kelvin (K).

The expression can be rearranged so that the amount of a gas in moles can be calculated at any temperature and pressure:

$$n = \frac{PV}{RT}$$

11.1 Review

SUMMARY

- The theoretical yield of a chemical reaction is the mass of the product that would be formed if the limiting reactant reacted completely.
- To calculate the percentage yield, divide the actual yield obtained by the theoretical yield that would be obtained, if the limiting reactant reacted completely and multiply by 100:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

- When a reaction proceeds by a number of steps, the overall percentage yield is reduced at each step.
- The overall yield of the product of a multistep reaction is found by multiplying the percentage yields of each step together and expressing as a percentage (multiplying by 100). For example, for the multistep reaction A → B → C → D with the yields: 90%, 50% and 60%:

$$\text{overall yield} = \frac{90}{100} \times \frac{50}{100} \times \frac{60}{100} \times \frac{100}{1}$$
$$= 27\%$$

KEY QUESTIONS

1 During a trial experiment for the industrial production of ethanol from ethene, 150 g of ethene was reacted with excess 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.

2 Calculate the percentage yield for the reaction in which 20.0 g of ethanol is oxidised to produce 21.5 g of ethanoic (acetic) acid according to the equation:

$$C_2H_5OH \xrightarrow{H^+/Cr_2O_7^{2-}} CH_3COOH$$

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 How would the overall yield be affected if the yield for B → C was only 10%?

4 Phosphoric acid is manufactured according to the equation:

$Ca_3(PO_4)_2(s) + 3H_2SO_4(l) \rightarrow 2H_3PO_4(l) + 3CaSO_4(s)$

In one industrial process, the percentage yield of phosphoric acid was 67%. If the initial mass of calcium phosphate, $Ca_3(PO_4)_2$ ($M = 310.18\,g\,mol^{-1}$), for this process was 1.500 kg, calculate the mass of phosphoric acid that was produced. Give your answer to the appropriate number of significant figures.

11.2 Calculations involving limiting reagents

In the previous section, you calculated the theoretical yield (or amount of product) that could be formed given the amount of one reactant. In chemistry, once you know the amount, in moles, of a reactant that is completely consumed in a chemical reaction, the amount of any other component can be determined from the balanced chemical equation.

In this section, you will learn how to perform stoichiometric calculations, in which two reactants are involved but the reactant that is completely consumed may not be obvious straight away. In this style of question, you are given sufficient information to allow you to calculate the amounts of both reactants present. But before you can calculate the amount of product that is formed, you will need to determine which reactant is completely consumed; that is, which reactant will be the limiting factor in the reaction.

STOICHIOMETRY PROBLEMS INVOLVING LIMITING REAGENTS

When two reactants are mixed to result in a chemical reaction, it is possible that they will be combined in just the right mole ratio as indicated in the equation for each to react completely. This is unlikely in the industrial context, because it is important that chemical processes are as economical as possible. One way in which this is achieved is to have one reactant in excess (more present than can possibly react) to ensure that most of the other, often more expensive, reactants will be consumed.

The amount of product formed in a reaction will depend on the quantities of reactants that are available. If one reactant is in excess, then another reactant will be the **limiting reagent**. The amount of the limiting reagent is used to calculate the quantities of products formed, the theoretical yield, in a reaction.

To illustrate this situation simply, first work on a problem that does not involve chemicals. Suppose that you have been given some skateboard decks and wheels and you want to make as many complete skateboards as you can. As you can see in Figure 11.2.1, a complete skateboard is made up of one deck and four wheels.

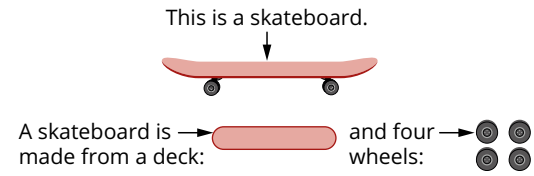


FIGURE 11.2.1 In order to make a complete skateboard, you must always use one deck and four wheels. This sets up the basic formula for a skateboard.

Now consider the situation shown in Figure 11.2.2. If you were given two decks and ten wheels, how many complete skateboards can you make from these materials?

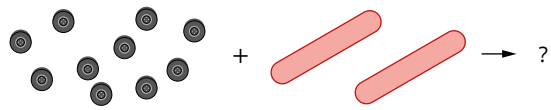


FIGURE 11.2.2 When provided with 10 wheels and two skateboard decks, how many complete skateboards can be made?

The answer is that you could make two complete skateboards and there would be two wheels left over (Figure 11.2.3).

FIGURE 11.2.3 When supplied with two decks and 10 wheels, the maximum number of skateboards that can be made is two. There will be two wheels that are not used.

In this example, you can say that the two wheels left over were in excess. Also, with the amount of decks and wheels that you were given, the total number of complete skateboards you could make was limited by the number of decks available.

A similar situation arises in chemical reactions if the quantities of reactants supplied are not in the stoichiometric ratio shown in the balanced equation for the reaction.

When this happens, the reactant that is:

- completely consumed is the limiting reagent
- not completely consumed is the excess reactant.

In a chemical reaction, the limiting reagent is completely used up.

Figure 11.2.4 shows three different scenarios for the reaction in which hydrogen gas and oxygen gas combine to form water, according to the equation:

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

Each of the diagrams provides examples to illustrate the concepts of limiting and excess reactants.

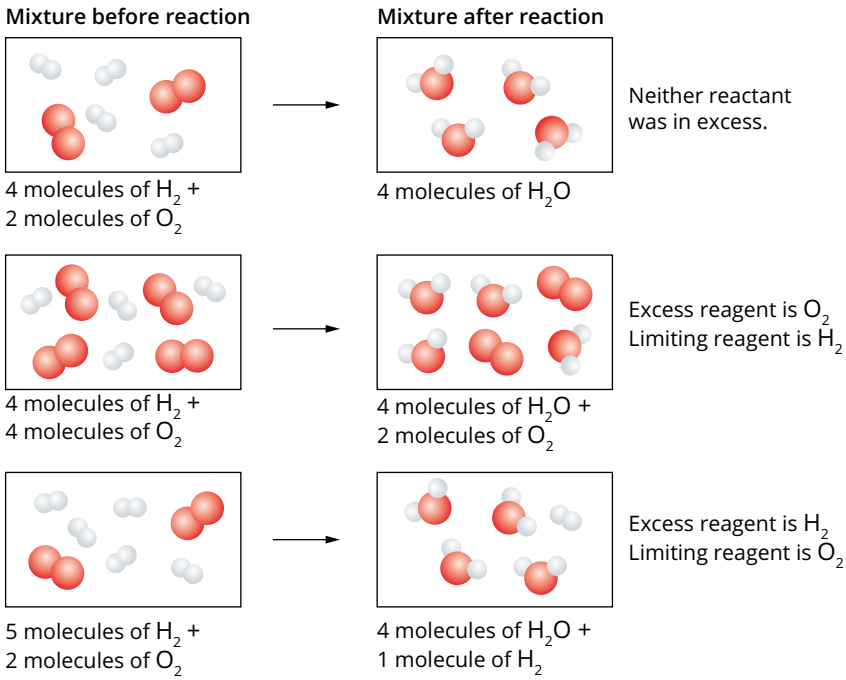


FIGURE 11.2.4 Different scenarios showing the concept of limiting reactant for the reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

Note that in each of the examples shown in Figure 11.2.4 the amount of product:

- formed is determined by the amount of the limiting reagent present in the reaction mixture
- cannot be determined from the amount of excess reactant.

In the skateboard example, it was the number of decks, not the number of wheels, that determined how many complete skateboards could be made.

> You must always use the amount of the limiting reagent to determine the amount of product that will be formed.

Steps in solving stoichiometry problems involving limiting reagents

To calculate which reactant is the limiting reagent, you must first convert the masses (for solids), volumes (for gases) or volumes and concentrations (for solutions) of the reactants to numbers of moles. Then use the mole ratio from the equation to determine which reactant is the limiting reagent. The steps for this process are outlined below for two reactants (Figure 11.2.5).

1
- Calculate the amounts of both known reactants.

2
- Choose one reactant (reactant A) and assume that all of it reacts.
- Use the mole ratio from the balanced equation to calculate how much of the other reactant (reactant B) would be needed to react with it.

3
- Compare this amount (of reactant B) with the amount of reactant B that is available.
- Ask yourself the question: Is there enough of reactant B to fully react with reactant A?

4
- If the answer is 'yes', then reactant A is the limiting reagent and therefore the 'known' for the reaction.
- If the answer is 'no', then reactant B is the limiting reagent and therefore the 'known' for the reaction.

5
- The amount of the limiting reagent can then be used to calculate the amounts of products formed in the reaction.

  Do this by multiplying by the mole ratio from the equation:

  $$\text{mole ratio} = \frac{\text{coefficient of unknown}}{\text{coefficient of known}}$$

FIGURE 11.2.5 Use these steps to determine which reactant is the limiting reagent in a chemical reaction.

Worked example 11.2.1

MASS–MASS STOICHIOMETRY CALCULATION WITH ONE REACTANT IN EXCESS

A solution containing 20.0 g of dissolved sodium hydroxide is added to a solution containing 25.0 g aluminium nitrate. An equation for the reaction is:

$3NaOH(aq) + Al(NO_3)_3(aq) \rightarrow Al(OH)_3(s) + 3NaNO_3(aq)$

a Which reactant is the limiting reagent?

b What is the mass of precipitate formed?

Thinking	Working
a Calculate the number of moles of each of the reactants in the equation using $n = \frac{m}{M}$ or $n = c \times V$ or $n = \frac{PV}{RT}$ as appropriate.	Use the equation $n = \frac{m}{M}$. For NaOH: $n(NaOH) = \frac{20.0}{40.0} = 0.500$ mol For $Al(NO_3)_3$: $n(Al(NO_3)_3) = \frac{25.0}{213} = 0.117$ mol
Use the coefficients of the equation to find the limiting reagent.	The equation shows that 3 mol of NaOH reacts with 1 mol of $Al(NO_3)_3$. So to react all of the $Al(NO_3)$ you will require $\frac{3}{1} \times n(Al(NO_3)_3$ of NaOH $\frac{3}{1} \times 0.117 = 0.352$ mol As there is 0.500 mol available, the NaOH is in excess. So, $Al(NO_3)_3$ is the limiting reagent (it will be completely consumed).
b Find the mole ratio of the unknown substance to the limiting reagent from the equation coefficients: $\text{mole ratio} = \frac{\text{coefficient of unknown}}{\text{coefficient of limiting reagent}}$	From the equation coefficients: $\frac{\text{coefficient of } Al(OH)_3}{\text{coefficient of } Al(NO_3)_3} = \frac{1}{1}$
Calculate the number of moles of the unknown substance using the number of moles of limiting reagent: $n(\text{unknown}) = n(\text{limiting reagent}) \times \text{mole ratio}$	$n(Al(OH)_3) = n(Al(NO_3)_3) \times \frac{1}{1}$ $= 0.117 \times \frac{1}{1}$ $= 0.117$ mol
Calculate the mass of the unknown substance using: $m(\text{unknown}) = n(\text{unknown}) \times \text{molar mass}$	Molar mass of $Al(OH)_3 = 78.0\,g\,mol^{-1}$ $m(Al(OH)_3) = 0.117 \times 78.0$ $= 9.15$ g

Worked example: Try yourself 11.2.1

MASS–MASS STOICHIOMETRY CALCULATION WITH ONE REACTANT IN EXCESS

A solution containing 0.600 g of lead(II) nitrate is added to a solution containing 2.60 g of potassium iodide. An equation for the reaction is:

$2KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$

a Which reactant is the limiting reagent?

b What is the mass of precipitate formed?

11.2 Review

SUMMARY

- Reactions in the chemical industry often have one reactant in excess to ensure that most of the other, often more expensive, reactant will be consumed.
- If quantities of more than one reactant are given, the limiting reagent needs to be determined; this will be the reactant that is consumed completely.
- The steps to determine which reactant is the limiting reagent and which reactant is in excess are shown in Figure 11.2.6.
- The limiting reagent is used to calculate the theoretical yield of product formed and the amount of the other reactant in excess.

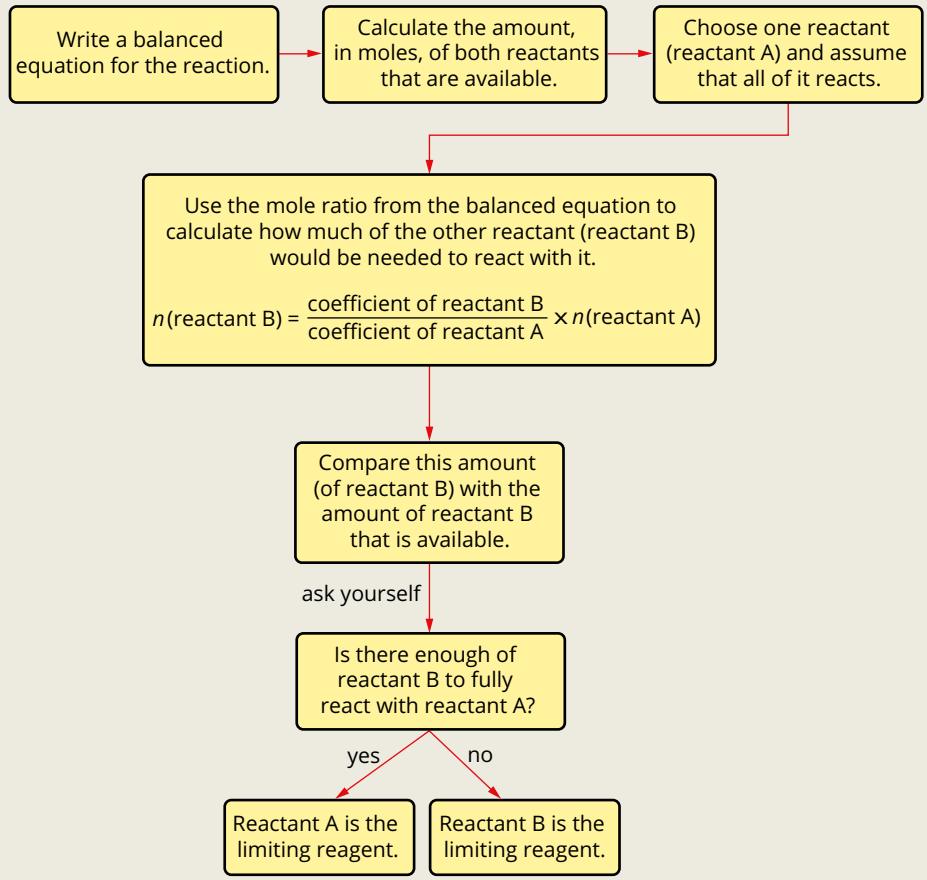


FIGURE 11.2.6 The steps to determine the limiting reagent in a chemical reaction

KEY QUESTIONS

1 Aluminium reacts with oxygen gas to form aluminium oxide. The balanced equation for the reaction is:

$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

In a particular reaction, 40 g of aluminium reacts with 35 g of oxygen gas. List the following steps in the order in which the calculations should be completed to determine the mass of aluminium oxide that will form.

I Use mole ratios to determine which reactant is limiting.
II Calculate the number of moles of aluminium and oxygen.
III Calculate the mass of aluminium oxide that forms.
IV Refer to the balanced equation.
V Calculate the number of moles of aluminium oxide that forms.

2 In three different experiments, different amounts of nitrogen and hydrogen reacted to form ammonia, according to the equation:

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

This table shows the amount of reactants and products in each experiment. Complete the table to indicate the amount of each substance remaining at the end of the reaction.

Nitrogen molecules available	Hydrogen molecules available	Ammonia molecules produced	Nitrogen molecules in excess	Hydrogen molecules in excess
2	10			
879	477			
9 mol	6 mol			

3 Sodium metal can react with chlorine gas to form sodium chloride. 25.0 g of sodium is reacted with 50.0 g of chlorine gas.

a Write the balanced equation for the reaction between sodium and chlorine.

b Calculate the mass of sodium chloride that will form in the reaction.

4 Potassium iodide and lead(II) nitrate solutions react together to form a precipitate of lead(II) iodide:

$2KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$

In each of the following cases, carry out the calculations to determine the quantities required.

a If 1.0 mol of potassium iodide reacts with 1.0 mol of lead(II) nitrate, determine which reactant is in excess and by how many moles.

b If 0.50 mol of potassium iodide reacts with 2.0 mol of lead(II) nitrate, determine which reactant is in excess and by how many moles.

c If 1.00 g of lead(II) nitrate reacts with 1.50 g of potassium iodide, determine which reactant is in excess and the mass of lead(II) iodide that forms.

d If 50.0 mL of 1.00 mol L^{-1} lead(II) nitrate solution reacts with 75 mL of 0.500 mol L^{-1} potassium iodide solution, determine which reactant is in excess and calculate the mass of lead(II) iodide that forms.

11.3 Some key products

AMMONIA

Ammonia is one of the most widely used chemicals in the world. Its unique properties and importance as a source of nitrogen make ammonia extremely versatile. The industrial-scale manufacture of ammonia is an important part of a developed country's agriculture industry.

World production of ammonia grew strongly from 62 million tonnes in 1974 to more than 140 million tonnes in 2016. More ammonia is produced industrially, per mole, than any other chemical. More than one-third of ammonia production occurs in China and India. More than 80% of the ammonia produced is used for the manufacture of ammonium salts, which are used as fertilisers.

Ammonia is also a good household cleaner when it is dissolved in water. Ammonia reacts slightly with water as a weak base to produce hydroxide ions (OH^-):

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

In addition to reacting with water, the polar NH_3 molecules form hydrogen bonds with H_2O molecules.

CHEMISTRY IN ACTION

Ammonia and explosives

As a fertiliser, ammonia has sustained food production for billions of people. On the other hand, as a result of its use in explosives, it has been estimated that ammonia has been responsible for the death of 150 million people.

In general, ammonium compounds and other compounds of nitrogen tend to be unstable. Ammonia is used as a raw material to make explosives such as ammonium nitrate, trinitrotoluene (TNT) and nitroglycerine.

Trinitrotoluene (Figure 11.3.1) is used as an explosive in the mining industry and by the military. It is manufactured in three steps by the reaction of nitric and sulfuric acids with toluene (Figure 11.3.2). Each step adds a nitro group (NO_2) to the benzene ring.

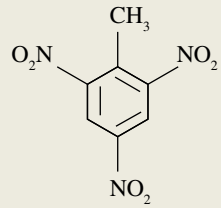


FIGURE 11.3.1 The structure of the explosive trinitrotoluene (TNT) (IUPAC name 2-methyl-1,3,5-trinitrobenzene)

The link between TNT and ammonia is in the production of nitric acid. Nitric acid is synthesised from ammonia in three reactions.

1 Oxidation of ammonia to nitrogen monoxide (NO):

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

2 Further oxidation of NO to nitrogen dioxide (NO_2):

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

3 Reaction of the NO_2 with water:

$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$

The NO produced in the final reaction is recycled for use in the second reaction.

As might be expected for an explosive, its detonation is a highly exothermic reaction. When detonated, TNT decomposes as follows:

$2C_7H_5N_3O_6 \rightarrow 3N_2 + 5H_2O + 7CO + 7C$

$2C_7H_5N_3O_6 \rightarrow 3N_2 + 5H_2 + 12CO + 2C$

Although TNT's decomposition is highly exothermic, the decomposition reaction has a relatively high activation energy compared to other explosives such as nitroglycerin, thus making it safer to handle and so a preferred explosive.

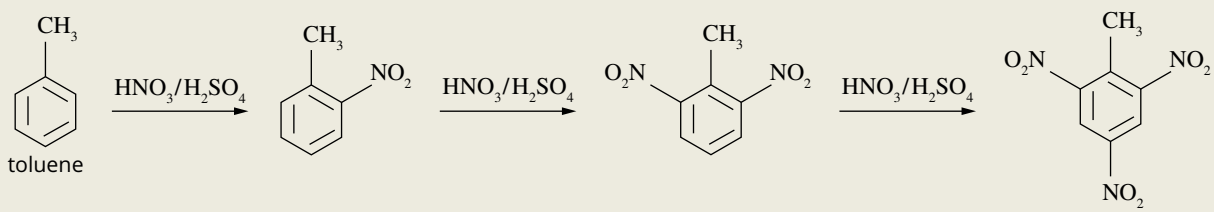


FIGURE 11.3.2 The conversion of toluene to the explosive trinitrotoluene. An NO_2 group is added to the benzene ring at each step.

Ammonia production

Ammonia is produced in large industrial plants. In Western Australia, there are several of these plants in the Pilbara region, including Yara Pilbara Fertilisers (Figure 11.3.3), which is one of the world's largest ammonia plants.

FIGURE 11.3.3 The Yara Pilbara Fertilisers ammonia plant in Western Australia is one of the world's largest ammonia plants, with an annual production capacity of approximately 850 000 tonnes.

The **Haber process** is used for the production of ammonia. It has been described as the reaction that feeds the world. The population growth that occurred during the 20th century was largely made possible by the Haber process. The ammonium fertilisers produced from ammonia are used by plants to make proteins, which you will study in Chapters 17 and 18. It has been estimated that more than 80% of the nitrogen in an average person's tissue is as a result of the Haber process.

Sourcing raw materials

Hydrogen and nitrogen are the raw materials needed for producing ammonia. The nitrogen is obtained from the atmosphere, since nitrogen makes up approximately 78% of the air. The nitrogen is separated from other components of air through liquefying the air and then using a process known as **fractional distillation**. Fractional distillation separates the components of a mixture, in this case air, according to their different boiling points.

The source of hydrogen depends on several factors, including the availability and cost of the raw materials and energy. Fossil fuels are often used, with natural gas, which is mainly methane, being the simplest and often the cheapest source. The hydrogen is obtained in a process known as steam reforming. The reactions that occur in the two-step process of steam reforming are represented by the equations:

Step 1: $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

Step 2: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

Haber process

In the industrial production of chemicals, reaction conditions such as temperature, pressure and catalysts need to be chosen very carefully. These conditions affect the rate of reaction and yield of the product. Ensuring a high yield gives the plant greater productivity and reduces waste, while a high reaction rate ensures the product is generated in a timely manner so that the plant can be economically viable.

Ammonia is manufactured from nitrogen and hydrogen gas in the Haber process. The reaction is exothermic:

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

The rate of a reaction can be increased by increasing the frequency with which reactants collide, and by increasing the proportion of collisions that have the required activation energy. This means that a higher reaction rate can be achieved when:

- the temperature is higher
- a catalyst is present
- the partial pressures of gaseous reactants are higher (higher pressure).

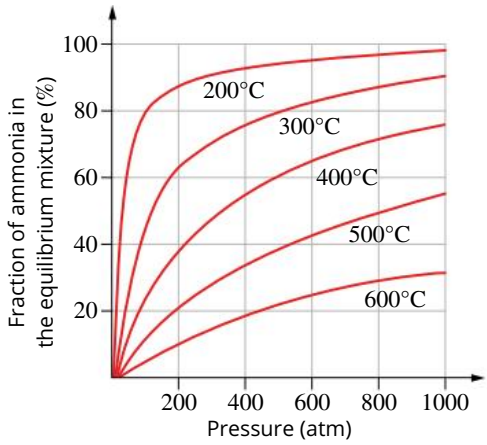


FIGURE 11.3.4 The percentage of ammonia present when a mixture of nitrogen and hydrogen has reached equilibrium.

Changing the temperature of a reaction changes the equilibrium constant of the reaction. The forward reaction in the Haber process is exothermic. This means that lowering the temperature increases the value of the equilibrium constant and increases the equilibrium yield of ammonia.

According to Le Châtelier's principle, the position of an equilibrium system shifts to partially oppose any changes imposed upon it. This means that increasing the pressure causes the system to partially oppose this pressure change, by shifting to the side of the equation with fewer gaseous particles to reduce the pressure. Since the equation for the Haber process has four gaseous reactant particles and two gaseous product particles, increasing the pressure causes a shift to the right and increases the amount of ammonia present at equilibrium.

The effects of changing temperature and pressure on the equilibrium are shown in Figure 11.3.4.

Table 11.3.1 summarises the effects of changing conditions on the reaction rate and equilibrium yield of ammonia in the reaction.

TABLE 11.3.1 Effects of catalyst, increased temperature and increased pressure on the reaction rate and equilibrium yield or ammonia

Condition	Effect on equilibrium yield	Effect on reaction rate
Catalyst present	No effect	Increased
Increased temperature	Decreased	Increased
Increased pressure	Increased	Increased

As you can see, a higher pressure favours both a high yield and a high reaction rate. In the Haber process, the economic benefits from the increased rate and yield outweigh the cost of maintaining high pressures. The pressure used in the Haber process is high, and varies between 100 and 250 atmospheres.

Table 11.3.1 shows that a higher temperature leads to a high reaction rate, but also leads to lower yields. Industrial plants use moderate temperatures, between 350°C and 550°C, to ensure that the yield is sufficient while maintaining a reasonable reaction rate. The use of a porous iron/iron oxide (Fe_3O_4) catalyst allows use of these moderate temperatures while producing the reasonable reaction rate required.

In the Haber process, nitrogen from the air and hydrogen from steam reforming are mixed and compressed before being pumped into the reactor where the ammonia is formed. In the reactor are several layers of iron/iron oxide catalyst mesh. The mixture then passes into another vessel where it is cooled, and gaseous ammonia is liquefied and collected. The unreacted nitrogen and hydrogen are compressed again and pumped back through the reactor. Figure 11.3.5 is a simplified depiction of the Haber process.

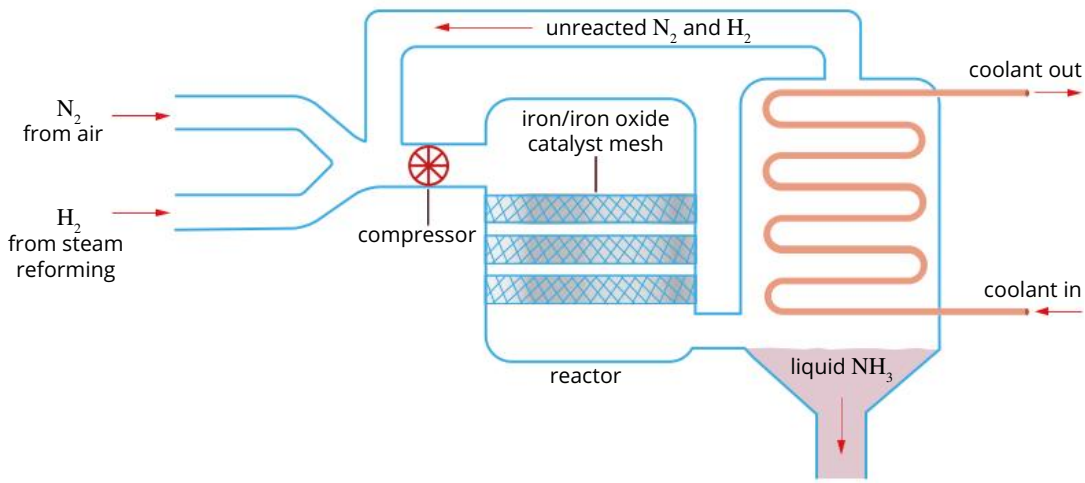


FIGURE 11.3.5 The main components of the Haber process, showing conversion of N_2 and H_2 to NH_3 and the subsequent collection of ammonia in liquid form

At each pass of the gases through the reactor, the yield of ammonia is about 20%. During commercial production of ammonia, the gas mixture is not given enough time to reach equilibrium. This ensures that ammonia is produced as quickly as possible.

The constant removal of ammonia from the reaction mixture ensures that a net forward reaction is always occurring. Since ammonia is the product of this reaction, removing it keeps the rate of the reverse reaction low. This gives an ultimate yield of 98%.

CHEMISTRY IN ACTION

Alternative sources of raw materials

Most of the hydrogen for the Haber process comes from the steam reforming of methane, which produces carbon dioxide as waste. Methane is the main component of natural gas, a fossil fuel. The use of fossil fuels to produce electricity for the process also releases carbon dioxide. Thus, much research is being undertaken into producing hydrogen from alternative methods.

The electrolysis of water by using electricity from renewable energy sources, such as hydroelectricity, has been the most commonly explored alternative.

The power cost of producing a tonne of ammonia by traditional methods is approximately $40, which is substantially lower than the $600 of power needed when using the electrolysis of water as the source of hydrogen. Nevertheless, improvements in electrolysis and hydroelectric technologies, and the rising cost of using fossil fuels, may one day see this become the primary way of sourcing hydrogen for producing ammonia.

Another area of research is methane cracking to obtain the hydrogen directly from the methane. The reaction is:

$$CH_4(g) \rightarrow C(s) + 2H_2(g)$$

This has the advantage that the carbon does not enter the atmosphere. However, a lot of energy is needed to break carbon–hydrogen bonds. They only start to break at about 550°C, and typically 800°C or over is needed. Catalysts can lower the reaction temperature, but the soot quickly coats the catalyst, making it inactive. Recent research has explored bubbling methane into a bath of molten metal. As methane bubbles through the metal, it is cracked with the hydrogen bubbling out of the top and the soot floating harmlessly to the top of the molten metal. A small-scale vessel using molten tin at 1000°C has operated successfully. There remain issues to be solved, including dealing with the estimated several cubic kilometres of soot that would be produced annually if this were scaled up to provide hydrogen at the volumes needed, but researchers believe there is potential for this approach.

SULFURIC ACID

Sulfuric acid (H_2SO_4) is a key chemical in a variety of industries. Sulfuric acid is so vital that a country's industrial capacity can be estimated simply by the mass of sulfuric acid it produces.

One of the many uses for sulfuric acid is as a dehydrating agent. Sulfuric acid extracts the hydrogen and oxygen from sugar in the form of water (Figure 11.3.6).

Sulfuric acid is a widely used chemical in industry because it has a range of useful properties. Most commonly, sulfuric acid is used as a strong acid or as a catalyst in its concentrated form.

FIGURE 11.3.6 Dehydration of sugar by concentrated sulfuric acid. The acid removes hydrogen and oxygen from the sugar in the form of water, leaving black carbon. The highly exothermic reaction drives most of the water off as steam.

CHEMFILE

Uses of sulfuric acid

As you can see in Figure 11.3.7, the most common use of sulfuric acid is in the production of a range of fertilisers, which accounts for 75% of its worldwide use.

Phosphorus, like nitrogen, is a key element in the growth of plants and is found in many fertilisers. Sulfuric acid is commonly used to convert insoluble calcium phosphate ($Ca_3(PO_4)_2$) into a soluble form of phosphorus that can be absorbed by plants.

One soluble form of phosphorus is produced in the following reaction, which takes several weeks to complete:

$$Ca_3(PO_4)_2(s) + 2H_2SO_4(l) + 4H_2O(l) \rightarrow Ca(H_2PO_4)_2(s) + 2CaSO_4{\cdot}2H_2O(s)$$

The combination of the solids produced in this reaction, $Ca(H_2PO_4)_2$ and $CaSO_4{\cdot}2H_2O$, is known as superphosphate. Superphosphate has been very important in the development of agriculture in Western Australia (and Australia more generally). Western Australian soils are very old and highly weathered. This has left them with low levels of natural phosphorus. Application of superphosphate to soils has contributed to the successful development of agriculture in Western Australia, particularly grain growing.

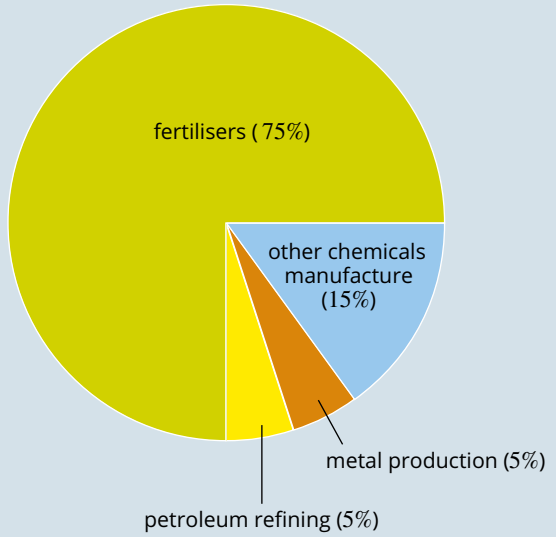


FIGURE 11.3.7 The uses of sulfuric acid worldwide

Sulfuric acid is a diprotic acid. When added to water, it can donate two protons in a two-step ionisation process:

$$H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq) \qquad \Delta H = -72 \text{ kJ mol}^{-1}$$

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq) \qquad \Delta H = -22 \text{ kJ mol}^{-1}$$

Production of sulfuric acid: the contact process

Annual worldwide production of sulfuric acid is over 240 million tonnes, more than any other industrially produced chemical in the world (although the production of ammonia is greater on a per mole basis). The **contact process**, which was originally patented in 1831, is still the primary way in which sulfuric acid is produced today.

In the contact process, sulfuric acid is manufactured in stages from sulfur dioxide. The overall process involves the oxidation of sulfur dioxide to sulfur trioxide, followed by conversion to the acid. The three stages of the process can be summarised as follows:

$$SO_2(\text{from various sources}) \rightarrow SO_3 \rightarrow H_2SO_4$$

Stage 1. Sourcing or producing sulfur dioxide

The sulfur dioxide used to produce sulfuric acid is obtained from two principal sources in Australia. These are the:

- combustion of sulfur recovered from natural gas and crude oil
- smelting of sulfide ores of copper, zinc or lead.

If sulfur extracted from natural gas or crude oil is used as a raw material for making sulfuric acid, the first stage of the manufacturing process involves spraying molten sulfur under pressure into a furnace. In this process, the sulfur burns in air to produce sulfur dioxide gas, as shown in Figure 11.3.8. The high surface area of the sulfur spray allows rapid combustion.

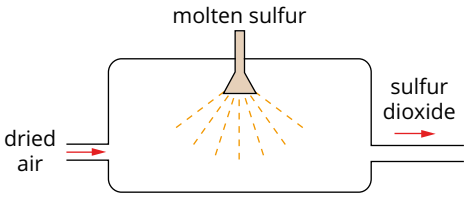


FIGURE 11.3.8 The burner in the contact process. In this vessel, molten sulfur is sprayed in and reacts with oxygen in the dried air.

The reaction is represented by the equation:

$$S(l) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H = -297 \text{ kJ mol}^{-1}$$

The sulfur dioxide gas is then cooled for the next stage in the process.

If sulfur dioxide is used as the raw material, then it must be dried (by bubbling through concentrated sulfuric acid) and pumped directly into the next stage of the process.

CHEMISTRY IN ACTION

Mining underground sulfur

A third source of sulfur is from the mining of underground deposits of elemental sulfur (Figure 11.3.9) by a method known as the Frasch process. While this process is now only used in a small number of plants worldwide, up until the end of the 20th century it was the most common way to obtain sulfur.

In the Frasch process, a hole is first drilled into the underground deposit and then three concentric pipes are placed into the deposit. Superheated water (about 170°C) is directed down the outer pipe into the sulfur deposit, melting the sulfur. Hot compressed air is injected into the sulfur through the inner pipe, which forces the molten sulfur up the middle pipe. Sulfur recovered in this process is about 90% pure.

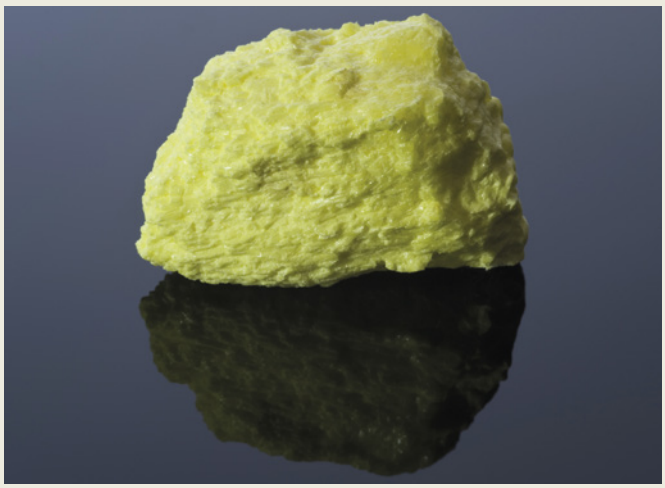


FIGURE 11.3.9 Elemental sulfur

Stage 2. Converting sulfur dioxide into sulfur trioxide

In the contact process, the main equilibrium step occurs in the converter, where sulfur dioxide gas is oxidised by oxygen to form sulfur trioxide gas:

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

Optimising both the equilibrium yield and rate of a reaction is vital to ensure that a plant is economically viable and to minimise waste emissions.

As for the Haber process, the reaction between sulfur dioxide and oxygen is exothermic and contains more gaseous reactant particles than gaseous product particles. Collision theory, Le Châtelier's principle and equilibria can be used to determine how changes in conditions will affect the yield and reaction rate.

A higher reaction rate can be obtained when a catalyst is present, the temperature is higher and the pressure is higher, while a higher yield can be obtained when the temperature is lower and pressure is higher. This is summarised in Table 11.3.2.

TABLE 11.3.2 Yield and reaction rates according to conditions

	Higher temperature	Higher pressure	Presence of catalyst
Equilibrium yield	Lower yield	Higher yield	No effect
Reaction rate	Higher reaction rate	Higher reaction rate	Higher reaction rate

Although a high pressure is used in the Haber process, this is not the case for the contact process. The cost of maintaining a high pressure outweighs any added benefits of a higher reaction rate and higher yield in the contact process, so atmospheric pressure is used instead.

As for many industrial processes, a conflict exists with the selection of a temperature. A high temperature produces a high reaction rate, but a low temperature is needed for a high equilibrium yield. Therefore, a moderate temperature of 400–500°C is used in conjunction with a vanadium(V) oxide (V_2O_5) catalyst. This ensures a high enough reaction rate is achieved while producing reasonable yields. Figure 11.3.10 shows the converter in which sulfur trioxide is formed in the presence of the catalyst.

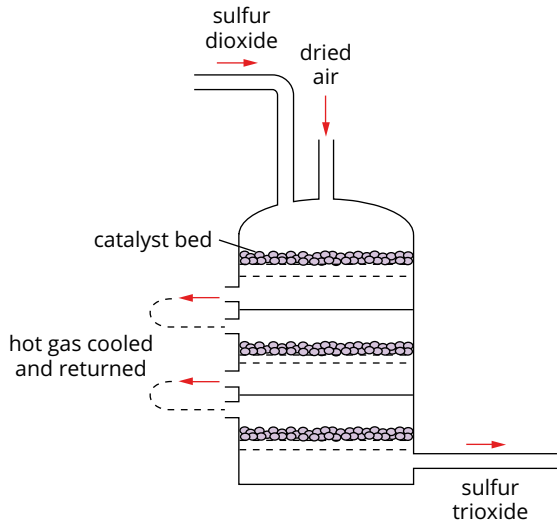


FIGURE 11.3.10 The converter of the contact process. The main equilibrium step for the contact process occurs in the converter, where sulfur dioxide is converted into sulfur trioxide as it passes over a series of vanadium(V) oxide catalyst beds.

To ensure that the gases are kept at the desired temperature, the gas mixture is cooled as it passes from one catalyst bed to the next. The conversion of SO_2 to SO_3 is improved by ensuring that an excess of the cheaper reactant O_2, from the air, is added.

Stage 3. Absorption of sulfur trioxide and conversion to sulfuric acid

Sulfur trioxide reacts with water to form sulfuric acid:

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq) \qquad \Delta H = -130 \text{ kJ mol}^{-1}$$

However, this direct reaction with water is not used because so much heat is generated that a fine mist of acid is produced. This fine mist is difficult to collect. Instead, sulfur trioxide gas is passed into concentrated sulfuric acid in an absorption tower. The reaction can be regarded as occurring in two steps:

1 The sulfur trioxide gas dissolves almost totally in the acid to form a liquid known as oleum ($H_2S_2O_7$):
$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$
2 Oleum obtained from the absorption tower is then carefully mixed with water to produce sulfuric acid:
$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$
The absorption tower is depicted in Figure 11.3.11.

In practice, the additional water is often trickled in, together with the concentrated sulfuric acid, to meet the incoming sulfur trioxide. This results in two molecules of sulfuric acid being produced for every one molecule of sulfuric acid that is introduced into the absorption tower. Unreacted sulfur dioxide can be recycled back into the converter in a process known as double absorption.

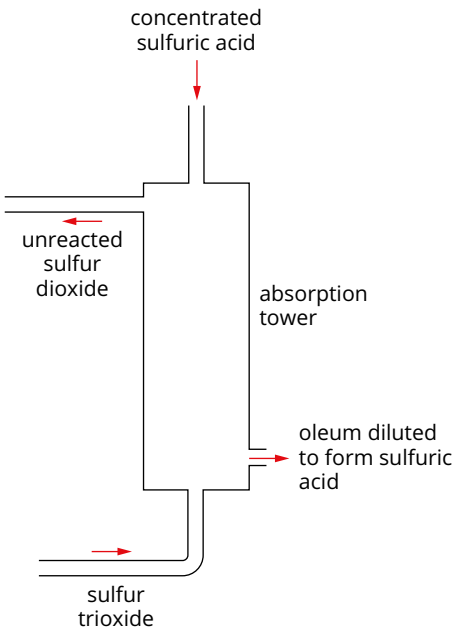


FIGURE 11.3.11 The absorption tower of the contact process. In this vessel, concentrated liquid sulfuric acid reacts with gaseous sulfur trioxide to produce oleum.

Waste management

From an environmental perspective, one positive feature of sulfuric acid plants is that they use sulfur or sulfur dioxide that is a by-product of other industries, such as metal smelting and petroleum refining.

Manufacturers of sulfuric acid must maximise the conversion of sulfur dioxide to sulfur trioxide because strict limits are set for sulfur dioxide emissions into the atmosphere, since sulfur dioxide can cause the formation of acid rain. The sulfur dioxide reacts with water in the rain and clouds to form sulfurous acid (H_2SO_3), which is a weak acid and donates a proton to water to form hydrogen sulfite ions:

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$$

$$H_2SO_3(aq) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + H_3O^+(aq)$$

It is also important to limit the emissions of sulfur dioxide gas because it corrodes metals and is harmful to the growth of plants and aquatic animals.

Most sulfuric acid plants built after 1970 use a double absorption process. As described above, sulfur trioxide is formed in the converter and converted to oleum in the absorption tower. Unreacted gases are then recycled back to the converter for one or two more passes over the catalyst beds before being returned for absorption. In this way, the percentage of sulfur dioxide converted to sulfur trioxide is increased from 98% to more than 99.6%. While this seems like a small increase, it reduces the amount of sulfur dioxide released into the environment by 80%.

CHEMISTRY IN ACTION

Compromises beyond temperature and pressure

To produce ammonia in the Haber process and sulfuric acid in the contact process, the economics of producing reasonable quantities in a reasonable time require compromises in temperature and pressure. In the Haber process, although high yield is favoured by using a low temperature, to provide an acceptable reaction rate a compromise moderate temperature is used. Similarly, in the contact process a moderate temperature is used for oxidation of sulfur dioxide to sulfur trioxide to give an acceptable reaction rate at the cost of yield. As well, in the oxidation of sulfur dioxide, even though high pressure gives a high yield and fast reaction, the cost of maintaining high pressures means atmospheric pressure is used.

The reasons for compromises in industrial processes go beyond just the reaction rates and equilibrium yields associated with pressure and temperature. When designing a process, chemical engineers need to consider many conditions that can affect the process, including possible unwanted side reactions and possible interactions between the various substances in the system.

Ethanol can be produced by reacting ethene with water:

$$CH_2CH_2(g) + H_2O(g) \rightarrow CH_3CH_2OH(g) \quad \Delta H = -45\,kJ\,mol^{-1}$$

Often in an industrial process, the cheapest reactant is used in excess to favour the forward reaction and improve yield. Although water is cheaper, ethene is used in excess. This compromise arises because of the nature of the catalyst used. The catalyst is phosphoric acid (H_3PO_4). The acid is coated onto a solid silicon dioxide support. If too much steam is used, the catalyst is diluted and may even wash off the solid support, making it ineffective.

Although a high pressure will give a fast reaction and high yield of ethanol, a moderate (in industrial terms) pressure of 60–70 atm is used. This compromise is needed not because of the high costs of maintaining high pressures, but because a high pressure causes the ethene to polymerise to produce polyethene (polyethylene).

11.3 Review

SUMMARY

- Ammonia is produced by the Haber process.
- Nitrogen needed for the Haber process is sourced from the air, and collected through fractional distillation.
- Hydrogen needed for the Haber process is primarily sourced from steam reforming of natural gas (mainly methane, CH_4) or other fossil fuels.
- The equation for the Haber process is:
  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\,kJ\,mol^{-1}$
- Sulfuric acid is produced in the contact process, which is summarised in Table 11.3.3.
- The steps in the contact process can be summarised as:
  $S(l) \rightarrow SO_2(g) \rightarrow SO_3(g) \rightarrow H_2S_2O_7(l) \rightarrow H_2SO_4(l)$
- The conditions chosen in any industrial process need to be selected carefully to ensure both a reasonable yield and reaction rate.
- In the Haber process, high pressures and moderate temperatures are chosen, and an iron/iron oxide mesh catalyst is used
- In the contact process, for conversion of sulfur dioxide to sulfur trioxide, atmospheric pressure and moderate temperatures, a vanadium(V) oxide catalyst and an excess of O_2 are used to ensure a greater conversion of sulfur dioxide to sulfur trioxide.

TABLE 11.3.3 Production of sulfuric acid using the contact process

Reaction vessel	Reaction(s)	Notes
Burner	$S(l) + O_2(g) \rightarrow SO_2(g)$	Sulfur for the process is generally sourced from other industrial processes, such as smelting metal ores or fossil fuel refining.
Converter	$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	V_2O_5 catalyst beds are used and the gaseous mixture is cooled between passes over the beds.
Absorption tower	Step 1. Absorption of sulfur trioxide: $SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$ Step 2. Dilution of oleum: $H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$	Sulfur trioxide is converted to sulfuric acid through a two-step process, initially forming an intermediate compound called oleum, $H_2S_2O_7$. This is because direct conversion to H_2SO_4 is very exothermic and forms a mist that is difficult to collect.

KEY QUESTIONS

1 Which of the following statements related to ammonia and its production are correct?

A Nitrogen for the Haber process is sourced from the air.

B Most ammonia is used to manufacture explosives for the mining industry.

C Extraction of hydrogen from methane in the steam reforming process does not contribute to global warming.

D The nitrogen in ammonia is the main contributor to the protein in humans.

E The overall yield in the Haber process is about 20%.

2 **a** The Haber process involves the reaction between nitrogen and hydrogen:

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

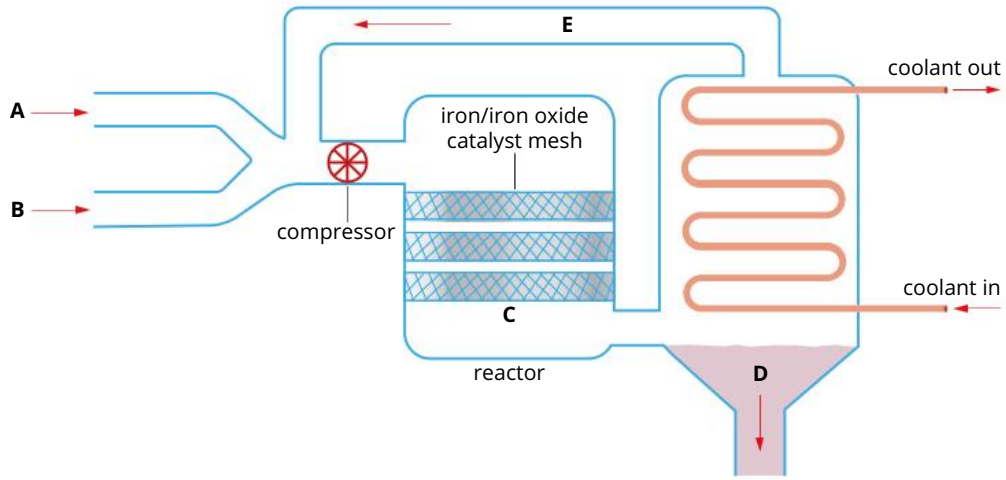
Use your knowledge of Le Châtelier's principle, equilibria and collision theory to categorise how the listed changes will affect both the equilibrium yield and reaction rate. Some changes may be listed in more than one category.

- Addition of a catalyst
- Increasing pressure
- Reducing temperature

	Increase	Decrease	No change
Reaction rate			
Equilibrium yield			

b Explain how increasing the partial pressure of nitrogen will affect the rate of production and the equilibrium yield of ammonia.

3 In the following diagram, label the chemicals A–E that would be present in higher concentrations in the different parts of the Haber process. Use state symbols to indicate the state of the chemicals. Note that in some parts of the system there will be more than one chemical at high concentration.



4 In which vessel of the contact process is oleum formed?

A dilution tower
B burner
C converter
D absorption tower

5 Match the following chemicals with the vessels of the contact process in which they react.

$O_2(g)$, $SO_3(g)$, $H_2SO_4(l)$, $SO_2(g)$, $S(l)$

Burner	Converter	Absorption tower

6 Why is it important to ensure that SO_2 emissions are as low as possible?

Chapter review

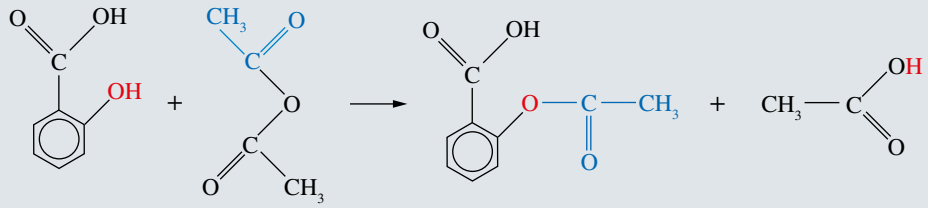
11

KEY TERMS

actual yield
contact process
fractional distillation
Haber process
ideal gas law
limiting reagent
percentage yield
theoretical yield
universal gas constant

Yield and the chemical industry

1 Aspirin can be synthesised by an esterification reaction according to the pathway shown 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.

2 Nitric acid can be manufactured in three steps.

Step 1 $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

Step 2 $2NO + O_2 \rightarrow 2NO_2$

Step 3 $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

a If the percentage yield in each step is, respectively, 95%, 80% and 90%, calculate the overall percentage yield of nitric acid.

b What theoretical mass of nitric acid will be produced if 1.500 tonnes of ammonia is reacted?

c What actual mass of nitric acid will be produced from this amount of ammonia?

3 Ammonia is produced in the Haber process by the reaction:

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

If the percentage yield of the reaction is 98%, what mass of hydrogen is needed to produce 5.50 tonnes of ammonia?

4 The three steps in the manufacture of sulfuric acid are represented by the equations:

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

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

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

Explain why compromise conditions may be required for the reaction of sulfur dioxide and oxygen, but not the other two steps of the process.

Calculations involving limiting reagents

5 In three separate experiments, different amounts of carbon and oxygen were reacted to form carbon dioxide, according to the equation:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

The table lists the amount of reactants and products in each of the three experiments. Complete the table to indicate the amount of product formed and the remaining reactant at the end of the reaction.

Carbon atoms available	Oxygen molecules available	Carbon dioxide molecules produced	Carbon atoms in excess	Oxygen molecules in excess
8	20			
1000	3000			
9 mol	6 mol			

6 Sodium can react with oxygen gas to form sodium oxide:

$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

3.0 mol of sodium is reacted with 0.8 mol of oxygen gas.

a Determine which reactant is in excess.

b How many moles of sodium oxide are produced in the reaction?

7 16.0 g of hydrogen sulfide is mixed with 20.0 g of sulfur dioxide and they react according to this equation:

$$2H_2S(g) + SO_2(g) \rightarrow 2H_2O(l) + 3S(s)$$

a Calculate the mass of sulfur produced.

b Calculate the mass of reactant left after the reaction.

8 In an ammonia production plant, 2.00 tonnes of nitrogen gas is mixed with 1.50 tonnes of hydrogen gas. Determine the mass of ammonia produced if the plant is 96% efficient. The reaction is:

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

9 One use of sulfuric acid is for the manufacture of superphosphate by reaction with rock phosphate, $Ca_3(PO_4)_2$, as shown below.

$$Ca_3(PO_4)_2(s) + 2H_2SO_4(l) + 4H_2O(l) \rightarrow Ca(H_2PO_4)_2(s) + 2CaSO_4{\cdot}2H_2O(s)$$

a Why can't rock phosphate be used directly as a fertiliser?

b If 800.0 kg of rock phosphate is mixed with 1220.0 kg of 62% by mass sulfuric acid solution, what mass of superphosphate will be produced, assuming complete reaction?

Some key products

10 In the manufacture of ammonia, nitrogen and hydrogen gases are mixed in the reactor where they produce ammonia. At each pass of the gases the yield of ammonia is about 20% and the mixture of N_2, H_2 and NH_3 gases in the reactor pass into a cooling chamber where the NH_3 condenses to a liquid and is removed from the chamber. Explain, using the appropriate chemistry principle, why only the NH_3 condenses.

11 Ammonia is used to manufacture a number of nitrate fertilisers, including ammonium nitrate and urea ($CO(NH_2)_2$).

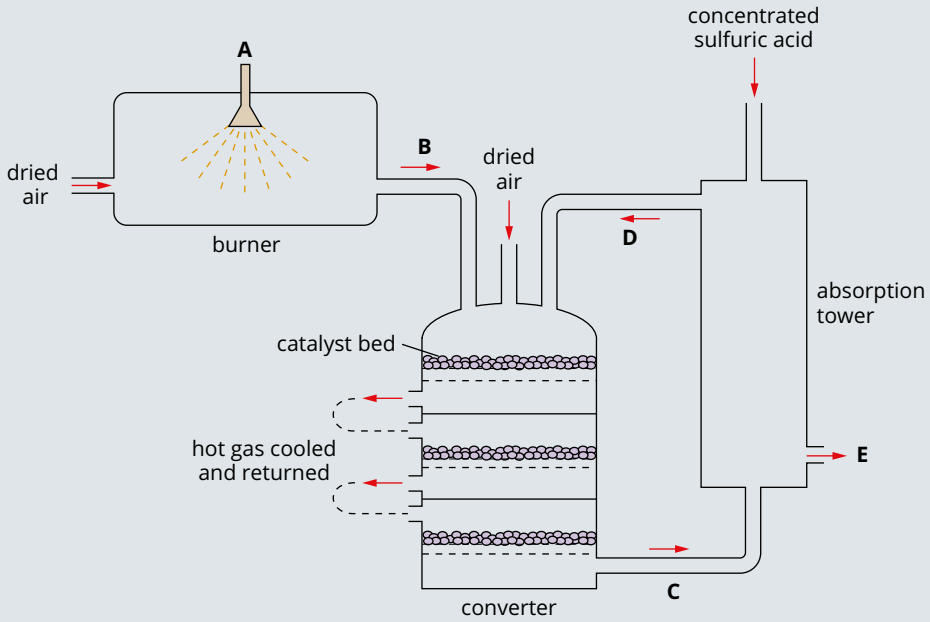
a Ammonium nitrate can be produced by bubbling ammonia gas into a concentrated solution of nitric acid. Write the balanced equation for the reaction.

b Urea can be produced by reacting ammonia with carbon dioxide. Write the balanced equation for the reaction.

c Which of these two nitrogen fertilisers provides more nitrogen per gram of fertiliser?

12 Describe the problems with sourcing hydrogen for the Haber process from methane.

13 **a** The following diagram shows the three parts of the contact process for manufacturing sulfuric acid. Label the chemicals at A–E.



b Use a balanced equation to explain why the air that goes into the burner needs to be dried.

14 The equilibrium reaction in the contact process is represented by the equation:

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

Complete the following sentences, using the terms: converter, moderate, cooled, absorption tower, SO_3, increase, SO_2, beds, V_2O_5, VO_5, burner, decrease, low, high, heated.

The main reaction in the contact process takes place in the _____. To ensure that the reaction rate is high enough a _____ catalyst and a _____ temperature are used. To ensure the yield is high, the gases are passed over several catalyst _____ with the gases being _____ between each pass. Unreacted _____ from the _____ is passed back through the _____ to increase the overall yield and decrease _____ emissions.

15 Why is it important to ensure that SO_2 emissions are as low as possible?

A SO_2 is a major contributor to photochemical smog.
B SO_2 causes the oceans and waterways to become more alkaline.
C SO_2 contributes to acid rain and corrosion.
D SO_2 creates holes in the ozone layer.

Connecting the main ideas

16 During the Haber process, the mixture of N_2, H_2 and NH_3 gases in the reactor pass into the cooling chamber. Which one of the following will not change when the gases enter the cooling chamber?

A equilibrium constant for the reaction
B rate of the forward reaction
C rate of the reverse reaction
D activation energy of reaction

17 The first step in the steam reforming process to get hydrogen for the Haber process is the reaction between methane and steam:

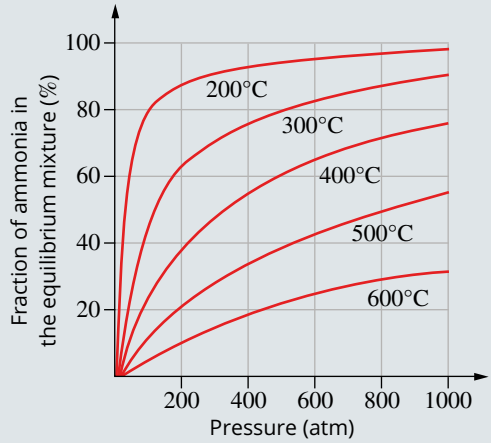
$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H = +206 \text{ kJ}$

a Give the set of conditions that would maximise the yield of hydrogen gas. Justify the conditions using Le Châtelier's principle.

b For the conditions you have given in part **a**, explain, using collision theory, their effect on the rate of reaction.

18 In most ammonia production plants, the reaction conditions chosen aim for about 20% ammonia in the equilibrium mixture of gases. To achieve this, one particular plant has operating conditions of 500°C and 200 atm. The plant operators decide to reduce the temperature to 400°C.

a Use the following graph to identify the pressure that needs to be used to maintain about 20% ammonia in the equilibrium mixture of gases.



b Use collision theory and Le Châtelier's principle to discuss how the change in temperature will affect the rates of the forward and reverse reactions at the new equilibrium compared to their rates at the original equilibrium, and how the change in temperature will affect the yield of NH_3.

c Use collision theory and Le Châtelier's principle to discuss how the change in pressure will affect the rates of the forward and reverse reactions at the new equilibrium compared to their rates at the original equilibrium, and how the change in pressure will affect the yield of NH_3. Thus, state why the change in pressure that you gave in **a** will keep the yield at about 20%.

19 A sulfuric acid production plant is located near a nickel refinery to use the sulfur dioxide that is produced by the roasting of nickel sulfide ores. The reaction of the ore is:

$$2NiS(s) + 3O_2(g) \rightarrow 2NiO(s) + 2SO_2(g)$$

a Calculate the volume of SO_2 gas produced, at 1 atm (101.3 kPa) and 30°C, from the roasting of 3.50 tonnes of ore. Assume complete reaction.

b The SO_2 is used to manufacture sulfuric acid in two further steps:
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$
If these steps both have a 98% yield, what mass of sulfuric acid solution with a concentration of 70% by mass H_2SO_4 can be produced?

20 Ammonia and sulfuric acid are commonly used to manufacture fertilisers. Ammonium sulfate is a fertiliser that is made by reacting ammonia and sulfuric acid with each other. It is particularly used on alkaline (high pH) soils to help decrease the soil pH.

a Write a balanced equation for the reaction of ammonia with sulfuric acid.

b Explain with the support of a balanced equation how this fertiliser can decrease soil pH.

CHAPTER

12 Resources and the environment

In a chemistry sense, our world is essentially a closed system; that is, there is no net gain or loss of matter in the world. The implications of this are two-fold. First, all physical natural resources are finite (cannot be replaced). Second, the products of the chemical industry will remain in the environment in one form or another.

This presents chemists with a delicate balancing act. On the one hand, society demands and expects a continuous supply of materials and goods, almost all of which involve a chemist in either their design or their production. On the other hand, there is growing concern regarding the long-term sustainability of resources and the health of the environment.

These seemingly contrasting notions are addressed by the philosophy underpinning green chemistry.

Science as a human endeavour

Scientific knowledge can be used to design alternative chemical synthesis pathways, taking into account sustainability, local resources, economics and environmental impacts (green chemistry), including the production of ethanol and biodiesel.

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12.1 Green chemistry

'Green chemistry' is a term that can be confused with 'environmental chemistry'. Environmental chemistry is the study of chemical processes that occur in a natural environment and how these processes are affected by human activities such as mining or pollution. **Green chemistry** is not a specific discipline of chemistry, but is an overarching philosophy related to **sustainable** and environmentally friendly chemical practices.

Environmental sustainability can be considered as the ability to balance the rates of resource use and pollution so that they can be continued indefinitely without harm to the environment.

The ultimate goal of green chemistry is to design more resource-efficient, environmentally friendly products and processes through technological and engineering solutions.

PRINCIPLES OF GREEN CHEMISTRY

The approach of green chemistry to industrial processes, and to a lesser extent laboratory and research activities, is underpinned by the 12 principles of green chemistry (Table 12.1.1).

TABLE 12.1.1 The 12 principles of green chemistry

Principle	Explanation
1 Prevent waste	Design chemical processes to prevent waste rather than treat waste or clean it up after it is formed.
2 Maximise atom economy	Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
3 Design less hazardous chemical syntheses	Design safer methods that use and generate substances with little or no toxicity to humans and the environment.
4 Design safer chemicals and products	Design chemical products to be fully effective, yet to have little or no toxicity.
5 Use safer solvents and reaction conditions	Avoid using toxic solvents to dissolve reactants or extract products.
6 Increase energy efficiency	Minimise energy requirements. Perform chemical reactions at room temperature and pressure whenever possible.
7 Use renewable raw materials	Use starting materials that are derived from renewable resources, such as plant materials, rather than from finite resources, such as fossil fuels.
8 Avoid chemical derivatives	When a chemical has to be produced from another chemical before it can be used, additional reagents are used and extra waste is generated.
9 Use catalysts, not excess reactants	Minimise waste by using small amounts of catalysts that can carry out a single reaction many times. Using a catalyst is preferable to using excess reactants, which creates waste.
10 Design chemicals and products that are biodegradable	Design chemical products that break down to harmless substances after use, so that they do not accumulate in the environment.
11 Analyse in real time to prevent pollution	Include continuous monitoring and control during the process to minimise or eliminate the formation of by-products.
12 Minimise the potential for accidents	Design chemicals and their forms (solid, liquid or gas) to minimise the potential for chemical accidents, including explosions, fires and releases to the environment.

SUSTAINABLE CHEMISTRY

One of the challenges facing politicians and lawmakers is to balance the need for economic growth and jobs with the desire to preserve and protect the natural environment. These are often seen as mutually exclusive, where you can have jobs and growth or a pristine natural environment, but not both.

However, the principles of green chemistry do not conflict with a productive and economically viable chemical industry. Through approaches such as developing alternative chemical syntheses, selecting safer **renewable** and locally sourced reagents, minimising waste and undertaking remediation (environmental clean-up), chemical industries can become sustainable, both environmentally and economically.

A renewable resource is a resource that is replenished naturally at a rate that compensates for its depletion through use.

Remediation is the act of remedying something.

Green syntheses

Industrial chemists design efficient methods for converting readily available starting materials into desired products. This process is known as the **synthesis** of a compound. The chemicals generated by industry could be compounds that have been designed to have exactly the right properties for their intended use, or compounds found in nature but not in large enough quantities required by society.

CHEMISTRY IN ACTION

Insulin: an example of chemical synthesis

In Australia, an estimated one million people have been diagnosed with diabetes. Many of these people require regular injections of insulin. Insulin is a hormone that plays an important role in regulating glucose levels in the blood. Insulin is naturally produced in the pancreas.

FIGURE 12.1.1 These pig pancreases are being examined upon delivery from the abattoir before being ground up for the rest of the extraction process.

When the study of insulin and its role in regulating blood sugar levels began in the early 1920s, the only source of insulin was living organisms, such as pigs and cattle (Figure 12.1.1). Insulin was extracted, purified and injected into people, mainly children, who were dying from diabetic ketoacidosis, in order to save their lives.

It was not until the early 1950s, when the amino acid structure of insulin (Figure 12.1.2) was characterised by British biochemist Frederick Sanger, that a synthesis was possible. Sanger was awarded the Nobel Prize in Chemistry in 1958 for his work.

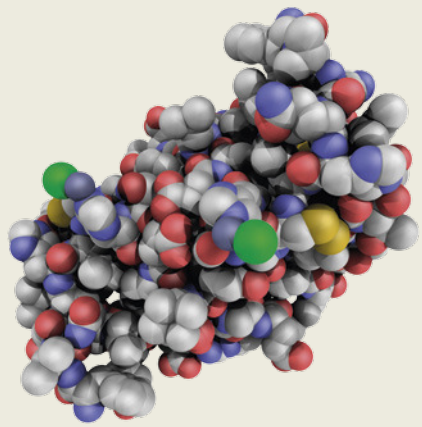


FIGURE 12.1.2 A computer-generated model of an insulin molecule. The chemical structure of insulin took almost 30 years to determine.

FIGURE 12.1.3 Nurofen is a well-known brand of ibuprofen pain killer.

In the past, chemists mainly concerned themselves with the yield and purity of the final products. They also considered time and cost as important factors. With an increasing awareness and concern for the environmental impact of human activities, chemists are trying to develop 'greener' synthesis pathways that minimise unwanted side-products, reduce waste and are energy efficient, while still being industrially feasible and economically viable.

Ibuprofen (Figure 12.1.3) is a common analgesic (pain reliever) that was first developed in the 1950s. Its 'brown' synthesis pathway (Figure 12.1.4) involved six distinct steps, in which only 40% of the atoms in the reactants ended up in the final product. Even if this reaction resulted in an impossible 100% yield, it would still mean that most of the atoms involved in the synthesis would be incorporated into waste and by-products. This represents a poor result environmentally and economically.

In 1992, a new 'green' synthesis pathway was developed involving only three separate steps (Figure 12.1.4), in which 77% of the atoms from reactants resulted in the final product. This value can be further improved to around 99% by regenerating and reusing some reactants. It is estimated that the worldwide production of ibuprofen is around 15 000 tonnes per year. Using the brown synthesis, this would also mean at least 15 000 tonnes of waste and by-products, but by utilising the green synthesis, this unnecessary waste is avoided.

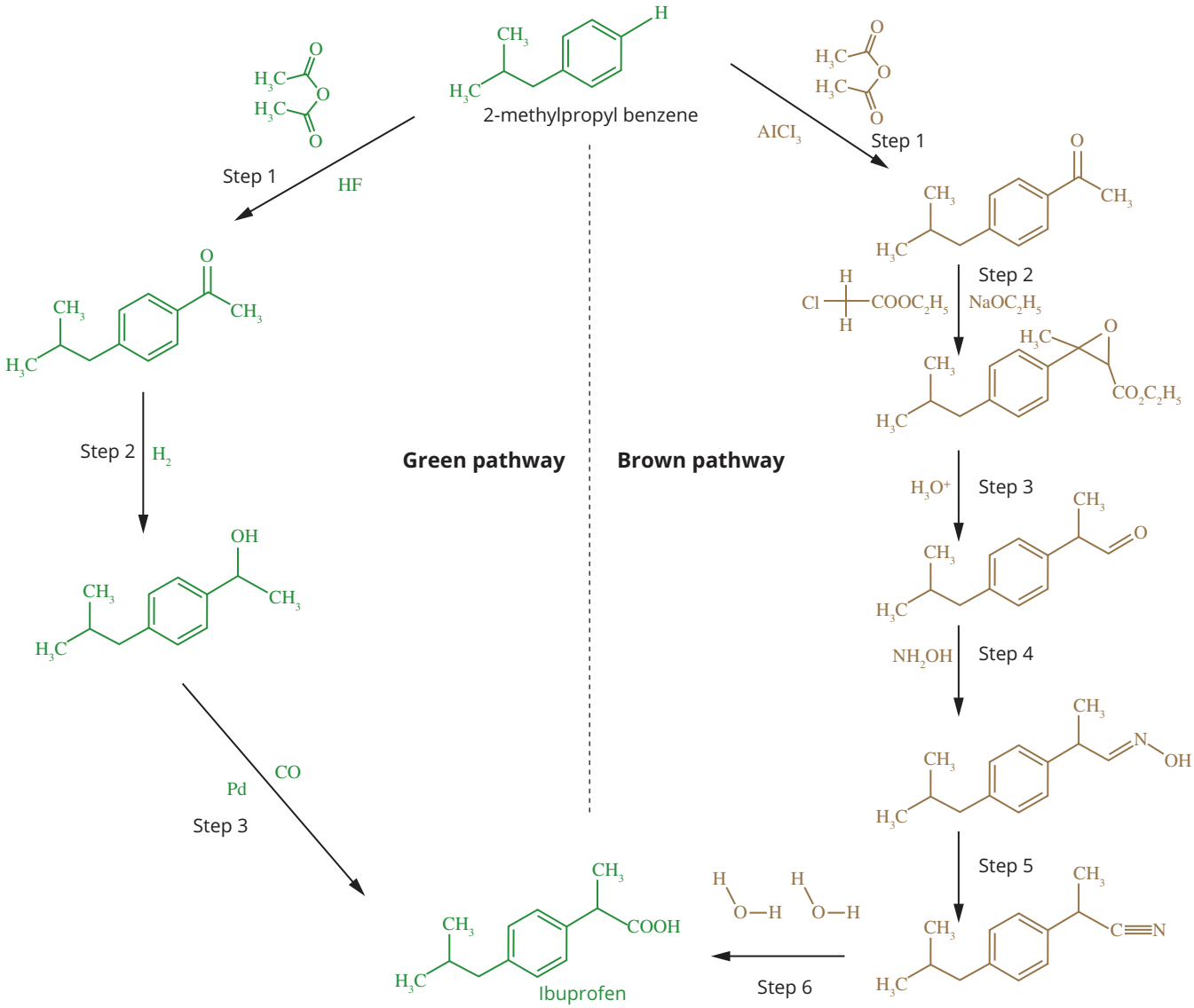


FIGURE 12.1.4 The older 'brown' and newer 'green' synthesis pathways for ibuprofen

EXTENSION

Atom economy

Today, chemists follow the philosophies represented by green chemistry and endeavour to design reaction pathways with the maximum 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 12.1.5, where the different coloured symbols represent atoms or groups of atoms, if the atom economy of a reaction is high, all or most of the atoms in the reactant molecules end up in the desired product molecule. If the atom economy of a reaction is low, fewer 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.

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.

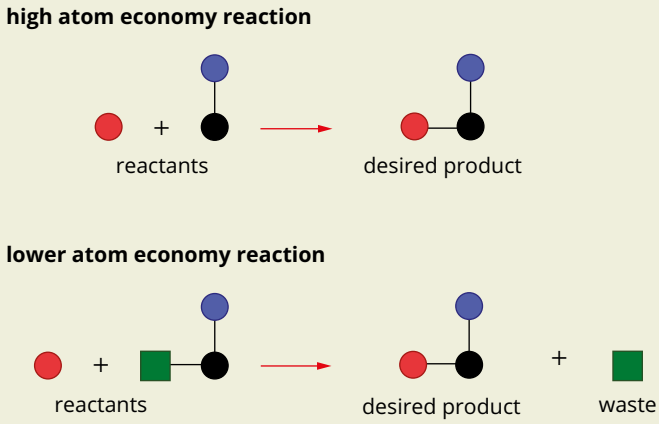


FIGURE 12.1.5 Examples of a high and low atom economy synthesis

Once the balanced equation for a reaction is known, the atom economy can be calculated from 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:

$$\text{atom economy} = \frac{\text{mass of desired product}}{\text{mass of all reactants}} \times 100$$

Use Worked Example 12.1.1 to help you with calculations of atom economy.

Worked example 12.1.1

CALCULATING ATOM ECONOMY

Calculate the atom economy for the production of ethanol from chloroethane. In this process, chloroethane is heated with a solution of sodium hydroxide. The equation for the reaction is:

$$C_2H_5Cl(aq) + NaOH(aq) \rightarrow C_2H_5OH(aq) + NaCl(aq)$$

Thinking	Working
Calculate the total molar mass of the reactants.	$M(C_2H_5Cl) + M(NaOH)$ $= [(2 \times 12.01) + (5 \times 1.008) + 35.45] + (22.99 + 16.00 + 1.008)$ $= 104.5\,g\,mol^{-1}$
Calculate the molar mass of the required product.	$M(C_2H_5OH)$ $= (2 \times 12.01) + (6 \times 1.008) + 16.00$ $= 46.07\,g\,mol^{-1}$
Calculate the atom economy for the reaction using the formula: $\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$	$\text{Atom economy} = \frac{46.07}{104.5} \times 100$ $= 44.1\%$ So in this process, only 44.1% of the starting materials are converted to the desired product. The remainder of the chemicals used is waste.

Worked example: Try yourself 12.1.1

CALCULATING ATOM ECONOMY

Calculate the atom economy for the formation of 1-iodopropane ($CH_3CH_2CH_2I$) from propan-1-ol.
The equation for the reaction is:

$$CH_3CH_2CH_2OH(aq) + NaI(aq) + H_2SO_4(aq) \rightarrow CH_3CH_2CH_2I(aq) + NaHSO_4(aq) + H_2O(l)$$

Green chemicals

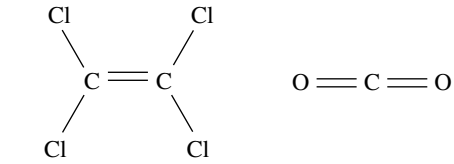
The history of chemistry is littered with infamous chemicals such as tetraethyl lead in petrol and the insecticide DDT. Although effective in their chosen roles, these chemicals posed significant health and environmental dangers. One of the 12 principles of green chemistry is to use equally effective, but safer and preferably renewable, chemicals.

Chemists are constantly searching for new, innovative and environmentally friendly chemicals to replace long-used, but often less safe, chemicals. One chemical that has been commonly used in dry-cleaning is perchloroethylene (PERC). PERC is the most commonly used dry-cleaning solvent. It is responsible for the characteristic smell of freshly dry-cleaned fabrics but is a recognised likely carcinogen that has been linked with other health conditions such as Parkinson's disease.

As can be seen in Figure 12.1.6, PERC is perfectly non-polar, which makes it ideal for dissolving hydrophobic substances such as oil and grease. A commonly available alternative to PERC that is also perfectly non-polar is carbon dioxide (Figure 12.1.6). The only problem with using carbon dioxide as a solvent is that at room temperature it is a gas, which makes it less suitable as a cleaning solvent than PERC, which is a liquid at room temperature. Simply cooling carbon dioxide to a liquid would mean reducing the temperature to –80°C, a temperature that would likely damage delicate fabrics.

To solve this problem, chemists use what is known as supercritical carbon dioxide. This is carbon dioxide, which at certain temperatures and pressures ($T > 31$°C and $P > 7.3$ MPa) demonstrates the properties of both a liquid and a gas at the same time. Using supercritical carbon dioxide with an appropriate detergent is an equally effective, yet significantly safer and environmentally friendly, alternative to perchloroethylene.

A carcinogen is a substance capable of causing cancer in living cells.



perchloroethylene (PERC) carbon dioxide

FIGURE 12.1.6 Perchloroethylene (PERC) and carbon dioxide both have non-polar structures, which make them suitable for removing grease and oil.

Hydrophobic substances are not attracted to, or will not mix homogenously, with water.

CHEMISTRY IN ACTION

Antibacterial handwashes—when soap became simply not enough

In the last few years, there has been a huge increase in the number of antibacterial handwashes and cleaning products (Figure 12.1.7) available to consumers. These handwashes are advertised as providing a greater level of protection from bacteria than simple soap and water. One of the major active ingredients in antibacterial products is triclosan.

FIGURE 12.1.7 Triclosan is the active ingredient in many antibacterial consumer products.

Triclosan (Figure 12.1.8) was developed in the 1960s and is an effective antibacterial and antifungal agent. However, a study carried out by the US Food and Drug Administration found no evidence that triclosan in soap provided any benefit compared with washing with regular soap and water.

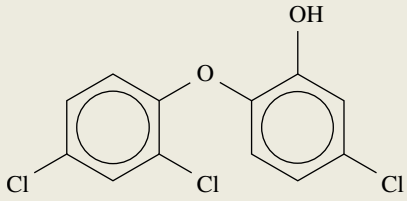


FIGURE 12.1.8 Triclosan is one of the major ingredients in antibacterial handwashes.

The potential adverse health effects of triclosan are still being investigated, but its impact on the environment is clear. In 2016, a study showed that the edible parts of plants that were irrigated with triclosan-contaminated water still contained triclosan months later. Triclosan primarily finds its way into the environment through sewage and waste waters. It is toxic to a range of aquatic bacteria and algae and has been detected in animals higher up the food chain, including fish and dolphins.

Numerous companies have voluntarily removed triclosan from their products in the face of mounting evidence of its environmental harm. Triclosan was banned for use in soap by the US Food and Drug Administration at the end of 2016 due to a lack of evidence of its efficacy. To date, triclosan is still legal in Australia.

Extracting gold in Western Australia

Gold mining (Figure 12.1.9) is the fourth largest commodity sector in Western Australia, valued at $10 billion each year. The industry standard method for gold extraction and refining involves gold cyanidation, where gold is leached from the ore as a water-soluble cyanide complex:

$$4Au(s) + 8CN^-(aq) + 2H_2O(l) + O_2(g) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

i Leaching is the process of extracting certain substances from a solid by dissolving them in a liquid.

FIGURE 12.1.9 The Kalgoorlie Super Pit is the second largest open-cut gold mine in Australia after the Newmont Boddington gold mine.

Once the gold is extracted by the carbon-in-pulp process, the tailings contain significant concentrations of cyanide, which is toxic. Often these waste streams are processed to detoxify them prior to storage, but processing does not completely eliminate the cyanide present in the tailings. Aqueous solutions of cyanide rapidly degrade in sunlight into harmless substances, but the cyanide-related cyanates and thiocyanates, although less toxic, may persist in the environment for a number of years. This makes the processing and storage of gold-refining wastes an expensive exercise.

Chemists at Curtin University in Perth have developed a gold extraction process in which the amino acid glycine, the simplest of the amino acids, is substituted for cyanide (Figure 12.1.10). Glycine demonstrates a number of benefits over cyanide: it is environmentally benign, cheaper and recyclable. Because glycine is non-toxic, it drastically reduces the environmental danger that mine tailings represent. Glycine is as accessible as cyanide and, because it is far safer, it lends itself to *in situ* leaching, reducing the need for vast open cut mines such as the Super Pit.

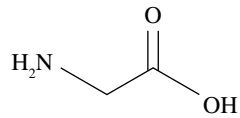


FIGURE 12.1.10 Glycine—the simplest amino acid—is being used in gold extraction.

CHEMISTRY IN ACTION

The 2014 Mount Polley mine disaster

Tailings are the materials left over after valuable minerals have been separated from the ore. Tailings usually consist of a slurry of fine particles of uneconomical metals, minerals and chemicals. Historically, tailings were disposed of in the most convenient manner—by being dumped into nearby downstream running water, such as rivers and streams. Today, tailings are often stored in large ponds or dams. The tailings are pumped into the ponds and sedimentation of the solids and evaporation of water is allowed to take place.

On 4 August 2014, there was a breach in a tailings pond at the Mount Polley copper and gold mine in British Columbia, Canada (Figure 12.1.11). This allowed 10 million cubic metres of waste water and 4.5 million cubic metres of tailings to pour into nearby Polley Lake. This spill raised the level of Polley Lake by 1.5 metres, and the lake then emptied into the nearby Quesnel Lake.

According to the mining company's documents, 326 tonnes of nickel, more than 400 tonnes of arsenic, 177 tonnes of lead and 18400 tonnes of copper and their compounds had been placed into the tailings pond in the previous year. Owing to the spill, much of this will have ended up in the local environment, including lakes and streams.

This is often considered the biggest environmental disaster in modern Canadian history and the true extent of the damage to the environment is likely to remain unknown for years or decades to come.

FIGURE 12.1.11 The Mount Polley tailings dam breach caused much destruction in the local environment.

Waste minimisation and remediation

Producing large amounts of waste is not economically or environmentally sustainable. Industries spend a lot of money and time to optimise operations and reduce inefficiencies, including waste generation. The key financial losses associated with waste are two-fold. First, reagents that end up in wastes do not end up in marketable product. Second, treating and storing waste is expensive. Applying the principles of green chemistry is one way in which a company can improve their profitability through reducing costs related to waste treatment and disposal while at the same time reducing the environmental impact of their business and becoming more sustainable.

One way that greener industries can be developed is to base a process on another industry's waste. This drastically reduces operating costs because businesses are usually happy to sell a waste that they would otherwise have to dispose of at an associated cost.

Chemical industries often locate themselves close to other industries on which they rely. This minimises material transport costs and allows several industries to make the most of existing infrastructure such as ports and rail networks. This synergy of industries is a common strategy aimed at increasing profitability, but it can also be used to develop green chemistry solutions to treating waste products.

The contact process used to produce sulfuric acid needs a steady source of sulfur dioxide as its key starting material. This sulfur dioxide can be obtained by burning solid sulfur in air, or using waste sulfur dioxide from another industry. When sulfide ores are roasted, one of the waste products is sulfur dioxide, which, if released into the air, contributes to environmental problems such as acid rain. The contact process is used south of Kalgoorlie to create sulfuric acid, a marketable product, from the nickel smelter's waste product.

One of the most significant waste products produced by the Alcoa aluminium refinery in Kwinana is 'red mud'. Red mud is the tailings produced after the extraction of alumina from bauxite ore and consists of a highly alkaline slurry of sediment particles and waste water. This red mud is pumped into tailings ponds (Figure 12.1.13) where it is left to dry through evaporation, and then the sediment is stored (dry stacking). Despite the tailings in the refinery being washed, the red mud remains highly alkaline due to the bases used in the extraction process. This is the major obstacle in the disposal of the tailings as the high alkalinity poses a risk to surface and ground water resources.

FIGURE 12.1.13 The tailing ponds at Alcoa's Kwinana aluminium refinery. You can see the 'red mud', which is highly alkaline.

A collaborative exercise between the Alcoa aluminium refinery and the nearby CSBP ammonia plant has found a green chemistry solution to both their waste products. The hydrogen required in the Haber process is produced by steam reforming of methane. One of the by-products of this is carbon dioxide, a greenhouse gas. This carbon dioxide is then used to neutralise the high alkalinity of Alcoa's tailings in a process called carbonation. This reduces the pH of the tailings to levels closer to that of the surrounding soils, making the tailings safer for disposal.

Rendering the waste product of an industry safe so that it can be disposed of makes a lot of sense environmentally, but not so much economically because this waste still needs to be disposed of at some cost. Economically, the ideal scenario would be to turn your waste product into a marketable commodity and have someone pay you for your waste.

CHEMFILE

Lobster is on the menu at the University of Western Australia

FIGURE 12.1.12 Dr Mohamed Makha

Dr Mohamed Makha (Figure 12.1.12) and a team of researchers at the University of Western Australia have developed a new and environmentally friendly extraction process that turns discarded lobster shells into a valuable manufacturing material.

Chitin (pronounced ky-tin) is a long-chain polymer that is found throughout nature. It forms the cell walls of fungi and the exoskeletons of arthropods, including lobsters. It is used in a number of different industrial processes, from pharmaceuticals, to a food additive, to manufacturing biodegradable plastics.

The new extraction process utilises a new, renewable, environmentally friendly solvent and utilises energy-efficient microwaves as a heat source. What was once discarded from kitchens could be the basis for a new, green, manufacturing industry in Western Australia.

FIGURE 12.1.14 This farmer from the Peel region is holding a lump of Alkaloam that was spread on his paddocks.

The fine-grained tailings residue produced after the carbonation process has found a use as a beneficial soil additive known as Alkaloam (Figure 12.1.14). Alkaloam provides a number of benefits to a typical sandy Perth soil, including raising the pH and increasing phosphate retention by up to 70%. It has been shown that Alkaloam is safe to use on grazing land used by livestock and it has found particular use in treating another environmental problem in the Peel–Harvey Estuary.

The Peel–Harvey Estuary has become eutrophic; that is, it experiences low oxygen levels due to rapid plant and algae growth resulting from increased nutrient concentrations in its waters (Figure 12.1.15). The surrounding Peel–Harvey catchment area contains a large horticultural industry that applies fertilisers to the soil as part of its operating procedure. Perth's sandy soils are typically very poor at retaining nutrients, particularly phosphates, which leach from the soils into the Peel–Harvey Estuary, contributing to the eutrophication problem. The application of Alkaloam to nearby farmland is seen as a viable method of preventing a large portion of the applied phosphate fertilisers from ending up in the estuary, thus reducing the eutrophication problem.

Eutrophication is the accelerated growth of plants and algae in water as a result of elevated nutrient levels.

FIGURE 12.1.15 Algal blooms form as a result of eutrophication.

The term 'waste' does not only apply to physical materials produced by the process; it also applies to energy liberated by reactions. The central reaction in the Haber process is exothermic; simply liberating the vast quantities of heat generated by this reaction into the air is another form of waste. The heat removed in condensing the ammonia produced at the end of the process is used to heat the feed gases of hydrogen and nitrogen. In this way, the heat energy is recycled, avoiding the need for the plant to use additional energy to generate more heat, saving both the environment and money.

EXTENSION

A green future for Western Australia

Two of the key chemical products in Western Australia are ammonia and sulfuric acid. These are economically important industries that other industries rely upon.

Ammonia is produced by the Haber process in the Pilbara. Sulfuric acid is produced by the contact process in Kalgoorlie. These two industries intersect at the CSBP fertiliser plant in Kwinana, where they are used to manufacture ammonium sulfate according to the reaction:

$$2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

You can compare the environmental impact and sustainability of the manufacture of the reagents used by each of these processes and suggest changes that could be made to each process through the application of green chemistry principles.

You could consider:

- the environmental impact of how the reagents are sourced, including wastes generated
- any existing examples of how green chemistry has been applied to the processes
- any possible alternative sources for the reagents and their comparable environmental impact
- the atom economy of the syntheses used.

12.1 Review

SUMMARY

- Green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.
- The philosophy of green chemistry is underpinned by 12 principles.
- The chemical method used to convert starting reagents to product is known as the synthesis of the product.
- Atom economy is a measure of the proportion of atoms from the reagents that end up in the desired product.
- The application of the principles of green chemistry should not have to come at significant economic cost.

KEY QUESTIONS

1. What is green chemistry?
2. How is green chemistry different from environmental chemistry?
3. What are some ways chemists can make a synthesis 'greener'?
4. Why is using renewable materials important?
5. Why would the new ibuprofen synthesis (shown in Figure 12.1.4) be as, if not more, profitable than the old one?
6. Why would water not be a suitable replacement for perchloroethylene as a dry-cleaning solvent?
7. What are the advantages of using glycine as a leaching agent over cyanide for metal extraction?
8. Suggest other ways to reduce the eutrophication in the Peel–Harvey Estuary.

Chapter review

12

KEY TERMS

green chemistry
renewable
sustainable
synthesis

Green chemistry

1 Which of the following is an aim of green chemistry?
- **A** Design chemical processes that maximise profits.
- **B** Design new chemicals.
- **C** Learn about the chemical processes that occur in the natural environment.
- **D** Design safer chemical products and processes and reduce or eliminate the generation of hazardous substances.

2 Which of the following is not a principle of green chemistry?
- **A** Use less energy.
- **B** Reduce the risk to people and the environment.
- **C** Avoid using artificial chemicals.
- **D** Prevent or reduce waste.

3 True or false? Under green chemistry philosophy, industries must sacrifice profits in order to become greener.

4 Considering the philosophy of green chemistry, which of the following alternatives is the best?
- **A** Turn your waste product into a profitable commodity.
- **B** Avoid any waste.
- **C** Dispose of waste responsibly.
- **D** Store waste in tailing ponds.

5 True or false? Organic farming is always an example of green chemistry.

6 What attributes would be required for an alternative chemical synthesis to be considered a 'green' synthesis?

7 Why could changing to a 'greener' chemical synthesis make good economic sense for a company?

8 Why is the use of catalysts integral to green chemistry?

9 How can using locally sourced resources reduce the environmental impact of an industrial process?

10 In many industries in the past, waste materials were simply incinerated. What possible environmental impacts would this have had?

11 How can you, as a student, ensure your laboratory experiments are 'green' experiments and reduce their environmental impact?

12 Use the MSDSs of carbon dioxide and perchloroethylene to compare the associated health risks of each.

CHAPTER

13 Structure of organic molecules

At the end of this chapter, you will appreciate the significance of the compounds that are formed between carbon, hydrogen and other elements, such as oxygen and nitrogen. Carbon is only the eleventh most abundant element in the universe, yet it forms more compounds than all other elements except hydrogen.

The prevalence of carbon in living things is why the study of the compounds of carbon and hydrogen is known as organic chemistry. You make use of these compounds in so many aspects of your life: from the polymer case of your phone to the pasta that you may eat for dinner.

In this chapter you will start to explore some of the many families of carbon compounds. You will investigate the properties of these compounds and how they are named and identified.

Science understanding

- organic molecules have a hydrocarbon skeleton and can contain functional groups, including alkenes, alcohols, aldehydes, ketones, carboxylic acids, esters, amines and amides; functional groups are groups of atoms or bonds within molecules which are responsible for the molecule's characteristic chemical properties
- structural formulae (condensed or showing bonds) can be used to show the arrangement of atoms and bonding in organic molecules that contain the following functional groups: alkenes, alcohols, aldehydes, ketones, carboxylic acids, esters, amines and amides
- IUPAC nomenclature is used to name organic species, including those with a parent chain of up to 8 carbon atoms with simple branching and one of the following functional groups: alkenes, alcohols, aldehydes, ketones, carboxylic acids, esters, amines and amides
- isomers are compounds with the same molecular formulae but different structures; different types of isomerism include chain and position structural isomerism and *cis–trans* isomerism
- organic compounds display characteristic physical properties, including boiling point and solubility in water and organic solvents; these properties 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
- empirical and molecular formulae can be determined by calculation and the structure of an organic compound established from the chemical reactions they undergo, and other analytical data

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13.1 Diversity of carbon compounds

Carbon forms more compounds than all other elements combined. This is because:

- carbon has four valence electrons, so it can potentially form covalent bonds with four other atoms
- carbon atoms can form strong covalent bonds with other carbon atoms, partly due to the relatively small size of the carbon atom
- covalent bonds formed by carbon atoms can be single, double or triple bonds.

Because of this, carbon can bond to itself to form molecules of varied length and shape. The different structures have different properties and applications.

Carbon-based molecules are all around you. Caffeine, petrol, pesticides, plastics and artificial flavours are all carbon-based compounds. Many of these compounds are produced from **crude oil**. Crude oil is formed over millions of years by the effects of heat and pressure on dead animals, plants and microorganisms trapped in the Earth's crust, buried beneath sediment. The study of the chemistry of carbon compounds is known as organic chemistry.

HYDROCARBONS

The simplest **organic molecules** are the **hydrocarbons**. Although hydrocarbons only contain the elements carbon and hydrogen, the different ways their atoms can be arranged to form molecules results in an enormous diversity of compounds. As you learnt in Year 11, hydrocarbon families can be simplified by grouping the millions of different molecules that exist into families called **homologous series**.

Compounds that are members of the same homologous series have:

- similar structures
- similar chemical properties
- the same general formula
- a pattern to their physical properties.

Homologous series contain members that have increasingly longer chains. The chains grow by the addition of a $-CH_2-$ unit to the previous member of the series. The hydrocarbons consist of three homologous series: the alkanes, the alkenes and the alkynes. Alkynes are not covered in this course and will not be discussed in detail.

The concept of homologous series can be applied to other types of organic molecules encountered later in this chapter.

Alkanes and alkenes are the most common hydrocarbon homologous series. The chains grow by the addition of a $-CH_2-$ unit.

ALKANES

Hydrocarbons can be classified into several groups or series. Methane is the first of a series of compounds known as the **alkanes**. Alkanes are hydrocarbons that contain only single bonds. All the carbon–carbon bonds in alkanes are single covalent bonds. Molecules such as this are said to be **saturated**.

Each member of the alkane series differs from the previous member by a $-CH_2-$ unit. You will recall that a series of molecules in which each member differs by $-CH_2-$ from the previous member is known as a homologous series.

CHEMISTRY IN ACTION

The diverse uses of hydrocarbons

The simplest homologous series is the alkanes. Alkanes are a homologous series of molecules that consist entirely of hydrogen and carbon atoms. Figure 13.1.1 shows methane, the simplest hydrocarbon. Methane is the gas used in most laboratory Bunsen burners. Propane (Figure 13.1.2) also belongs the alkane homologous series. Like methane, propane is a commonly used fuel contained in portable gas bottles. Alkenes such as ethene (Figure 13.1.3) contain a carbon-to-carbon double bond. Ethene is commonly used to make polymers that are found in many household plastics. Some hydrocarbons can also form ring structures, like those shown in Figures 13.1.4 and 13.1.5. These rings may form from single carbon-to-carbon bonds or even double bonds like those shown in benzene in Figure 13.1.5.

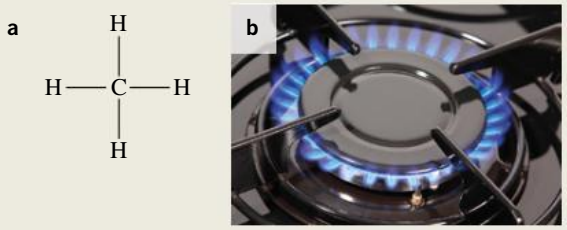


FIGURE 13.1.1 (a) Methane (CH_4) contains one carbon atom with four single covalent bonds to four hydrogen atoms. (b) Methane is the gas used in most laboratory Bunsen burners and household gas stoves.

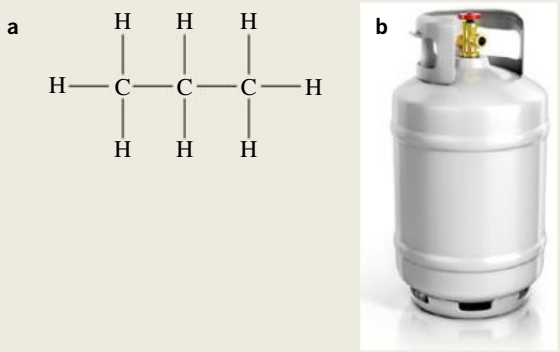


FIGURE 13.1.2 (a) Propane (C_3H_8) contains only single bonds. (b) Propane is the fuel contained in many portable gas bottles.

FIGURE 13.1.3 (a) Carbon can form compounds that contain carbon–carbon double bonds. These compounds include ethene (C_2H_4). (b) Among other uses, ethene is used to make the polymers in these food storage containers.

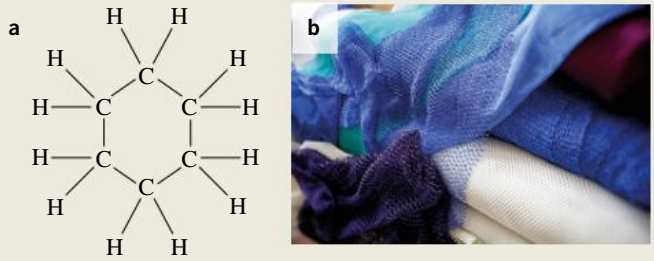


FIGURE 13.1.4 (a) Hydrocarbons can form ring structures with single bonds, such as cyclohexane (C_6H_{12}). (b) Cyclohexane is used by industry to make the starting materials for the manufacture of nylon.

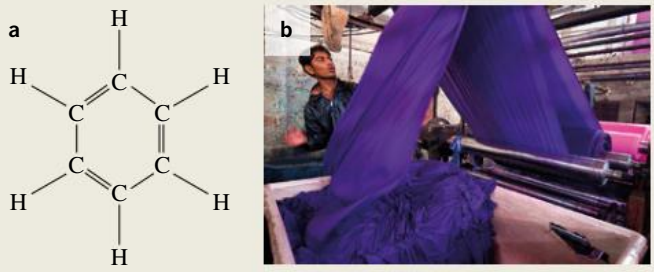
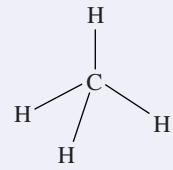
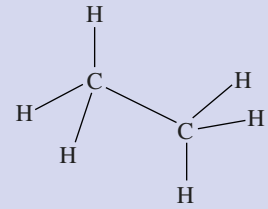
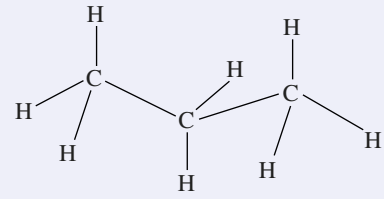


FIGURE 13.1.5 (a) Some molecules containing rings are unsaturated, such as benzene (C_6H_6), which is found in crude oil. (b) In this image, fabric is dyed using a dye based on benzene.

Table 13.1.1 shows the first three members of the alkane series. Note that the bonds around each carbon atom adopt a tetrahedral shape and the boiling points increase as the molecules become larger.

TABLE 13.1.1 Structure, properties and some uses of the first three alkanes

Name and molecular formula	Structural formula	Properties	Uses
Methane, CH_4		Non-polar, gas, boiling point (BP) –164°C	Cooking, Bunsen burners, gas heating
Ethane, C_2H_6		Non-polar, gas, BP –87°C	Conversion to ethene
Propane, C_3H_8		Non-polar, gas, BP –42°C	Liquid petroleum gas (LPG)

REPRESENTING ORGANIC MOLECULES

Before exploring organic molecules further, you should revise the different ways that the formulae of molecules can be represented. The formulae used in this course are:

- molecular formulae
- structural formulae
- condensed (or semistructural) formulae.

Molecular formulae

Molecular formulae, such as C_2H_6O and $C_4H_8O_2$, indicate the number and type of atoms of each element present in a molecule. However, they do not indicate how the atoms are arranged.

Structural formulae

Structural formulae show the spatial location of atoms relative to one another in a molecule, as well as the number and location of covalent bonds. Non-bonding electrons (lone pairs) are generally not shown.

As you learnt in Year 11, when four single bonds are formed around a carbon atom, the pairs of electrons in each bond act as a negatively charged cloud. **Valence shell electron pair repulsion (VSEPR) theory** tells you that these electron pairs repel each other so the bonds are as far apart as possible, at an angle to each other of nearly 109.5°. The structure of methane, shown in Figure 13.1.6, is described as a **tetrahedral** shape because the four single bonds are pointing to the corners of a tetrahedron (shown in red).

Molecules consisting of long chains of carbon atoms joined by single bonds are often referred to as 'straight-chain' molecules. However, because of the tetrahedral distribution of each carbon's bonds, the chain actually has a zig-zag shape. Structural formulae showing a tetrahedral arrangement of bonds can become

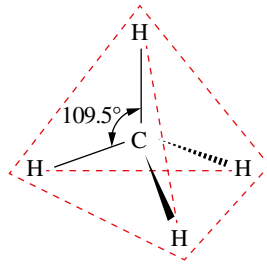


FIGURE 13.1.6 The structure of a molecule of methane (CH_4) showing the tetrahedral geometry. The solid wedge represents a bond coming out of the page, whereas the dashed wedge represents a bond going into the page.

complicated and difficult to interpret. To make the structure of these molecules clearer, the bonds are often drawn at right angles. These two representations are shown in Figure 13.1.7.

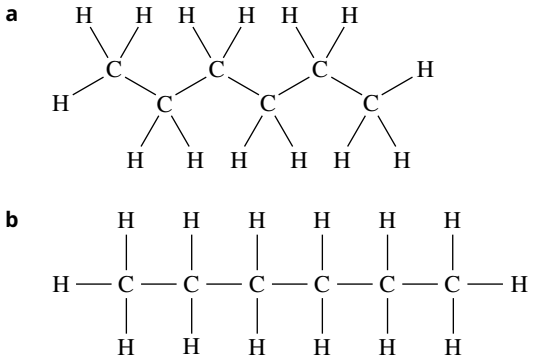


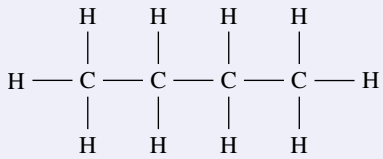
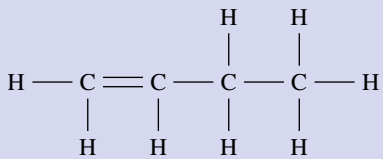
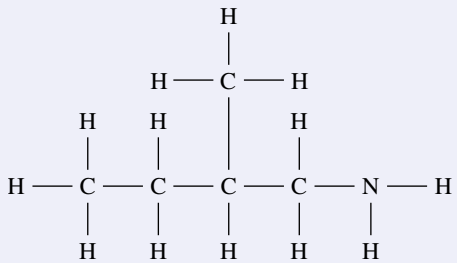
FIGURE 13.1.7 (a) The six carbon chain of hexane (C_6H_{14}). There is a tetrahedral arrangement of bonds around each carbon atom. (b) The chain can be drawn in a straight line for convenience.

Condensed formulae

A **condensed formula** is used to indicate the connections in the structure of a compound without showing the three-dimensional arrangement of atoms. The term **semistructural formula** is also used to describe this type of formula.

In a condensed formula, the carbon chain is represented on one line of text. The carbon atoms in the chain, and all the atoms attached to each of them, are listed in the order that they appear in the structural formula. Single bonds are not shown, but double carbon–carbon bonds are often shown. Groups of atoms that form branches in a molecule are written in brackets after the carbon atom to which they are attached. Some examples of structural, condensed and molecular formulae are shown in Table 13.1.2.

TABLE 13.1.2 Examples of structural, condensed and molecular formulae

Structural formula and name	Condensed (semistructural) formula	Molecular formula
 Butane	$CH_3CH_2CH_2CH_3$	C_4H_{10}
 But-1-ene	$CH_2{=}CHCH_2CH_3$	C_4H_8
 2-Methylbutan-1-amine	$CH_3CH_2CH(CH_3)CH_2NH_2$	$C_5H_{13}N$

NAMING ORGANIC MOLECULES

As you learnt in Year 11, the IUPAC (International Union of Pure and Applied Chemists) system is used to name organic molecules. In Year 12, you will be using this system to name a range of molecules, including **isomers** (molecules that have the same molecular formula but a different arrangement of atoms), from different homologous series of organic substances. The following section revises some of the naming techniques that you used in Year 11.

The **stem names** used for molecules with between one and eight carbon atoms are listed in Table 13.1.3.

TABLE 13.1.3 Stem names used for molecules with between one and eight carbon atoms

Stem (parent) name	Number of carbon atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8

Naming alkanes

The systematic naming of carbon compounds is controlled by IUPAC. Under the IUPAC system, the name of the compound provides details of its structure. The following rules apply when naming alkanes.

1 Identify the longest unbranched carbon chain.
2 Number the carbon atoms in the chain from the end of the chain that will give the smallest numbers to branching groups.
3 Name the alkyl groups after the alkane from which they are derived.
4 Place the number and position of each of the alkyl groups at the beginning of the compound's name.
5 If two identical side chains are present, use 'di-' as a prefix; for three, use 'tri-'.
6 If there is more than one type of alkyl side chain on the molecule, list them in alphabetical order at the start of the name, with their numbers to indicate their respective positions.

Carefully check that you have identified the longest unbranched carbon chain. Sometimes the longest carbon chain is not drawn in a straight line.

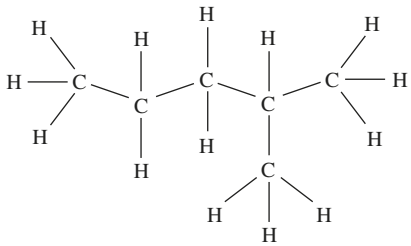
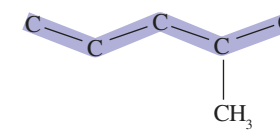


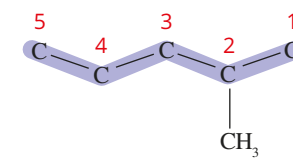
FIGURE 13.1.8 The IUPAC system will be used to name this isomer of hexane.

The following steps show the process of naming the isomer of hexane shown in Figure 13.1.8.

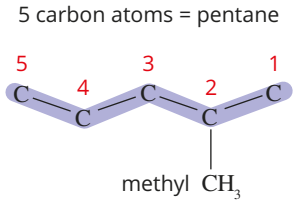
1 Identify the longest unbranched carbon chain.



2 Number the carbons, starting from the end closest to the branch.



3 Name the side branches and main chain.



4 Combine all components to write the full name: 2-methylpentane

Figure 13.1.9 shows examples where these rules have been applied. Note the use of the prefix 'di-' to indicate the presence of two methyl side branches and the numbering to indicate their position along the longest continuous carbon chain (for example, 3,3-indicates that both side branches are attached to the third carbon atom).

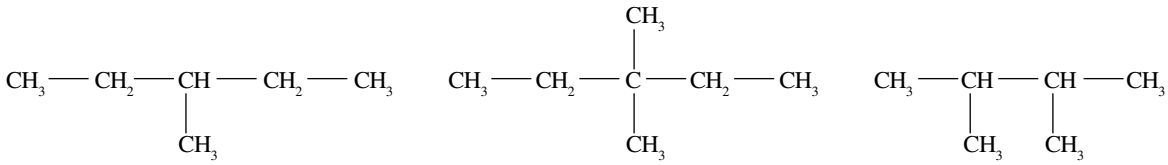


FIGURE 13.1.9 IUPAC systematic names for three alkanes. Note that there are no spaces in the names of these compounds.

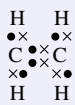
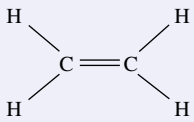
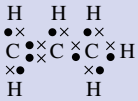
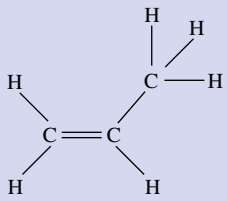
ALKENES

Alkenes are unsaturated hydrocarbons and contain at least one double carbon–carbon bond, so must contain two or more carbon atoms.

Writing formulae of alkenes

As with alkanes, there are a variety of ways for writing the formulae of alkenes. Table 13.1.4 shows different ways of representing ethene and propene.

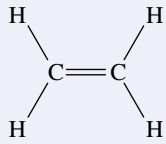
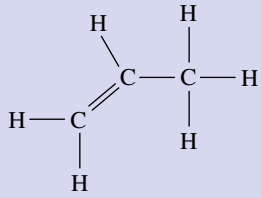
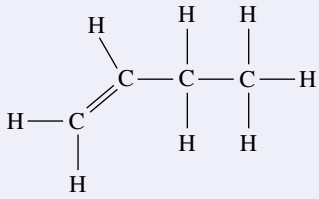
TABLE 13.1.4 Different ways of representing alkenes

Alkene	Molecular formula	Electron dot diagram (Lewis structure)	Condensed structural formula	Structural formula
Ethene	C_2H_4		CH_2CH_2	
Propene	C_3H_6		CH_2CHCH_3	

The molecular, structural and condensed formulae of the first three members of the homologous series of alkenes are shown in Table 13.1.5. You can see that successive members differ by a $-CH_2-$ unit. Alkenes have the general formula C_nH_{2n}.

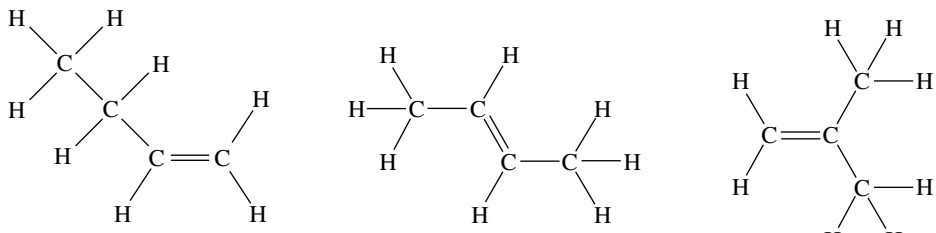
Alkenes with four or more carbon atoms can have **structural isomers**, where the location of the double bond changes, as well as ***cis–trans* isomers**, where the geometry of groups around the double bond changes.

TABLE 13.1.5 Formulae of the first three members of the alkene homologous series

Name	Molecular formula	Structural formula	Condensed structural formula
Ethene	C_2H_4		$CH_2=CH_2$
Propene	C_3H_6		$CH_2=CHCH_3$
But-1-ene	C_4H_8		$CH_2=CHCH_2CH_3$

Structural isomers of alkenes

For alkene molecules that contain more than three carbon atoms, structural isomers will exist. As you can see in Figure 13.1.10, isomers may result from branches in the carbon chain, or if the carbon–carbon double bond is in different positions.



but–1–ene but–2–ene methylpropene

FIGURE 13.1.10 Isomers of butene. Isomers of alkenes can have branches in the carbon chain or the double bond at different points in the carbon chain.

When naming alkene isomers, the carbons are numbered from the end of the carbon chain that gives the lowest number to the first carbon in the double bond. The location of the double bond in the molecule is indicated by this number. In Figure 13.1.10, you can see that the double bond in but-1-ene is between carbons 1 and 2. The double bond in but-2-ene is between carbons 2 and 3.

Naming alkenes

The rules for naming alkenes follow the rules used for alkanes. In addition, the following conventions are applied.

- Use the ending '-ene' 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'.
- Indicate *cis* and *trans* isomers by writing '*cis*-' or '*trans*-' in front of the compound's name.

The flowchart in Figure 13.1.11 shows the steps involved in naming an alkene.

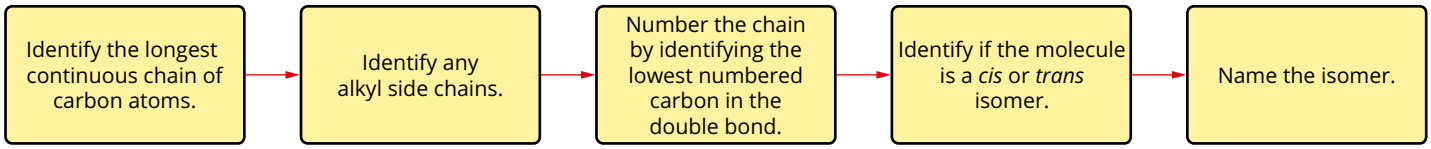
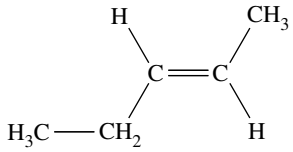


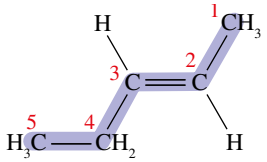
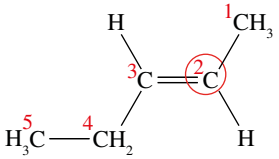
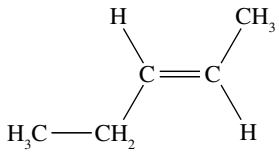
FIGURE 13.1.11 The steps used to name alkenes

Worked example 13.1.1

NAMING A *cis–trans* ISOMER OF AN ALKENE

Write the systematic name of the following alkene.

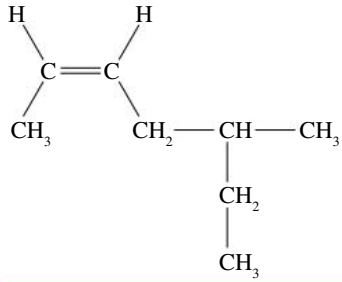


Thinking	Working
Identify the parent name by counting the longest continuous chain of carbon atoms that contains the carbon–carbon double bond.	 There are five carbon atoms in the longest continuous chain, so the parent name is pentene.
Identify any alkyl side chains by counting the number of carbon atoms in any branches.	There are no alkyl side chains.
Number the continuous chain from the end closest to the double bond and identify the lowest numbered carbon atom in the double bond.	 The lowest numbered carbon atom in the double bond is 2, so the parent name becomes pent-2-ene.
Number any alkyl side chains using the numbers of the carbon atoms to which they are attached.	There are no alkyl side chains.
Identify whether the molecule is a *cis* or *trans* isomer.	 Both of the carbons in the double bond are attached to a hydrogen atom and another carbon in the chain. The carbon atoms are on opposite sides of the double bond so this is a *trans* isomer.
Name the isomer.	The name of the isomer is *trans*-pent-2-ene.

Worked example: Try yourself 13.1.1

NAMING A *cis–trans* ISOMER OF AN ALKENE

Write the systematic name of the following alkene.



BENZENE RINGS

In 1825, Michael Faraday isolated a new hydrocarbon, named benzene (C_6H_6). The structure and properties of benzene puzzled scientists for 40 years. It is now known that benzene has a ring structure, but it does not have alternating double and single bonds (Figure 13.1.12).

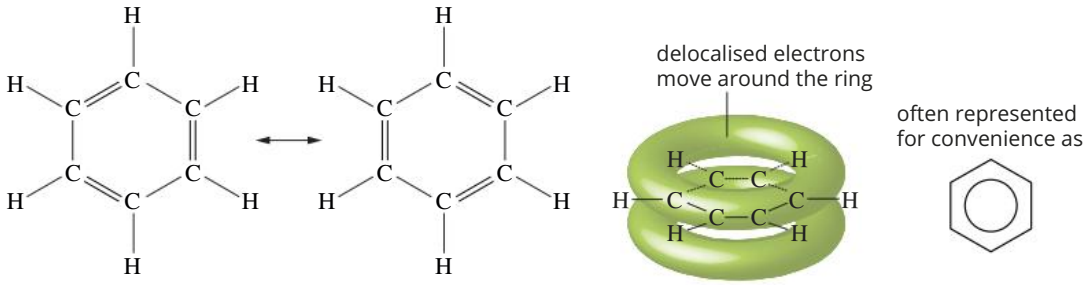


FIGURE 13.1.12 Representations of benzene. All six carbon atoms and six hydrogen atoms in the benzene molecule are in the same plane. There are no double bonds in benzene: the electrons are delocalised.

The electrons that make up the double bonds are not in fixed positions; they are delocalised and can move around the ring. Each carbon–carbon bond is the same length and the molecule is more stable than you would expect an unsaturated molecule to be.

In Year 11, you saw that benzene is a substance that can exist on its own. Benzene rings can also exist within more complex molecules, or as a side group on a molecule. In this context, the benzene ring is called a phenyl group, and later in this chapter you will encounter substances, such as phenylamine (used as an artificial sweetener in drinks), that contain benzene rings.

13.1 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 the same general formula. Alkanes are an example of a homologous series.
- Alkanes are saturated hydrocarbon molecules that contain only single bonds and have a general formula C_nH_{2n+2}.
- Structural isomers are molecules with the same molecular formula but different arrangements of atoms.
- Hydrocarbon molecules can be drawn using structural formulae or condensed structural formulae.
- The IUPAC naming system is used to provide systematic names for hydrocarbon molecules. Names are based on the longest unbranched carbon chain.
- Alkenes are a homologous series of hydrocarbons that contain a carbon–carbon double bond.
- Alkenes have the general formula C_nH_{2n}.
- Alkenes can have both structural and *cis–trans* isomers.

KEY QUESTIONS

1 From which one or more of the following sources does crude oil originate?

A plant material
B forest animals that have recently died
C dinosaurs only
D marine microorganisms

2 Methane is the smallest hydrocarbon molecule.

a What is the molecular formula of methane?
b Why is methane a hydrocarbon?
c Why does the carbon atom in a methane molecule bond to four, rather than two, three, five or any other number of hydrogen atoms?
d Draw the structural formula of methane. Why does methane have this particular arrangement of hydrogen atoms around each carbon atom?

3 Answer the following questions relating to the hydrocarbon with the molecular formula C_3H_8.

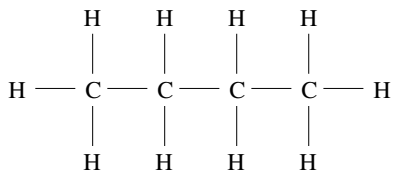
a What is the name of this hydrocarbon?
b Write a balanced chemical equation for the complete combustion of this hydrocarbon. This hydrocarbon exists as a gas at room temperature.
c Draw the structural formula of this hydrocarbon.
d Write the condensed structural formula of this hydrocarbon.

4 Write the systematic names of these alkanes based on their condensed structural formulae.

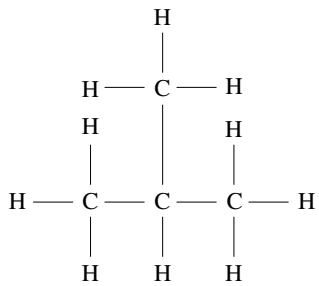
a $CH_3CH_2CH_2CH_3$
b $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
c $CH_3CH_2CH_2CH(CH_3)_2$
d $CH_3CH(CH_3)CH_2CH_3$
e $CH_3CH(CH_3)CH_2CH(CH_3)_2$

5 Write the systematic names of the alkanes shown here based on their structural formulae.

a

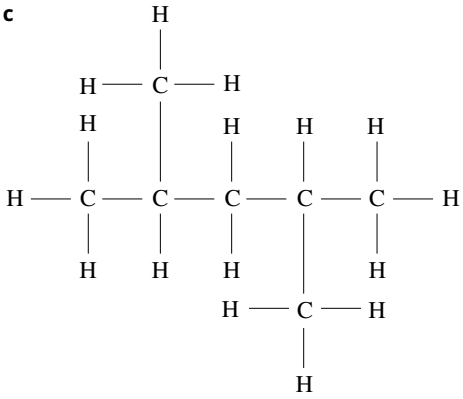


b

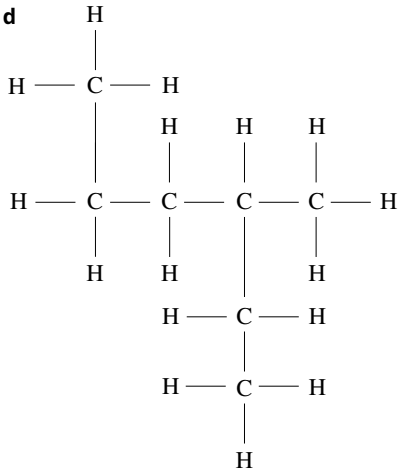


13.1 Review *continued*

c



d

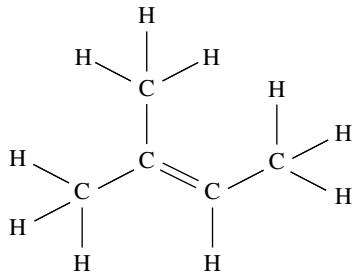


6 Draw the structural formulae of these alkanes based on their systematic names.

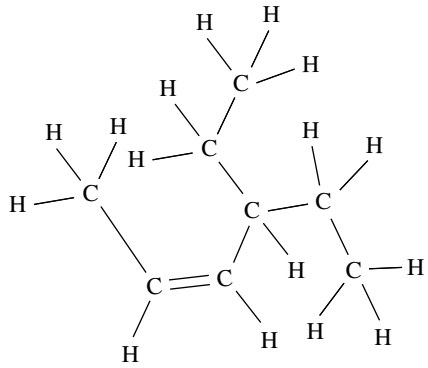
a hexane
b 3-methylhexane
c 3,3-dimethylpentane
d 3-ethyl-2-methylpentane

7 Name the following molecules.

a



b



8 Draw the structure of 2,3-dimethylpent-2-ene.

13.2 Functional groups

Most organic compounds can be regarded as derivatives of hydrocarbons that have one or more hydrogen atoms replaced by other atoms or groups of atoms called a **functional group**.

The presence of a particular functional group in a molecule gives a substance certain physical and chemical properties. For example, vinegar and wine (Figure 13.2.1) 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.

FIGURE 13.2.1 (a) Vinegar and (b) wine contain molecules with two carbon atoms. Vinegar contains ethanoic (acetic) acid with a carboxyl functional group and wine contains ethanol with a hydroxyl group.

In this section, you will explore these homologous series:

- alcohols
- primary amines
- carboxylic acids
- primary amides
- esters
- aldehydes
- ketones.

You will learn about the functional groups in each of these families of molecules, as well as how to name them.

ALCOHOLS

Ethanol is a member of the homologous series of alcohols. **Alcohols** contain a **hydroxyl** (–OH) **functional group** attached to a saturated carbon atom. A representation of the hydroxyl group is shown in Figure 13.2.2.

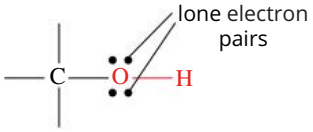


FIGURE 13.2.2 Alcohols contain the hydroxyl functional group –OH (in red above). There are two pairs of non-bonding electrons on the oxygen atom.

Figure 13.2.3 shows the structural and condensed formulae of three alcohols. You can think of the hydroxyl group as taking the place of a hydrogen atom in an alkane.

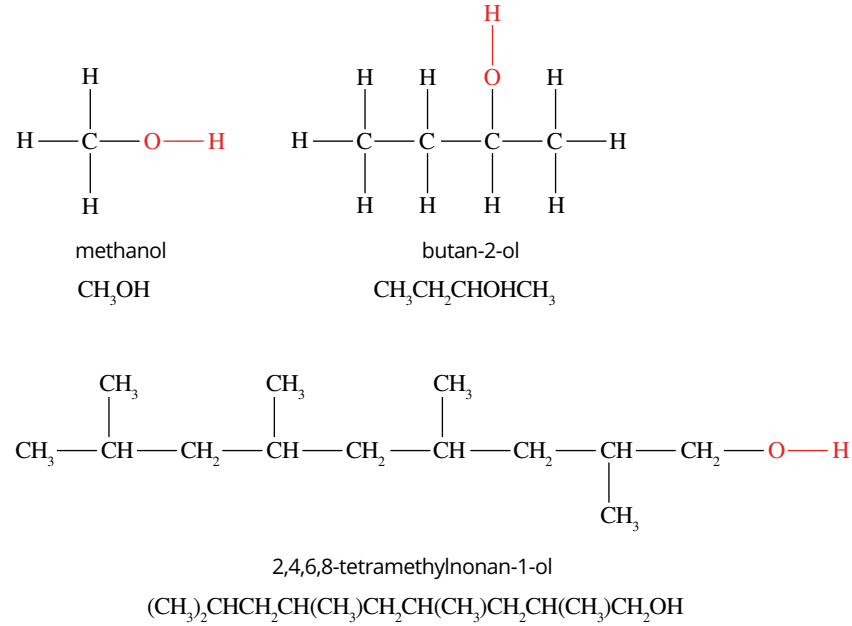


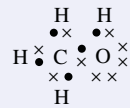
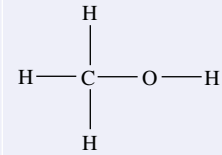
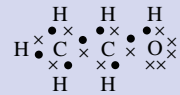
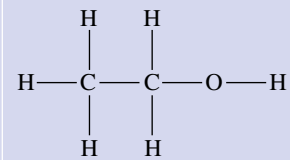
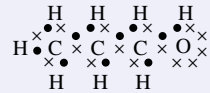
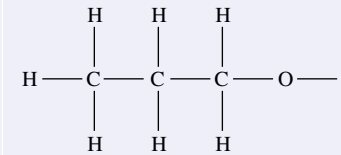
FIGURE 13.2.3 Structural and condensed formulae of three alcohols. Each contains the hydroxyl functional group (shown in red). Note that the non-bonding electron pairs on the oxygen atom are often omitted in structural formulae.

Formulae and structure of alcohols

The functional group in alcohols is made up of an oxygen atom bonded to a hydrogen atom. This –OH group is known as a hydroxyl group and replaces one hydrogen in the structure of an alkane. Successive members of this homologous series differ by a $–CH_2–$ unit.

When naming alcohols, a similar systematic naming process to the one used for alkanes and alkenes applies. The number of carbon atoms in the molecule is indicated by the stem name, e.g. meth-, eth-, prop-, but-. However, the suffix (ending) of the name of an alcohol is always '-ol'. Table 13.2.1 shows different ways to represent alcohols.

TABLE 13.2.1 The first three members of the homologous series of alcohols

Alcohol	Molecular formula	Electron dot formula (Lewis structure)	Structural formula	Condensed structural formula
Methanol	CH_3OH			CH_3OH
Ethanol	C_2H_5OH			CH_3CH_2OH
Propanol	C_3H_7OH			$CH_3CH_2CH_2OH$

Structural isomers of alcohols

The position of the hydroxyl (–OH) functional group influences the chemical and physical properties of alcohols. Alcohols with more than two carbon atoms have more than one position where the hydroxyl functional group may be found. For example, the hydroxyl group in propanol (C_3H_7OH) can be bonded to the first or the second carbon atom. This gives two different molecules: $CH_3CH_2CH_2OH$ and $CH_3CH(OH)CH_3$. The name of the alcohol must reflect the structure of the molecule, so a system of nomenclature is used.

Naming alcohols

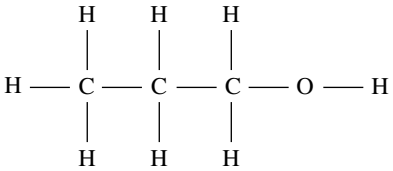
You can determine the name of an alcohol as follows.

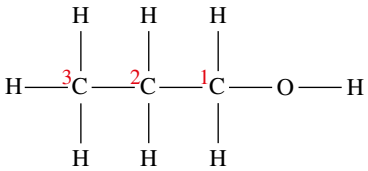
- Start with the name of the parent alkane, remove the 'e' from the end and add the suffix '-ol'.
- Number the atoms in the longest carbon chain from the end that is closest to the –OH functional group.
- Indicate the number of the atom that the hydroxyl group is bonded to before the -ol ending and separate it by hyphens.

Worked example 13.2.1

IUPAC NAMING SYSTEM FOR ALCOHOLS

Write the systematic name for the following molecule.

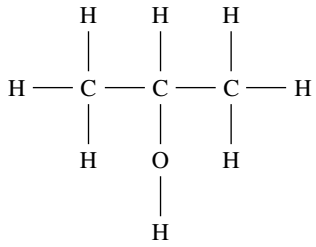


Thinking	Working
Identify the longest carbon chain in the molecule. The name of the molecule is based on this longest chain.	There are three carbons in the longest chain. The name is based on propane.
Identify the functional group that is present.	There is a hydroxyl group present.
Number the carbon atoms, starting from the end closest to the functional group.	
Identify the position(s) and type(s) of branches.	There are no branches in this molecule.
Combine all components. Place the number for the position of the branch 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 propan-1-ol.

Worked example: Try yourself 13.2.1

IUPAC NAMING SYSTEM FOR ALCOHOLS

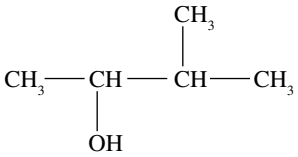
Write the systematic name for the following molecule.

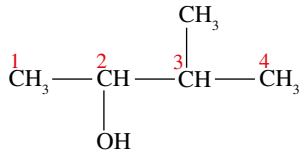


Worked example 13.2.2

IUPAC NAMING SYSTEM FOR ALCOHOLS

Write the systematic name for the following molecule.

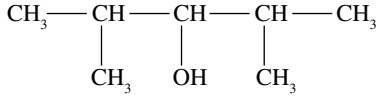


Thinking	Working
Identify the longest carbon chain in the molecule. The name of the molecule is based on this longest chain.	There are four carbons in the longest chain. The name is based on butane.
Identify the functional group that is present.	There is a hydroxyl group present.
Number the carbon atoms, starting from the end closest to the functional group.	
Identify the position(s) and the type(s) of branches.	There is a methyl ($-CH_3$) group bonded to carbon C3 so the prefix 'methyl' is used.
Combine all components. Place the number for the position of the branch 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.

Worked example: Try yourself 13.2.2

IUPAC NAMING SYSTEM FOR ALCOHOLS

Write the systematic name for the following molecule.



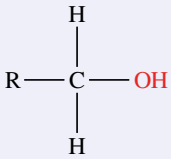
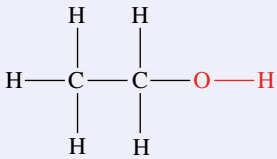
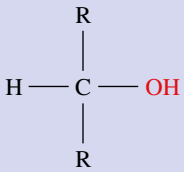
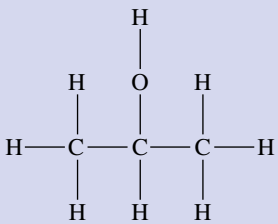
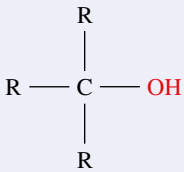
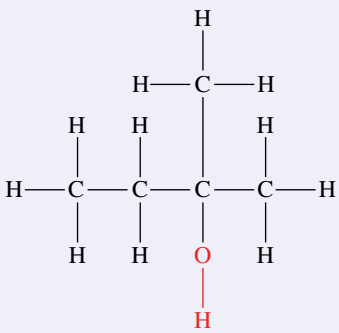
Types of alcohols

Alcohols are classified according to the number of alkyl groups attached to the carbon atom that is 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 13.2.2. Alkyl groups are represented by the general symbol R.

TABLE 13.2.2 The three different types of alcohols. The hydroxyl group is shown in red

Type of alcohol	Definition	General formula	Example
Primary	The carbon bonded to the –OH group is only bonded to one alkyl group.		
Secondary	The carbon 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.		

PRIMARY AMINES

Amines are a homologous series of organic compounds that contain the amino functional group. An amino functional group consists of one nitrogen atom covalently bonded to two hydrogen atoms, as shown in Figure 13.2.4.

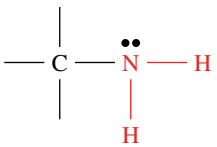
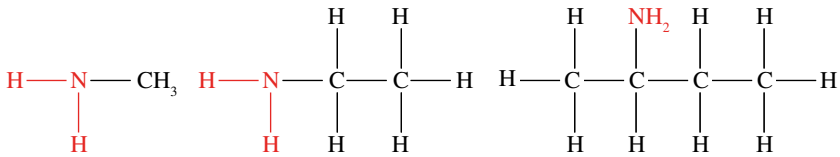


FIGURE 13.2.4 Primary amines contain the amino functional group $-NH_2$ (in red). There are two non-bonding electrons on the nitrogen atom.

Amino functional groups with two hydrogens and one alkyl group are called **primary amines**. Unlike alcohols, 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 course. Some primary amines are shown in Figure 13.2.5.



methanamine
CH_3NH_2

ethanamine
$CH_3CH_2NH_2$

butan-2-amine
$CH_3CHNH_2CH_2CH_3$

FIGURE 13.2.5 Structural and condensed structural formulae of three primary amines. The amino functional group is shown in red. Primary amines have one carbon atom bonded to the nitrogen atom.

CHEMFILE

Amines, chocolate and happiness!

An active ingredient in chocolate (Figure 13.2.6) is the primary amine 2-phenylethanamine.

2-Phenylethanamine is also produced in the pleasure centres of the brain and has the effect of generating a general sense of wellbeing or happiness, as well as temporarily raising blood pressure and blood glucose levels.

Eating chocolate provides you with a boost of 2-phenylethanamine, so the reason that eating chocolate might make you feel happy is partly due to organic chemistry!

FIGURE 13.2.6 Chocolate contains an amine that makes people feel happy.

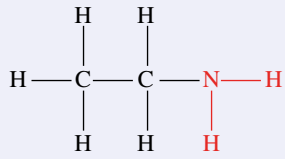
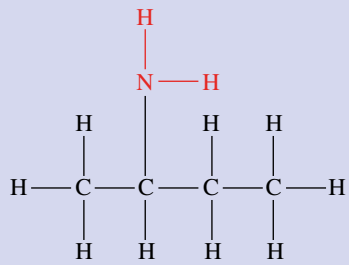
Naming amines

Amines are named in a similar way to alcohols. You can determine the name of an amine as follows.

- Replace the '-e' at the end of the parent alkane's name with the suffix '-amine'.
- If structural isomers are possible, insert a number before '-amine' to indicate the carbon to which the amino functional group is attached.

Table 13.2.3 shows two examples of naming amines.

TABLE 13.2.3 Examples of naming amines

Name	Condensed formula	Structural formula
Ethanamine	$CH_3CH_2NH_2$	
Butan-2-amine	$CH_3CHNH_2CH_2CH_3$	

CARBOXYLIC ACIDS

Formulae and structure of carboxylic acids

Carboxylic acids are a homologous series that contain the carboxyl functional group (Figure 13.2.7). In this functional group, a carbon atom has a double bond to one oxygen atom and a single bond to a second oxygen atom. This second oxygen atom is also bonded to a hydrogen atom. This –COOH group can be regarded as replacing one hydrogen in the structure of an alkane. The bonds around the carbon atom have a trigonal planar arrangement with the O–C–O angle being about 120°, as shown in Figure 13.2.8.

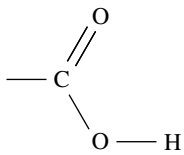


FIGURE 13.2.7 Structure of the carboxyl functional group

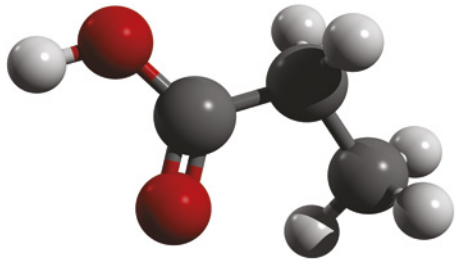


FIGURE 13.2.8 A carboxylic acid has a tetrahedral arrangement of atoms in the hydrocarbon part of the molecule, but there is a trigonal planar arrangement of atoms in the carboxyl functional group.

The **carboxyl functional group** is represented in a condensed formula as –COOH and is always located at one end of a hydrocarbon chain. Figure 13.2.9 shows the structural and condensed formulae of three carboxylic acids.

Naming carboxylic acids

The prefixes that are used to indicate the number of carbon atoms in alkanes are also used with carboxylic acids. You can determine the name of a carboxylic acid as follows.

- Use the suffix '-oic acid'.
- Count the carbons in the functional group in the chain used to name the carboxylic acid. For example, C_2H_5COOH has three carbons and is called propanoic acid.
- Always number the carboxyl carbon as number 1.

The general formula of a carboxylic acid is often represented as RCOOH, where R is an alkyl group, such as $–CH_3$ and $–C_2H_5$. The first three members of the carboxylic acid homologous series are listed in Table 13.2.4. Successive members of the series differ by a $–CH_2–$ unit.

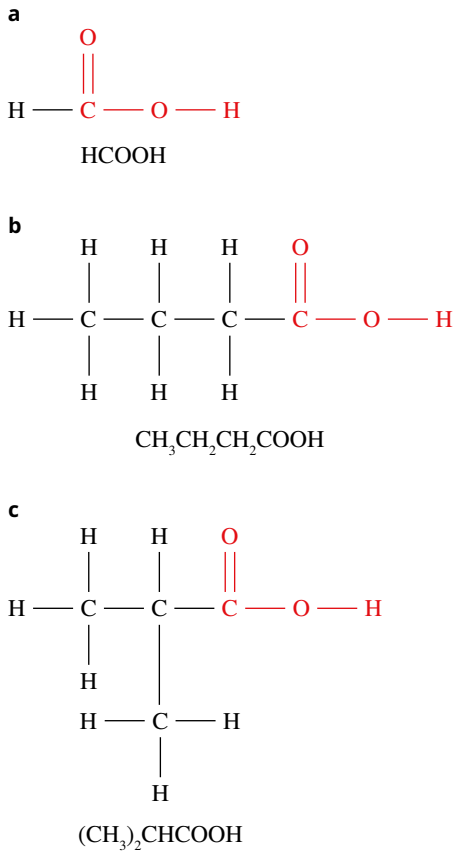
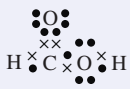
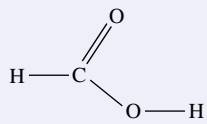
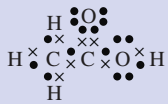
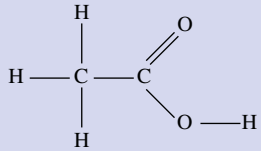
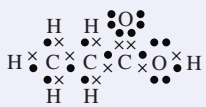
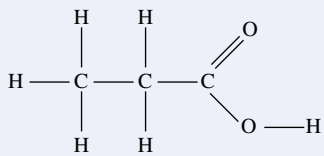


FIGURE 13.2.9 Structural and condensed structural formulae of three carboxylic acids. The carboxyl functional group is shown in red. Note that molecules (b) and (c) are isomers with the molecular formula $C_4H_8O_2$.

TABLE 13.2.4 The first three members of the homologous series of carboxylic acids

Name	Molecular formula	Electron dot formula (Lewis structure)	Structural formula	Condensed structural formula
Methanoic acid	HCOOH			HCOOH
Ethanoic acid	CH_3COOH			CH_3COOH
Propanoic acid	C_2H_5COOH			CH_3CH_2COOH

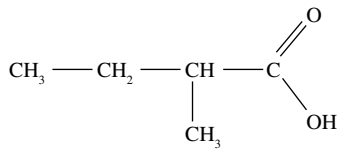
Structural isomers of carboxylic acids

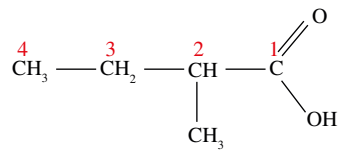
The carboxyl group can only occur on the end of a molecule because the carbon atom in the carboxyl group has a double bond to one oxygen and a single bond to another oxygen. Carboxylic acids can form isomers with different branches, but the carbon atom in the carboxyl group is always carbon number 1.

Worked example 13.2.3

IUPAC NAMING SYSTEM FOR CARBOXYLIC ACIDS

Write the systematic name for the following molecule.

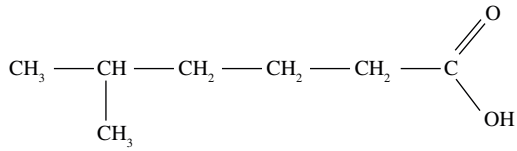


Thinking	Working
Identify the functional group that is present.	There is a carboxyl group present.
Identify the longest carbon chain that includes the carboxyl carbon. This atom will be C1. The stem name of the molecule is based on this longest chain.	There are four carbons in the longest chain, so the stem name is based on butane.
Number the carbon atoms, starting from the end incorporating the functional group.	
Identify the position(s) and the type(s) of branches.	There is a methyl group on C2.
Combine all components. Place the number for the position of the branch in front of the prefix and use the ending -oic acid.	The name of the molecule is 2-methylbutanoic acid.

Worked example: Try yourself 13.2.3

IUPAC NAMING SYSTEM FOR CARBOXYLIC ACIDS

Write the systematic name for the following molecule.



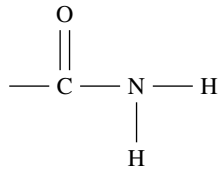


FIGURE 13.2.10 Structure of the amide functional group in a primary amide.

PRIMARY 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 $–NH_2$ (Figure 13.2.10).

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 formula as

–$CONH_2$ and is always located at one end of a hydrocarbon chain. The structural and condensed structural formulae of three primary amides are shown in Figure 13.2.11.

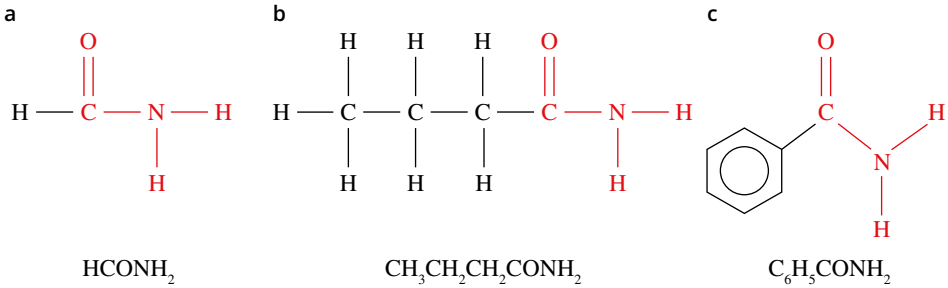


FIGURE 13.2.11 Structural and condensed structural formulae of three amides, with the amide functional group shown in red.

Naming amides

You can determine the name of an amide as follows.

- Identify the length of the parent chain.
- Given the amide group in primary amides is found at one end of the chain, number this carbon as carbon 1.
- Use the prefix for the parent name and add the suffix 'amide' to represent this functional group.

For example, in Figure 13.2.11a, the carbon chain is made up of only one carbon and therefore given the prefix meth-. It has only single bonds so the name of this molecule is methanamide. Figure 13.2.11b is called butanamide because it is made up of four carbons and the amide functional group.

CHEMFILE

Urea and organic chemistry

The amide urea ($(NH_2)_2CO$) is the end product of the breakdown of proteins by mammals and is excreted in urine. This naturally produced urea can be used as a source of nitrogen to promote plant growth (see Figure 13.2.12).

FIGURE 13.2.12 Urea is used commercially in fertiliser.

Friedrich Wöhler, a German chemist, synthesised urea in his laboratory in 1828 by treating silver cyanate with ammonium chloride. In a letter to a colleague, Wöhler excitedly wrote: 'I must tell you that I can make urea without the use of kidneys, either man or dog'.

Wöhler's synthesis of urea was remarkable because it was the first time someone had made an organic molecule. This discovery established the field of synthetic organic chemistry, which is responsible for millions of products in our society.

ESTERS

Esters are produced by the reaction of a carboxylic acid with an alcohol. The **ester functional group** (Figure 13.2.13) contains a carbonyl group attached to an oxygen linked to another carbon. It is similar to a carboxyl group, but the hydrogen of the –OH is replaced by an alkyl group.

Figure 13.2.14 (page 330) shows the structural and condensed structural formulae of three esters. In condensed structural formulae, the ester functional group is usually written as –COO– or $–CO_2–$

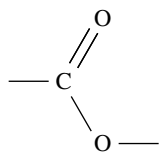


FIGURE 13.2.13 Structure of the ester functional group

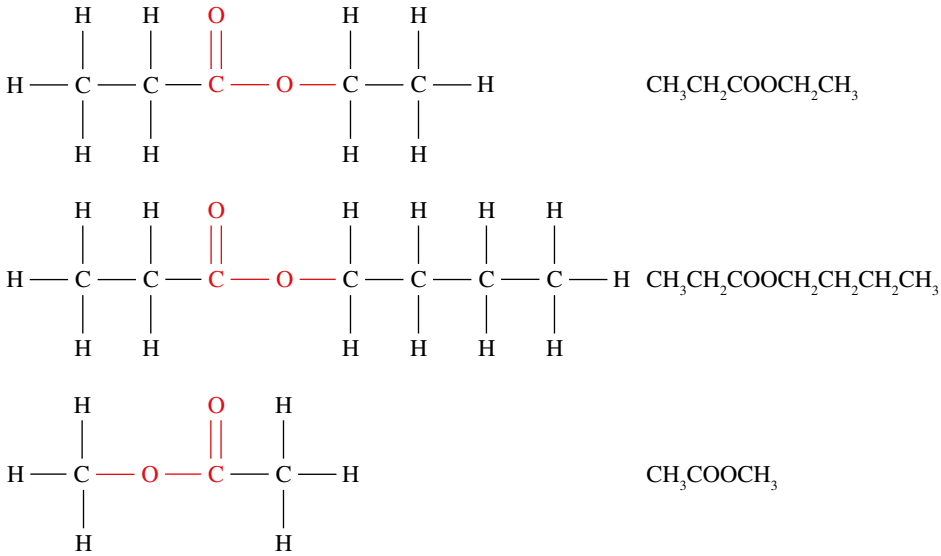


FIGURE 13.2.14 Structural and condensed structural formulae of three esters. Each contains the ester functional group shown in red.

The general formula of an ester may be represented as R–COO–R′ where R and R′ are alkyl groups, which may or may not be identical.

Esters are formed when carboxylic acids are heated with alcohols in the presence of sulfuric acid. Sulfuric acid acts as a catalyst because it increases the rate of reaction, but is not consumed by the reaction.

In Figure 13.2.15, you can see that an ester functional group is formed from the **esterification reaction** between the carboxyl functional group of the carboxylic acid and the hydroxyl functional group of the alcohol. Because a small molecule (in this case water) is formed, the reaction is also a **condensation reaction**.

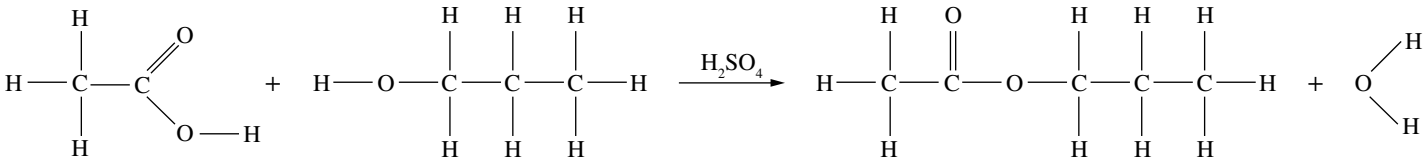


FIGURE 13.2.15 Reaction of a carboxylic acid and an alcohol to form an ester

Naming esters

The name of the ester is made up of the two compounds that react to form the ester—an alcohol and a carboxylic acid, as shown in Figure 13.2.16.

You can determine the name of an ester as follows.

- Locate the functional group and the carbonyl carbon.
- Starting from this carbon, determine the number of carbon atoms in the chain attached to it. Name it according to the stem name, adding the suffix '-oate'. This carbonyl-containing portion of the ester is derived from the carboxylic acid.
- Then add the alkyl group bonded to the singly bonded oxygen atom in front of the name. This portion of the ester is derived from the alcohol.

Use Worked Example 13.2.4 to develop your skills in naming esters.

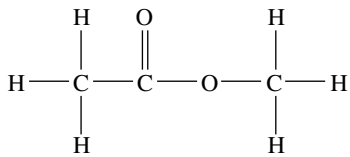
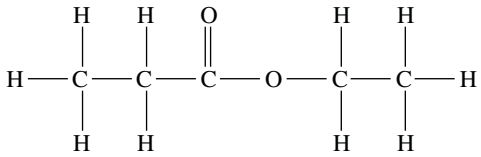


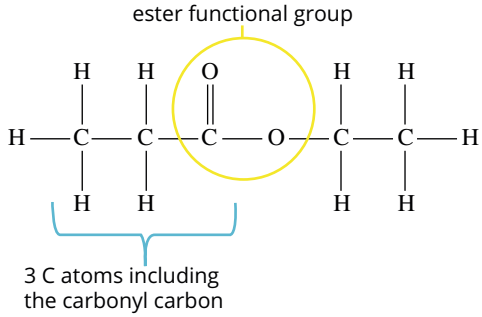
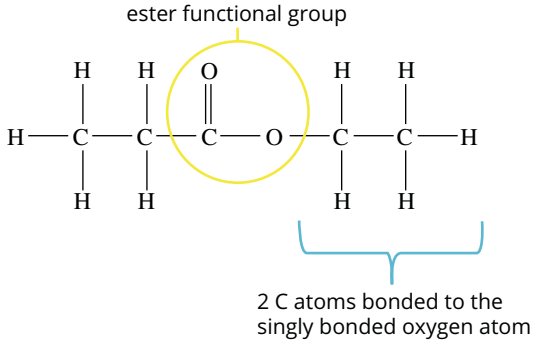
FIGURE 13.2.16 Methyl ethanoate (acetate) is an ester formed by the reaction of methanol with ethanoic acid.

Worked example 13.2.4

IUPAC NAMING SYSTEM FOR ESTERS

Write the systematic name for the following molecule.



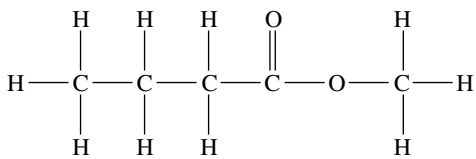
Thinking	Working
Locate the ester functional group. Starting from the carbonyl carbon, determine the number of carbon atoms in the chain attached to it and name according to the stem name, adding the suffix '-oate'.	 There are three carbons in the chain, including the carbonyl carbon, so the last part of the ester's name is propanoate.
Count how many carbons are bonded to the singly bonded oxygen atom. The alkyl group bonded to the singly bonded oxygen atom is then added in front of the name.	 There are two carbon atoms bonded to the singly bonded oxygen atom, so the alkyl group is ethyl.
Combine the two components, placing the alkyl part of the name first.	The name of the molecule is ethyl propanoate.

The name of the ester can easily be determined if you know the names of the carboxylic acid and alcohol that it is made from. The alkyl group name is derived from the name of the alcohol; for example, methanol becomes methyl. The -oic acid portion of the carboxylic acid name is replaced with -oate; for example, ethanoic (acetic) acid becomes ethanoate (acetate). The name of the example ester would be methyl ethanoate.

Worked example: Try yourself 13.2.4

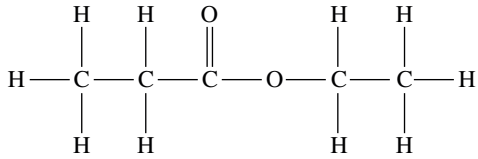
IUPAC NAMING SYSTEM FOR ESTERS

Write the systematic name for the following molecule.

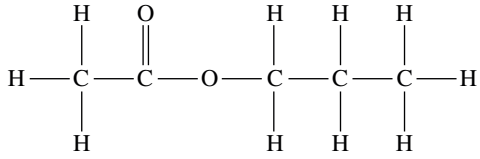


Structural isomers of esters

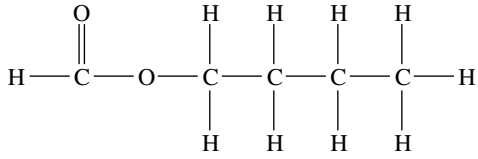
The position of the ester group can vary within a molecule and create structural isomers. Figure 13.2.17 shows three esters that are structural isomers with the molecular formula, $C_5H_{10}O_2$. The position of the ester functional group is shown by the naming of the ester, rather than by using numbers.



ethyl propanoate



propyl ethanoate



butyl methanoate

FIGURE 13.2.17 Three esters that are structural isomers with the molecular formula $C_5H_{10}O_2$

ALDEHYDES AND KETONES

Molecules of aldehydes, ketones, carboxylic acids, amides and esters all contain a **carbonyl functional group**, as shown in Figure 13.2.18. A carbonyl functional group 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 bonds are 120°.

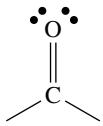


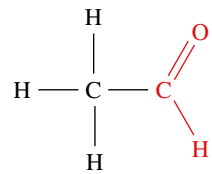
FIGURE 13.2.18 The carbonyl functional group. The non-bonding pairs of electrons shown on the oxygen atom are often not included in structural formulae.

Aldehydes

In **aldehydes**, the carbonyl group is always at the end of the hydrocarbon chain. As shown in Figure 13.2.19, 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.

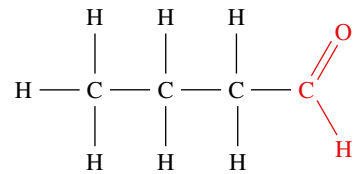
The simplest aldehyde, methanal (HCHO), is also commonly known as formaldehyde and is used to preserve biological specimens, including embalming human remains.

a



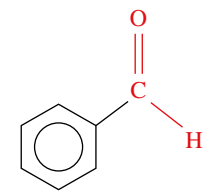
CH_3CHO

b



$CH_3CH_2CH_2CHO$

c



C_6H_5CHO

FIGURE 13.2.19 Structural and condensed formulae of three aldehydes. Each contains a carbonyl functional group with a hydrogen atom attached, shown in red.

Naming aldehydes

You can determine the name of an aldehyde as follows.

- Locate the functional group and the carbonyl carbon.
- Starting from this carbon, determine the number of carbon atoms in the chain attached to it. Name it according to the stem name, adding the suffix '-al'.

For example, the structure in Figure 13.2.19a has two carbons in the chain, so is given the prefix 'ethan-'. Being an aldehyde, it is given the suffix '-al'. Therefore, the name of this aldehyde is ethanal. Figure 13.2.19b is composed of a chain made up of four carbon atoms with the carbonyl hydrocarbon. Therefore, it is called butanal.

Ketones

In **ketones**, the carbonyl carbon is attached to other carbon atoms. This means that the carbonyl group is never at the end of the molecule, as you can see in the examples in Figure 13.2.20. In condensed structural formulae, the carbonyl functional group in a ketone is simply written as –CO–.

The simplest ketone, propanone (CH_3COCH_3), is commonly called acetone and is a useful polar organic solvent, frequently found in nail polish remover and paint thinner.

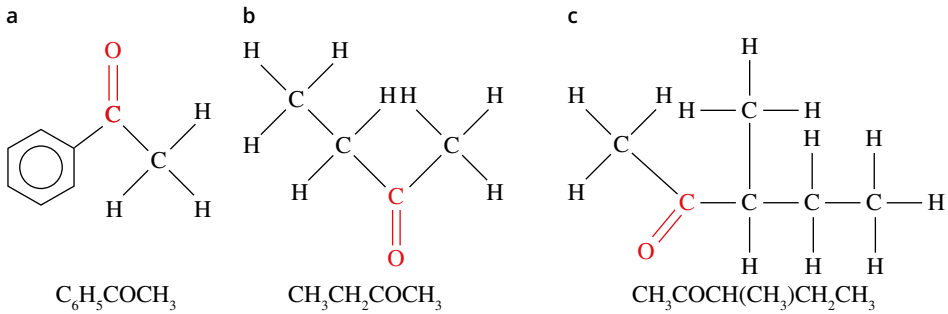


FIGURE 13.2.20 Structural and condensed formulae of three ketones. Each contains a carbonyl functional group (shown in red) attached to two hydrocarbon groups.

Naming ketones

You can determine the name of a ketone as follows.

- Identify the end of the hydrocarbon chain closest to the functional group and number the carbons from this end of the molecule.
- If there is a branched alkane, write the number and name of the alkyl group.
- Use the prefix for the number of carbon atoms present in the chain and suffix '-one', indicating the position of the double bonded oxygen by inserting the number between the prefix and suffix in the final part of the name.

For example, in Figure 13.2.20b, the chain is four carbons long. The position of the carbonyl group is attached to the second carbon, so this is butanone. Figure 13.2.20c has a methyl group attached to the third carbon in the chain. This ketone is named 3-methylpentan-2-one.

Figure 13.2.20a has a benzene group as well as a methyl group. The chain is essentially the same as propanone, with a benzene ring making up the position of the third carbon in the chain. It is given the name 1-phenylethan-1-one. This name has a prefix of phenyl to indicate the benzene ring and overall '-one' suffix to indicate the presence of the carbonyl group.

13.2 Review

SUMMARY

- Alcohols are a homologous series that contain a hydroxyl (–OH) group.
  - Alcohols are named by replacing the '-e' at the end of the parent alkane with the suffix '-ol'.
  - Alcohols are differentiated from each other as primary, secondary or tertiary alcohols, depending on the number of alkyl groups to which they are bonded.
- Primary amines are a homolgous series that contain an amino ($–NH_2$) functional group.
  - Primary amines are named by replacing the '-e' at the end of the parent alkane with the suffix '-amine'.
- When isomers exist, a number is used to specify the position of the functional group.
- The carbonyl group (–CO–) is a component of a number of functional groups.
- Aldehydes and ketones are homologous series that contain a carbonyl group on its own.
  - Aldehydes are named by replacing the '-e' at the end of the parent alkane with the suffix '-al'.
  - Ketones are named using with the suffix '-one', with a number used to identify the position of the carbonyl group.
- The carbonyl group is at the end of a hydrocarbon chain in aldehydes and within a hydrocarbon chain in ketones.
- 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'.
- Primary amides are a homologous series of molecules that contain the amide group ($–CONH_2$) at the end of the hydrocarbon chain.
- Esters are a homologous series of molecules that contain an ester group (–COO–) within the hydrocarbon chain.
- Esters have a two-word name.
  - The first part of the name comes from the part derived from an alcohol and the '-ol' suffix is changed to '-yl'.
  - The second part of the name is derived from the part that comes from a carboxylic acid and the suffix '-oic acid' is changed to '-oate'.

KEY QUESTIONS

1 Draw the structure and then write the name of a tertiary alcohol with the molecular formula $C_5H_{12}O$.

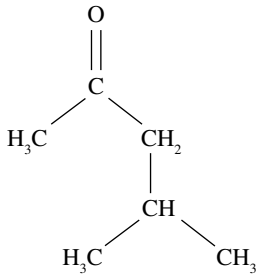
2 Give the systematic names of:

a $CH_3(CH_2)_3CH_2OH$

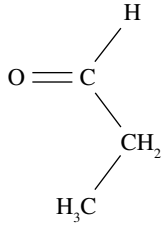
b $CH_3(CH_2)_3CHNH_2(CH_2)_2CH_3$

3 What homologous series do each of the following molecules belong to?

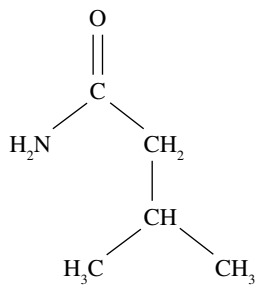
a



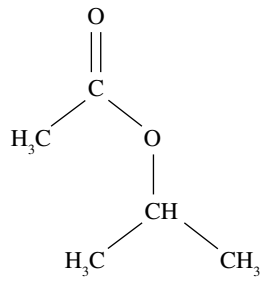
b



c



d



4 Write the systematic name for the following molecules.

a $HCOOCH_3$

b $HCOOH$

c $CH_3CH_2CH_2COOCH_2CH_2CH_3$

d CH_3COOCH_3

e $CH_3(CH_2)_4COOCH_2CH_3$

5 Draw and name an isomer of $HCOOCH_3$.

13.3 Properties of organic compounds

The functional groups that are present in organic compounds are responsible for many of their chemical and physical properties. For example, the properties of methanoic acid (formic acid, HCOOH) (Figure 13.3.1) are largely determined by the presence of the polar, acidic carboxyl functional group in its molecules.

FIGURE 13.3.1 Green tree ants weave leaf nests in the Gardner Plateau on the Kimberley Coast in Western Australia. Weaver ants can inflict painful bites and often spray methanoic acid directly at the bite wound, resulting in intense discomfort.

In this section you will consider the effect of functional groups on physical properties such as boiling point, solubility and viscosity. Differences in chemical properties will also be linked to the ability of functional groups to form different intermolecular interactions.

PHYSICAL PROPERTIES OF ALKANES AND ALKENES

Boiling points of alkanes

Table 13.3.1 lists the boiling points of the first six alkanes from methane to hexane. The boiling points increase as the size of the alkane molecule increases.

TABLE 13.3.1 Boiling points of the first six 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

Because alkane molecules are non-polar, the only intermolecular forces of attraction between them are weak **dispersion forces**. As the length of the carbon chain increases, the overall forces of attraction between molecules also increase (Figure 13.3.2). The dispersion forces between molecules increase because of the increased strength of temporary dipoles within the molecules. Because the boiling point of a molecular substance is determined by the strength of the intermolecular forces, boiling points increase as alkane chain length increases.

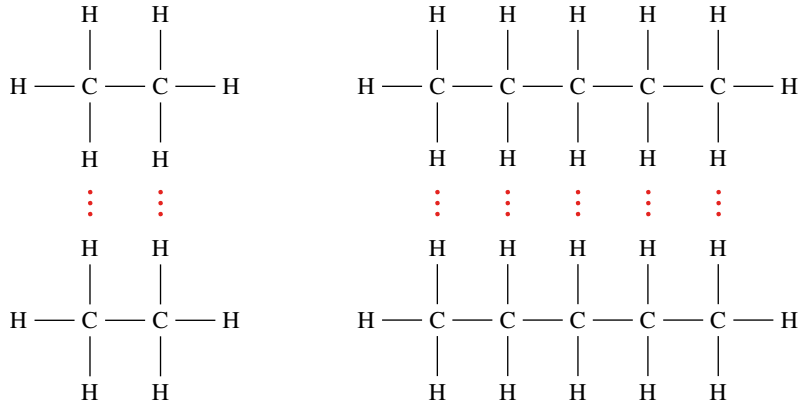
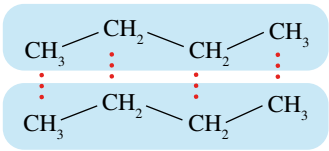


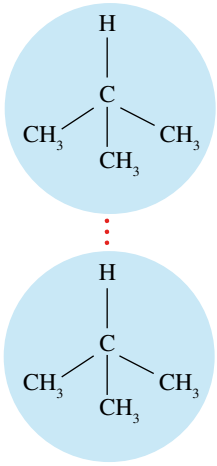
FIGURE 13.3.2 Dispersion forces are the strongest forces between alkane molecules. As molecules become longer, the dispersion forces become stronger.

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 come as close together in the bulk substance.

Figure 13.3.3 shows how the shapes of butane and its branched isomer methylpropane influence the strength of the dispersion forces between the molecules. Butane ($CH_3CH_2CH_2CH_3$) boils at –0.5°C, whereas methylpropane ($(CH_3)_3CH$) boils at –11.7°C. Although both molecules have the same molecular formula of C_4H_{10}, molecules of $CH_3CH_2CH_2CH_3$ have a greater surface area and can fit more closely together, allowing more contact between the molecules and forming stronger intermolecular bonds.



butane
- less compact molecule
- molecules are closer
- boiling point –0.5°C



methylpropane
- more compact molecule
- molecules are further apart
- boiling point –11.7°C

FIGURE 13.3.3 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 come closer together.

> **The strength of dispersion forces between molecules depends on the size and shape of the molecules.**

Boiling points of alkenes

Alkenes are non-polar and the forces of attraction between them are only weak dispersion forces. As you can see in Table 13.3.2, members of this homologous series have relatively low boiling points, similar to those observed for the alkanes with the same number of carbon atoms.

As for the alkanes, the boiling points of alkenes increase with molecular size as the strength of dispersion forces between molecules increases.

TABLE 13.3.2 Boiling points of molecules containing four carbons with different functional groups

Compound	Boiling point (°C)
Butane (C_4H_{10})	–0.5
But-1-ene (C_4H_8)	–6.3

CHEMFILE

Have you got the patience for slow science?

The longest running laboratory experiment in the world was set up in 1927 at the University of Queensland in Brisbane. The long-running 'pitch drop' experiment is designed to show that pitch, a mixture of highly viscous hydrocarbons, is actually a liquid. Pitch, otherwise known as bitumen (Figure 13.3.4), appears solid on first inspection and shatters if you strike it with a hammer.

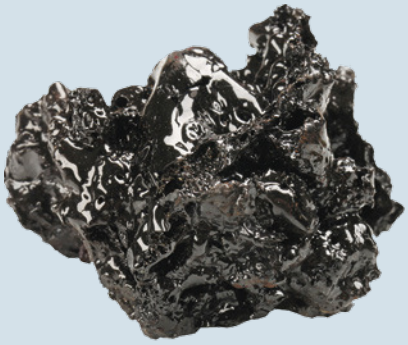


FIGURE 13.3.4 A sample of pitch at room temperature appears solid and shatters when hit with a hammer.

Professor Thomas Purnell set up the pitch experiment, as shown in Figure 13.3.5, by placing a sample of pitch into a funnel encased in a sealed container. He wanted to demonstrate to students that pitch was indeed a liquid—just a very, very viscous one. Over time, the pitch has settled and slowly flowed through the funnel, producing on average a drop once every decade. The ninth drop was recorded in April 2014.

Today, bitumen is used extensively, forming the main component of road surfaces. Under normal conditions, the road surface appears solid. However, heating reduces the viscosity and road workers are able to work the pliable bitumen.

FIGURE 13.3.5 Professor Thomas Purnell set up the famous University of Queensland pitch drop experiment in 1927. Professor John Mainstone, shown here, oversaw the experiment for many years.

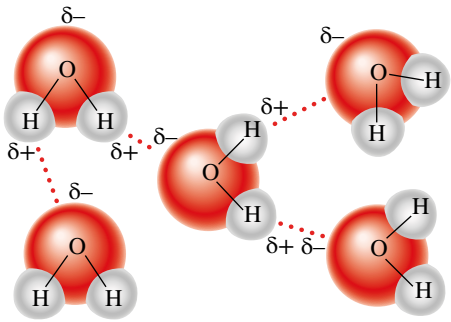


FIGURE 13.3.6 Water molecules are held to each other by hydrogen bonding.

Solubility in water

The non-polar nature of alkanes and alkenes makes them insoluble in water. You will recall from Year 11 Chemistry that water molecules are polar and held together by strong **hydrogen bonds** (Figure 13.3.6). The weak dispersion forces between water molecules and hydrocarbon molecules are not strong enough to overcome the strong attraction between water molecules, so 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 because hexane is less dense than water and the two liquids cannot dissolve in each other. 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 13.3.7, has a drastic effect on beaches and wildlife.

FIGURE 13.3.7 Oil spills at sea can contaminate shorelines and are very difficult to clean due to the lack of solubility of the oil in water. Other non-polar solvents or physical methods are required to disperse or remove the oil.

FIGURE 13.3.8 White spirit contains a mixture of alkanes. It is a useful solvent for other non-polar liquids.

Solubility in organic solvents

Alkanes mix with other non-polar liquids, such as alkenes and symmetrical haloalkanes. This is because the forces of attraction between molecules of these liquids are also weak dispersion forces and of similar strength to the alkane–alkane forces of attraction. Therefore, these liquids are **miscible**; that is, they are soluble in each other.

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 13.3.8).

PHYSICAL PROPERTIES OF ALCOHOLS, CARBOXYLIC ACIDS, AMINES AND AMIDES

Compounds from the four homologous series alcohols, carboxylic acids, amines and amides will be considered together because their molecules contain functional groups that can form hydrogen bonds. The ability of molecules to form hydrogen bonds has a significant effect on their properties.

The addition of polar functional groups to a hydrocarbon increases the boiling point for molecules of a similar size compared to the non-polar alkanes.

Boiling points

Hydrogen bonds are the strongest of the intermolecular forces and, as a result, molecules that can form hydrogen bonds generally exhibit higher boiling points. You can see in Table 13.3.3 that alcohols, carboxylic acids, amines and amides have higher boiling points than alkanes of similar molecular mass.

TABLE 13.3.3 Comparison of boiling points of compounds with different functional groups based on molecular mass

Homologous series	Compound	Formula	Molar mass ($g\,mol^{-1}$)	Boiling point (°C)
Alkane	Butane	C_4H_{10}	58	–1
Alcohol	Propan-1-ol	C_3H_7OH	60	97.2
Carboxylic acid	Ethanoic acid	CH_3COOH	60	118
Amine	Propan-1-amine	$C_3H_7NH_2$	59	49
Amide	Ethanamide	CH_3CONH_2	59	210

Boiling points of alcohols

The higher boiling points of the alcohols are due to the presence of hydrogen bonds between neighbouring alcohol molecules. In contrast, the only types of bonding present between non-polar alkane molecules are much weaker dispersion forces.

You will recall from Year 11 Chemistry that oxygen is a more **electronegative** atom than hydrogen, so the oxygen–hydrogen bond in the hydroxyl functional group is a polar bond. Figure 13.3.9 shows how hydrogen bonding occurs between the partially charged hydrogen atom in the –OH group 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.

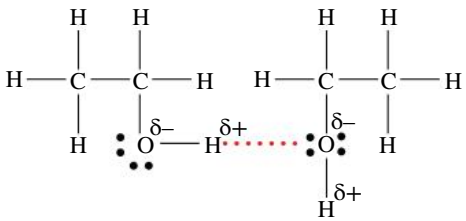


FIGURE 13.3.9 The red dotted line shows the hydrogen bonds that form between molecules such as ethanol that contain the polar hydroxyl functional group.

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 13.3.10.

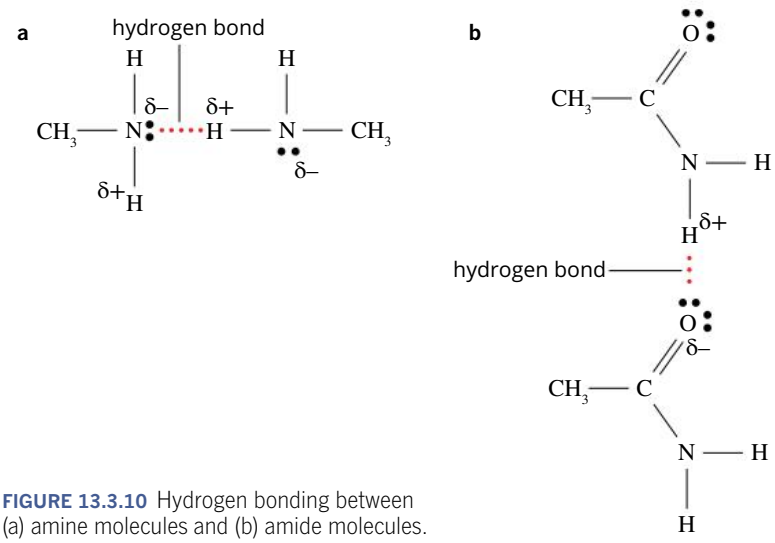


FIGURE 13.3.10 Hydrogen bonding between (a) amine molecules and (b) amide molecules.

In amines, the hydrogen bonds form between the non-bonding pair of electrons on the electronegative nitrogen atom and the partially positive hydrogen atom on another amine molecule. In amides, hydrogen bonds form between the non-bonding electron pairs on the oxygen atoms of one molecule and the partially positive hydrogen atom on a neighbouring molecule. The strength of the hydrogen bonding between molecules explains the relatively high boiling points of amines and amides when compared to hydrocarbon molecules of similar size.

Boiling points of carboxylic acids

Hydrogen bonding also has a marked effect on the boiling points of carboxylic acids. Figure 13.3.11 shows how two molecules of a carboxylic acid in the liquid state can form **dimers**, in which two hydrogen bonds form between the molecules.

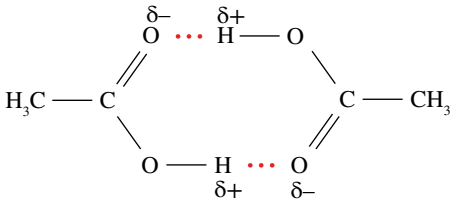


FIGURE 13.3.11 Hydrogen bonding between two ethanoic acid molecules results in the formation of a dimer.

The dimer produced is a stable species with a molar mass that is double that of a 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 higher dispersion forces combined with the hydrogen bonds between molecules result in the higher boiling point observed for carboxylic acids when compared to most other organic molecules of similar size.

Figure 13.3.12 highlights the higher boiling points of the carboxylic acid homologous series compared to alcohols.

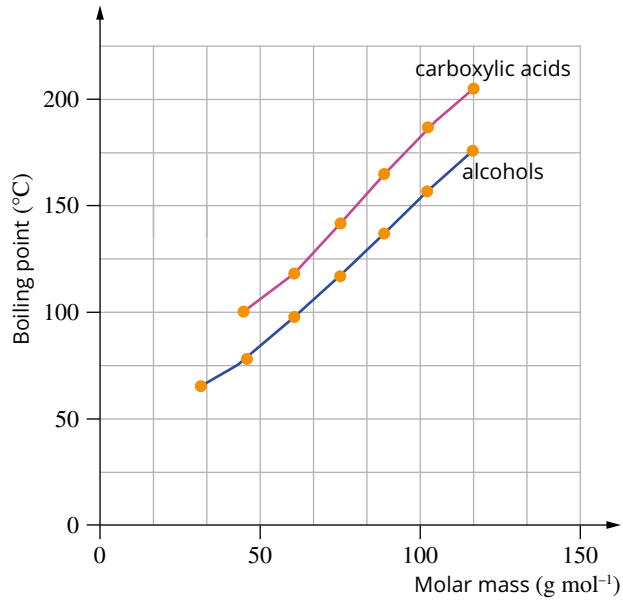


FIGURE 13.3.12 Boiling points of the carboxylic acid homologous series increase with increasing molar mass. The boiling points are higher than the boiling points of alcohols because of the formation of dimers stabilised by hydrogen bonds between molecules.

Effect of chain length on boiling point

The boiling points of alcohols, amines, amides and carboxylic acids increase as molar mass increases. For example, in alcohols the intermolecular hydrogen bonding between the –OH groups result in the higher boiling points. As the length of the hydrocarbon chain or 'tail' increases from one member of the homologous series to the next, the molar mass of the alcohols increases. With the increase in molecular size, the dispersion forces between molecules also become stronger. So the boiling points of alcohols increase as molar mass increases (Figure 13.3.13).

The three-dimensional structure of molecules can also affect the boiling point of a compound. In the case of alcohols, in addition to the impact of branching on the strength of dispersion forces, the position of the hydroxyl group within the molecule affects the hydrogen bonding. Figure 13.3.13 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.

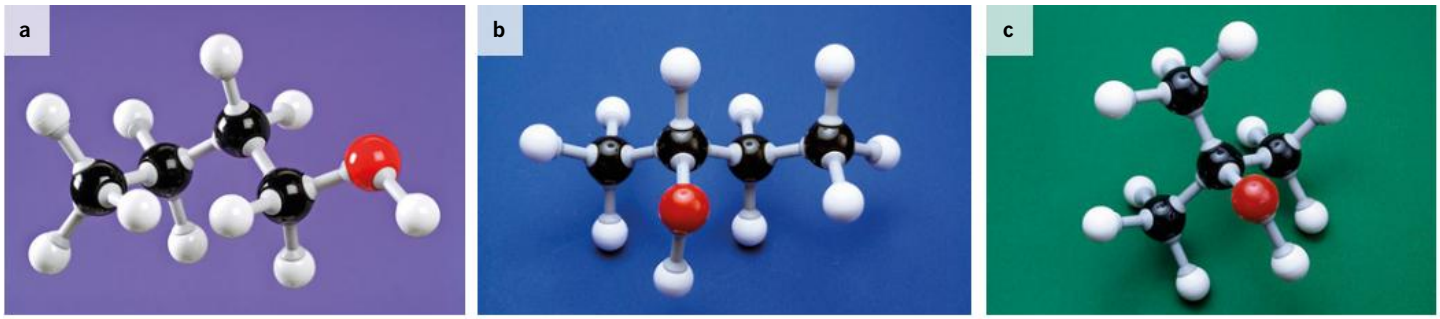


FIGURE 13.3.13 Molecular models of the three isomers of butanol: (a) butan-1-ol, (b) butan-2-ol and (c) 2-methylpropan-2-ol

You can see from the models that the hydroxyl group becomes increasingly 'crowded' from the primary alcohol through to the secondary and tertiary alcohol isomers. The presence of the alkyl groups restricts a molecule's ability to form hydrogen bonds with other molecules. For this reason, the boiling points of these alcohols decrease in the sequence from primary to secondary to tertiary alcohol, as seen in Table 13.3.4.

TABLE 13.3.4 The boiling point 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

Solubility

Solubility in water

Small alcohols and amines dissolve well in water because hydrogen bonds can form between the polar functional groups of the molecules and adjacent water molecules. For alcohols, the hydrogen bonds form between the partially positive hydrogen atom of the hydroxyl group and the lone-pair electrons of an adjacent water molecule (Figure 13.3.14a). There is also attraction between the partially positive hydrogen within the water molecules and the lone-pair electrons on the alcohol. This is how ethanol dissolves in water in alcoholic drinks, such as beer or wine.

When amines interact with water molecules (Figure 13.3.14b), hydrogen bonds can form between the lone-pair electrons of the nitrogen and the partial positive hydrogen of an adjacent water molecule or between the hydrogen of an amine group and an oxygen of an adjacent water molecule.

Amide and carboxylic acid molecules with short carbon chains are also soluble in water. 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 (Figure 13.3.15).

The high solubility of the carboxylic acid, citric acid, and the substance vitamin C, means they are found in a range of solutions, such as orange and lemon juice (Figure 13.3.16).

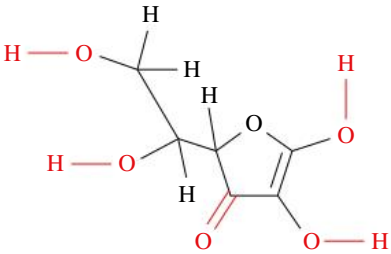


FIGURE 13.3.16 The presence of a large number of polar carbonyl and hydroxyl functional groups in a molecule of vitamin C makes it highly soluble in water. (Carbon atoms in the structure have been omitted for clarity.)

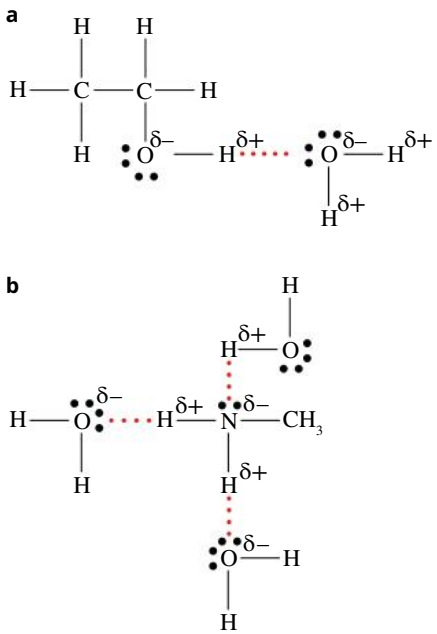


FIGURE 13.3.14 Hydrogen bonding between water molecules and (a) an ethanol molecule and (b) an amine molecule.

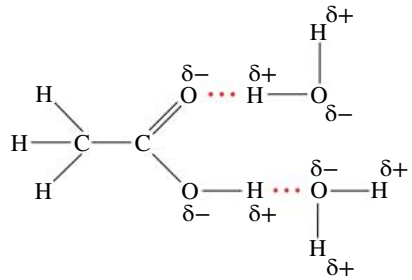


FIGURE 13.3.15 A small carboxylic acid molecule, such as ethanoic acid, is soluble in water due to hydrogen bonding between the carboxyl functional group and water molecules.

Solubility and chain length

The graph in Figure 13.3.17 shows the solubility of three alcohols. The solubility of alcohols, amines, amides and carboxylic acids in water decreases with increasing length of the carbon chain.

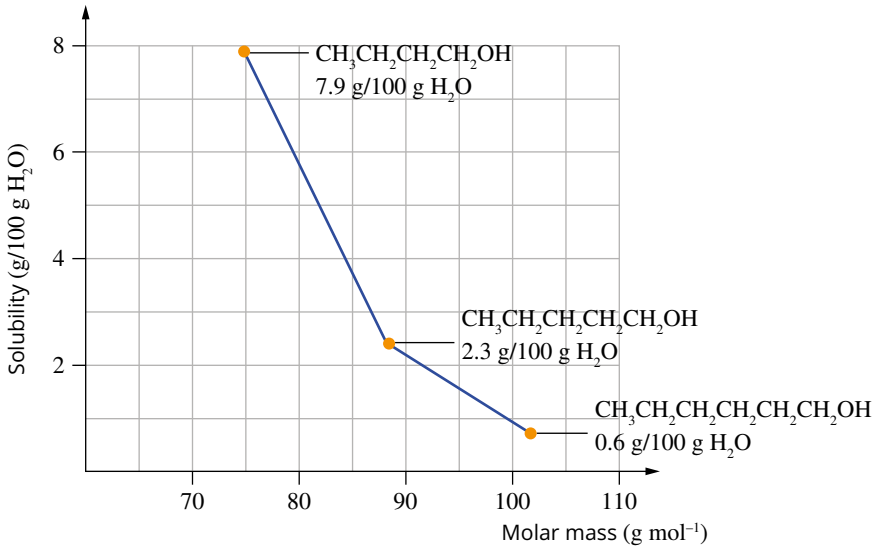


FIGURE 13.3.17 The solubility of alcohols in water decreases with increasing carbon chain length. This trend is also observed for other polar hydrocarbons such as amines, amides and carboxylic acids.

The longer hydrocarbon chains disrupt the hydrogen bonds between water molecules. While the hydroxyl group of an alcohol, for example, can form hydrogen bonds with water molecules, the hydrocarbon 'tail' cannot. Only dispersion forces occur between the hydrocarbon chain and water molecules, which are not as strong as hydrogen bonds, opposing the tendency for the molecule to dissolve. As chain length increases, the non-polar nature of the molecule also increases and the alcohol becomes less soluble.

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 amines, amides and carboxylic acids in organic solvents show similar trends to those of alcohols.

Properties and uses of alcohols

Many small alcohols are useful as fuels. Ethanol can be used as a fuel on its own or mixed with petrol. The combustion of ethanol produces carbon dioxide and water:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

The boiling points of alcohols increase as the size of the alcohol molecule increases. However, the boiling points of the alcohols are all higher than those of the corresponding alkanes. All the alcohols are liquids at room temperature, in contrast to the alkanes and alkenes, many of which are gases. The trend in boiling points of the first six alcohols is shown in Figure 13.3.18.

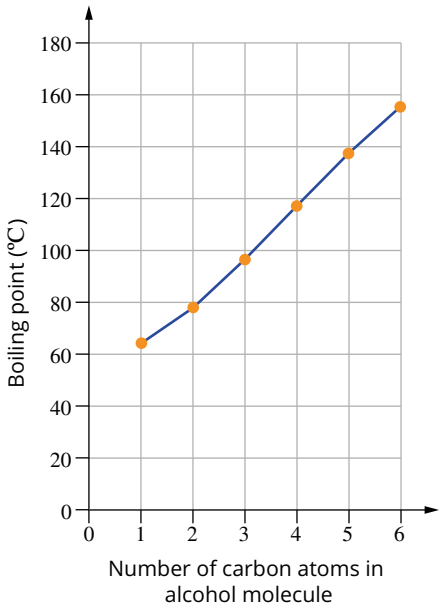


FIGURE 13.3.18 As the number of carbon atoms in an alcohol molecule increases, the boiling point increases.

The higher boiling point of alcohols is due to the presence of the –OH group, which allows hydrogen bonding to occur between molecules and strengthens the intermolecular bonding.

Hydrogen bonding also influences the solubility of the alcohols in water. The presence of the –OH group allows hydrogen bonds to form between water molecules and alcohol molecules (Figure 13.3.19). For smaller alcohols, such as methanol and ethanol, this allows the alcohol to dissolve readily in water. The solubility of the other alcohols decreases as the length of the carbon chain attached to the –OH group increases. A longer carbon chain means that more of the molecule is non-polar and the molecule becomes less polar overall.

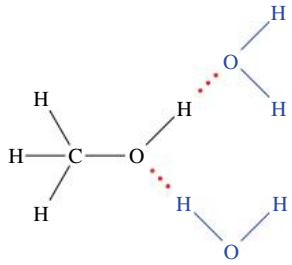


FIGURE 13.3.19 Hydrogen bonds form between the hydroxyl group of a methanol molecule and water.

CHEMFILE

Making champagne

The solubility of ethanol in water is essential in the production of alcoholic drinks. Champagne and wine are made by the fermentation of glucose ($C_6H_{12}O_6$) obtained from grapes. In the presence of yeast, ethanol and carbon dioxide are formed:

$$C_6H_{12}O_6(aq) \xrightarrow{\text{yeast}} 2C_2H_5OH(aq) + 2CO_2(g)$$

When a carefully selected mixture of grapes is fermented in bottles to make champagne, the ethanol and some carbon dioxide dissolves in the aqueous solution. Because the sparkle of the carbon dioxide is required in the final product, the yeast must be removed from the bottles very carefully while keeping the carbon dioxide in solution.

When it is time to remove the yeast from the fermented champagne solution, the bottle is inverted and the yeast is frozen in the neck of the bottle (Figure 13.3.20). The stopper and yeast are then quickly removed and the stopper is replaced.

FIGURE 13.3.20 An inverted bottle of champagne in the Moet & Chandon champagne cellar, Epernay, France. The yeast can be seen near the temporary cap of the bottle.

Properties and uses of carboxylic acids

Carboxylic acids are organic acids. They are commonly found in nature, giving a sour taste to lemon juice and vinegar, or making an ant bite or a nettle prick sting. Figure 13.3.21 shows the structures of these carboxylic acids.

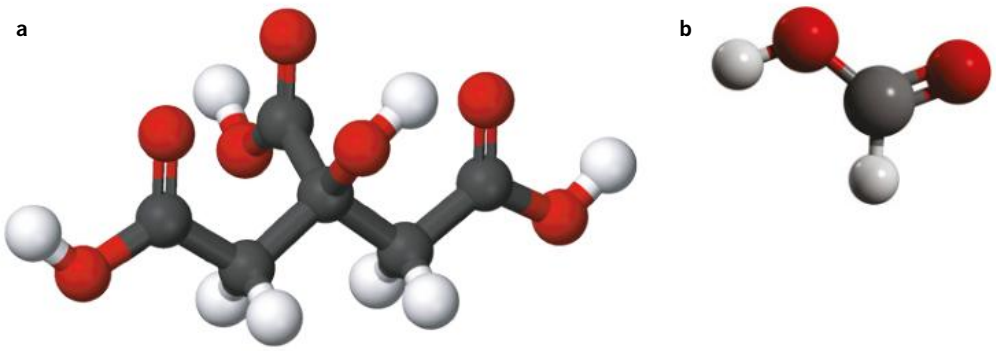


FIGURE 13.3.21 Carboxylic acids are found in nature. (a) Citric acid is in lemons and (b) methanoic acid is present in stinging nettles and ants.

As shown in Figure 13.3.22, the carboxyl functional group is made up of a **carbonyl group** (C=O) and a hydroxyl (–OH) group. Both of these groups are polar, with oxygen being much more electronegative than carbon and hydrogen. The electrons are drawn away from the hydrogen atom, enabling it to react in water to form an $H^+(aq)$ ion, so the functional group can act as an acid.

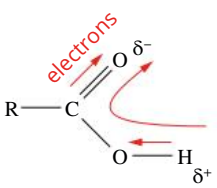


FIGURE 13.3.22 Electrons are drawn away from the hydrogen of the carboxyl functional group, allowing the hydrogen to be donated as a H^+ ion in an acid–base reaction.

CHEMFILE

Butter bombs

When butter goes rancid, the unpleasant odour is due to butanoic acid that has been released from the fats in the butter.

In its pursuit of Japanese whaling ships between 2005 and 2010, the crew of Sea Shepherd ships threw stink bombs made of rancid butter onto the decks of the whaling ships (Figure 13.3.23). While the members of Sea Shepherd maintained that they were throwing essentially harmless food material at the manned whaling ships, the butanoic acid in the rancid butter would not be a pleasant material to get in your eyes.

FIGURE 13.3.23 Sea Shepherd crew members throw butanoic acid in the form of rancid butter onto a Japanese whaling ship.

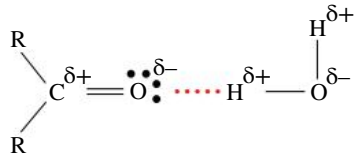


FIGURE 13.3.25 Hydrogen bonds form between the negatively charged electron pair on the oxygen atom in a carbonyl group and the positively charged hydrogen atom in a water molecule.

Carboxylic acids are weak acids and are often found in food. When foods go bad, carboxylic acids can be formed. For example, ethanoic acid is produced when wine is left open to oxygen in the atmosphere. We describe the taste of this wine as 'vinegary' because it actually has changed to vinegar. This reaction is used deliberately in the manufacture of the many different varieties of vinegar, such as apple cider vinegar.

PHYSICAL PROPERTIES OF ALDEHYDES, KETONES AND ESTERS

Aldehydes, ketones and esters can be considered together because they are composed of molecules that are held together by dipole–dipole attractions. Their molecules cannot form hydrogen bonds with each other because they do not have a hydrogen atom bonded to an oxygen atom or a nitrogen atom in their molecules.

Boiling points

Aldehydes, ketones and esters all contain a carbon–oxygen double bond. Oxygen is much more electronegative than carbon, so the carbon–oxygen double bond is polar. This means that molecules of aldehydes, ketones and esters contain a permanent dipole, which can form dipole–dipole attractions with nearby molecules. The dipole–dipole interactions that arise between ketone molecules are shown in Figure 13.3.24.

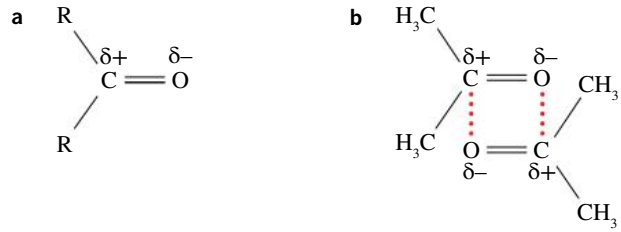


FIGURE 13.3.24 (a) A carbonyl bond is polar. (b) Dipole–dipole attractions between ketone molecules.

The strength of these dipole–dipole bonds between molecules give aldehydes, ketones and esters higher boiling points than similar sized alkanes. However, their boiling points are not as high as similar-sized alcohols because dipole–dipole bonds are not as strong as hydrogen bonds.

Effect of chain length on boiling point

As the hydrocarbon chain of aldehydes, ketones and esters increases in length, their boiling points increase because the strength of the dispersion forces between molecules also increases. This trend is similar to that observed for alcohols and other compounds described earlier.

Solubility

Solubility in water

Molecules of aldehydes, ketones and esters cannot form hydrogen bonds with each other. However, Figure 13.3.25 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, ketones and, to a lesser extent, esters soluble in water.

As for other soluble organic compounds such as alcohols, when the non-polar hydrocarbon chain length of aldehydes, ketones and esters increases, their solubility in water decreases.

Solubility in organic solvents

As the non-polar hydrocarbon chain of aldehydes, ketones and esters increases in length, they become more soluble in non-polar solvents. This is opposite to the trend observed in water.

EXTENSION

Flashpoint

When a candle burns, the solid candle wax must be converted to a vapour before it will ignite. The match used to light the candle first melts some of the wax soaked into the candlewick and vaporises it. It is the wax vapour, rather than the solid candle wax, that ignites and actually burns. Close observation of a burning candle, such as the one shown in Figure 13.3.26, confirms this.

FIGURE 13.3.26 Close observation of a candle shows that it is the candle-wax vapour rather than the solid wax that burns.

Similarly, for liquid fuels such as petrol and methylated spirits, it is the vapour that burns, rather than the liquid. As the temperature of a liquid fuel increases, the concentration of vapour above the surface of the liquid rises. At a certain temperature, there will be enough fuel vapour mixed with the air for the fuel to burn. The temperature at which a vapour ignites is called the flashpoint.

The flashpoint is defined as the lowest temperature at which a liquid forms sufficient vapour to ignite when an ignition source (such as a flame) is applied (Figure 13.3.27). The flashpoints of some common fuels are shown in Table 13.3.5.

TABLE 13.3.5 Flashpoints of some common fuels

Fuel	Flashpoint (°C)
Ethanol	16
Petrol	−43
Diesel	>52
Jet fuel	>38

The flashpoints of hydrocarbon fuels, such as petrol, diesel and kerosene, are related to the boiling points of the fuels. The boiling points of hydrocarbons are a property of the carbon–carbon chain length of the hydrocarbon molecules in the fuels. This trend is also observed when measuring flashpoints (Table 13.3.6).

TABLE 13.3.6 Flashpoints of a selection of alkanes with increasing molecular size

Alkane	Number of carbon atoms in chain	Flashpoint (°C)
Butane	4	−76
Methylpropane	4	−83
Hexane	6	−7
Heptane	7	25
Octane	8	56

The shape of a molecule can also affect a compound's physical properties. Methylpropane and butane are isomers, with a molecular formula of C_4H_{10}. The dispersion forces between methylpropane molecules are weaker than in butane, so methylpropane has a lower boiling point and lower flashpoint than butane.

While the low flashpoints of fuels make them useful in engines, their use also has dangers. That is why when putting petrol in a car, you should not smoke or use a naked flame of any kind. Gas supplies, including bottled gas, have additives with unpleasant odours that make it possible to detect and respond to gas leaks before an explosion occurs.

FIGURE 13.3.27 This apparatus measures the flashpoint of fuels. The fuel is heated steadily in a metal cup and, at intervals, a flame is brought above the liquid in the cup. The flashpoint is the lowest temperature at which the fuel will ignite when the flame is brought above it.

Properties and uses of esters

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.

Although esters are polar, they have no free hydroxyl groups, so they cannot form hydrogen bonds with each other. Therefore, they have lower boiling points than carboxylic acids and alcohols of similar relative molecular mass (Figure 13.3.28).

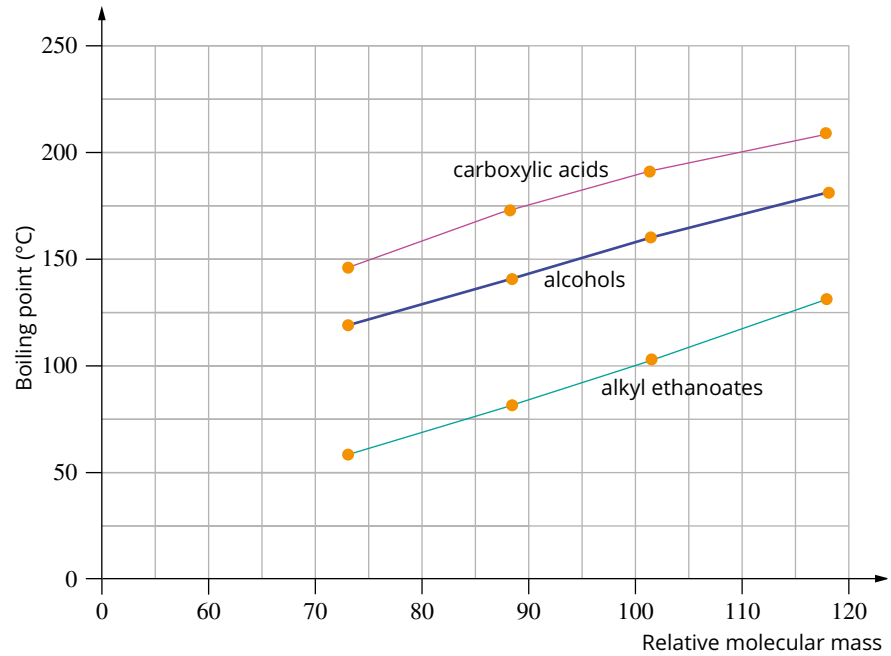


FIGURE 13.3.28 Boiling points of alkyl ethanoates (a series of esters) compared to carboxylic acids and alcohols of similar relative molecular mass.

Smaller esters are liquids at room temperature. They are good solvents for many organic compounds. For example, butyl ethanoate is used as a paint thinner and ethyl ethanoate is found in nail polish removers. Many esters are large molecules and exist as oils and waxes. For example, beeswax is largely composed of an ester called triacontanyl palmitate (Figure 13.3.29).

FIGURE 13.3.29 Beeswax is largely composed of an ester called triacontanyl palmitate.

CHEMFILE

Esters, sweet flavours and strong aromas

Esters are responsible for some of the natural and synthetic flavours and smells found in ice creams, lollies, flowers and fruit (Figure 13.3.30). Table 13.3.7 lists the names of some esters with distinctive smells or flavours.

FIGURE 13.3.30 Esters are responsible for many of the flavours and odours of fruit.

TABLE 13.3.7 Some sweet smelling esters

Ester	Smell or flavour
Pentyl propanoate	Apricot
Ethyl butanoate	Pineapple
Octyl ethanoate	Orange
2-Methylpropyl methanoate	Raspberry
Ethyl methanoate	Rum
Pentyl ethanoate	Banana

13.3 Review

SUMMARY

- The boiling points of organic molecules are determined by intermolecular forces. Dispersion forces are always present and there may also be dipole–dipole attractions or hydrogen bonds.
- The strength of dispersion forces between alkane molecules depends on the size and shape of the molecules.
- The only forces of attraction between molecules of the alkane and alkene homologous series are dispersion forces.
- Molecules of aldehydes, ketones and esters have polar carbonyl functional groups and they are attracted to each other by dipole–dipole attractions.
- Molecules of alcohols, carboxylic acids, amines and amides contain functional groups that can form hydrogen bonds with other molecules.
- Comparing molecules of similar size in different homologous series, it is generally true that their boiling points increase in the order: alkanes, alkenes < aldehydes, ketones, esters < alcohols, carboxylic acids, amines, amides.
- The solubility of organic molecules in water is determined by the way the water molecules interact with the molecules of the solvent. This is affected by the polarity of functional groups and the length of the non-polar hydrocarbon tails.
- Alkanes and alkenes are insoluble in water.
- The smaller members of the aldehyde, ketone, ester, alcohol, amine and amide homologous series are generally soluble in water. Solubility rapidly decreases as the chain length increases.
- Alkanes and alkenes are soluble in non-polar organic solvents.
- The solubility of aldehydes, ketones, esters, alcohols, amines and amides in non-polar organic solvents increases as the chain length of the molecules increases.

KEY QUESTIONS

1 Complete the following paragraph by filling in the gaps with the appropriate words.
Butane is a member of the _____ homologous series. The forces of attraction holding butane molecules to each other are _____. As the chain length of alkanes increases, their boiling points _____. Alkanes are _____ in water. This is because the forces of attraction between water molecules and alkane molecules are _____ than the _____ between water molecules.

2 Arrange the following compounds in increasing order of boiling point. Provide reasons for your answer.
$CH_3CH_2CH_2CH_3$, $CH_3CH(CH_3)CH_3$, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_3$

3 Arrange the following compounds in increasing order of boiling point.
$CH_3CH_2CH_2CH_3$, CHCH, CH_3CHCH_2, $CH_3CH_2CH_2CH_2OH$, $CH_3CH_2CH_2COOH$

13.4 Isomers overview

Isomers are molecules that contain the same number and type of atoms, arranged in different ways. The existence of isomers is a major reason that there are so many different carbon compounds. Isomers have the same molecular formula, but they can have different physical and chemical properties and so behave differently.

There are two main types of isomers considered in this course:

- structural (positional and chain) isomers
- **geometric** (*cis–trans*) **isomers**.

Structural isomers form when the atoms in molecules with the same molecular formula bond together in different arrangements. Two types of structural isomers are **chain isomers** and **positional isomers**.

CHAIN ISOMERS

Chain isomers form because of the branching that is possible in the carbon chains that form the backbone of any large organic molecule. Chain isomers of alkanes can contain more than one **alkyl group**; some molecules may also have more than one alkyl group attached to the same carbon atom.

Hexane is an example of an alkane with no branches. It has the molecular formula C_6H_{14} and its structure is shown in Figure 13.4.1.

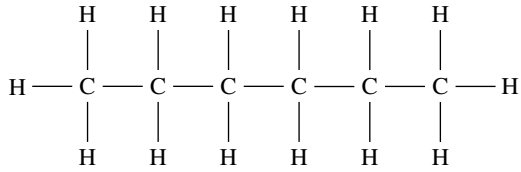


FIGURE 13.4.1 Hexane is a single-chain hydrocarbon with single bonds that contains six carbon atoms and fourteen hydrogen atoms.

Three of the chain isomers of hexane are shown in Figure 13.4.2. Each isomer has a different name that represents its exact molecular structure. The naming of chain isomers is described in the next section.

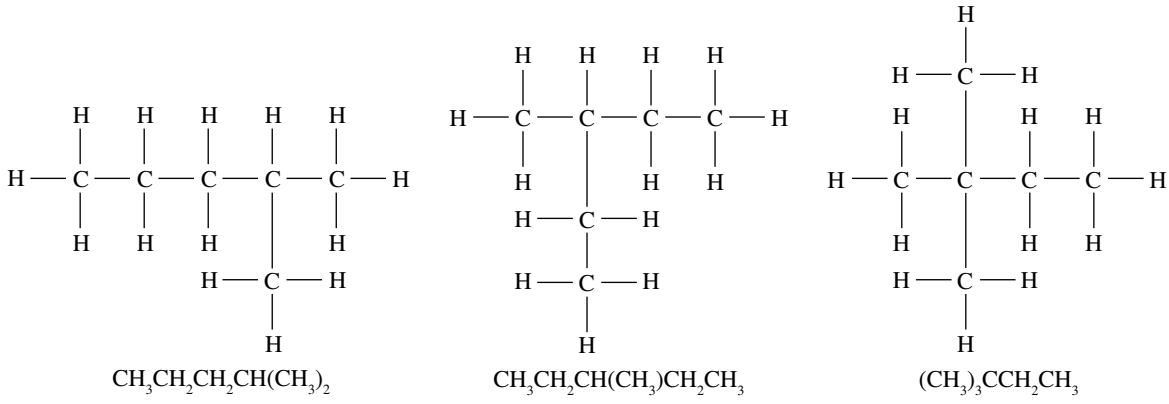


FIGURE 13.4.2 Three chain isomers of hexane

POSITIONAL ISOMERS

Positional isomers can occur for organic molecules that contain functional groups. Two molecules with the same carbon chain and functional group, but with the functional group in a different location in the molecule, are called positional isomers.

Alcohols are organic molecules that contain a hydroxyl (–OH) functional group. A number of positional isomers can be drawn for an alcohol with the molecular formula $C_4H_{10}O$. Like chain isomers, each positional isomer is given a different name. Figure 13.4.3 shows two positional isomers, butan-1-ol and butan-2-ol.

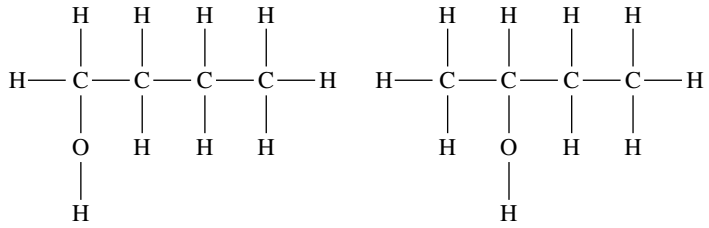


FIGURE 13.4.3 Two positional isomers of an alcohol with the formula $C_4H_{10}O$

It is important to realise that alkenes also contain functional groups—their double carbon–carbon bonds. This means that positional isomers can be formed when the double bond is in different locations. Figure 13.4.4 shows the two positional isomers of butene.

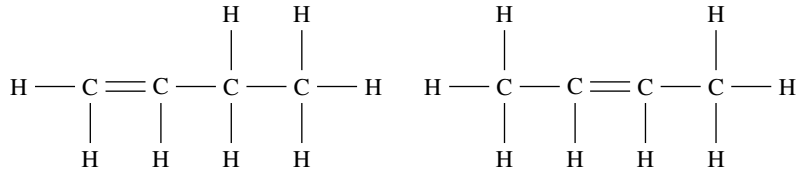


FIGURE 13.4.4 The two positional isomers of butene: but-1-ene and but-2-ene

Positional isomers only exist for molecules that contain a functional group and have a long enough carbon chain that different positions of 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 formulae of ethanol in Figure 13.4.5 do not represent positional isomers.

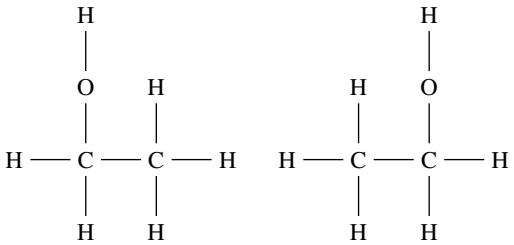


FIGURE 13.4.5 Two representations of the structure of ethanol (C_2H_6O). These are not positional isomers; if the first structure is flipped over, it is identical to the second.

It is possible for structural isomers to form both positional and chain isomers. Figure 13.4.6 shows two more isomers of an alcohol with the formula $C_4H_{10}O$. They are chain isomers of the molecules shown previously in Figure 13.4.5, and positional isomers of each other.

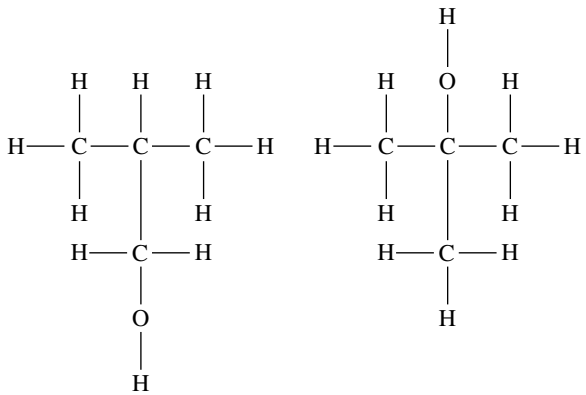


FIGURE 13.4.6 Two more molecules that are alcohols with the molecular formula $C_4H_{10}O$

GEOMETRIC (*CIS–TRANS*) ISOMERS

Geometric isomers can occur when there is restricted rotation somewhere in a molecule. Restricted rotation can occur about a carbon–carbon double bond or within a ring.

Two atoms joined by a single bond can rotate freely around the single bond. You might think that the two models shown in Figure 13.4.7 show different molecules, but they are models 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 molecule.

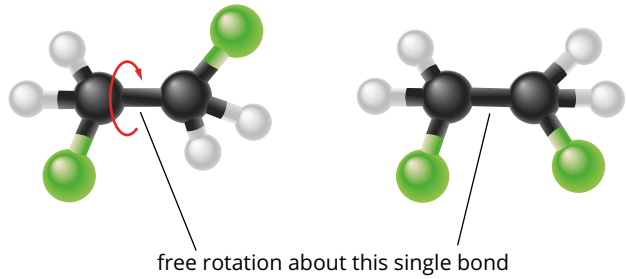


FIGURE 13.4.7 These two models represent the same molecule because the groups on either end can rotate around the single bond.

However, because of the way that the electrons are arranged in a double bond, groups attached to carbons on either side are unable to rotate freely. The models in Figure 13.4.8 represent two molecules that cannot be rotated to form the same structure because a double bond is present.

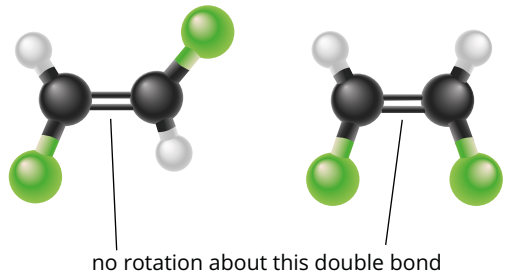


FIGURE 13.4.8 These two models represent different molecules because the groups on either end cannot rotate around the double bond.

cis–trans isomers can occur when there are two different groups attached to each carbon atom involved in the double bond. The different groups can be functional groups or hydrocarbon chains of different lengths. There are two possible arrangements: the groups can be on the same or opposite sides of the double bond. If the groups are on the same side, the isomer is called the ***cis* isomer**. If the groups are on opposite sides, the isomer is called the ***trans* isomer**.

Figure 13.4.9 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. If the bromine atoms are attached to different carbon atoms, then it is called 1,2-dibromoethene, which has the condensed structural formula BrCH=CHBr. There are two isomers that may form: *cis*-1,2-dibromoethene and trans-1,2-dibromoethene.

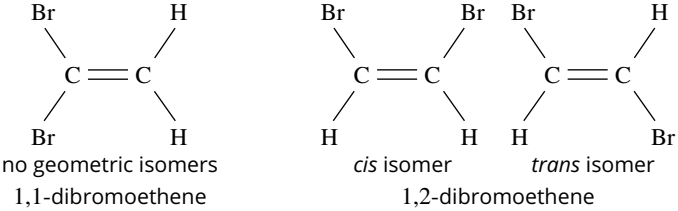
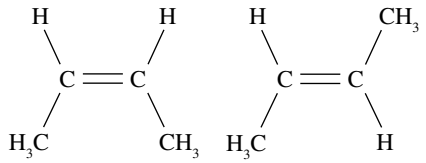


FIGURE 13.4.9 The possible structures of dibromoethene ($C_2H_2Br_2$). Note the position of the bromine atoms in the *cis* and *trans* isomers.

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 13.4.10 shows the *cis* and *trans* isomers of but-2-ene.



cis-but-2-ene *trans*-but-2-ene

FIGURE 13.4.10 The two isomers of but-2-ene both have the condensed structural formula $CH_3CH{=}CHCH_3$. 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.

CHEMISTRY IN ACTION

The correlation between *trans*-fatty acids and coronary heart disease

Trans-fatty acids occur in small amounts in nature, but are also produced from vegetable oils for use in many common foods such as margarine and for frying fast foods. *Trans*-fatty acids are hydrocarbon chains with a *trans* carbon–carbon double bond. This means the fatty acid chains pack together quite tightly (as opposed to *cis*-isomers). This tight packing gives them more desirable melting and boiling points.

In recent years, studies have shown there has been a correlation between the intake of *trans*-fatty acids in the diet and the risk of coronary heart disease. Coronary heart disease results when the coronary arteries get narrower, restricting the flow of blood to the heart. This narrowing is caused by fatty material (cholesterol) that gradually builds up inside the arteries. The recommendation from The Heart Foundation is that less than 1% of total energy should come from *trans*-fats.

13.4 Review

SUMMARY

- Carbon compounds can have structural isomers and geometric (*cis–trans*) isomers. Structural isomers include chain and positional isomers.
- Chain isomers have the same molecular formula but different branching of the carbon chain.
- Positional isomers have the same molecular formula, but at least one functional group in different positions on the carbon chain.
- Geometric (*cis–trans*) isomers 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 are geometric isomers of alkenes that occur when there are two different groups attached to the carbon atoms at each end of a carbon–carbon double bond.
- In *cis–trans* isomers of alkenes, the atoms in the isomers are joined in the same order, but have a different arrangement in space.

KEY QUESTIONS

1 **a** Which is the shortest alkane that can have chain isomers?

b Draw structural formulae for all the chain isomers of this alkane.

2 Explain why carbon chains in alkanes are not straight, as commonly drawn in structural formulae.

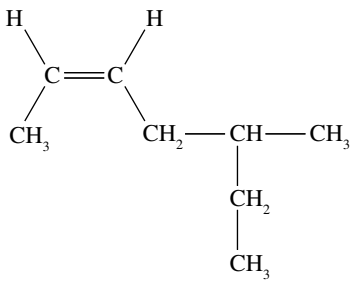
3 Look at the following alkenes, numbered i–iv.

a Which alkenes have *cis–trans* isomers?

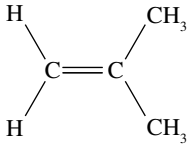
b Which alkenes are *cis* isomers?

c Which alkenes do have not *cis–trans* isomers? Explain why.

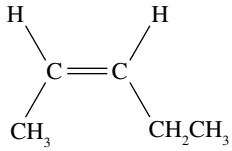
i



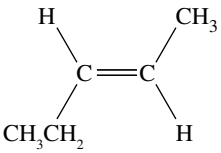
ii



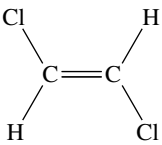
iii



iv



v



13.5 IUPAC nomenclature overview

In the early 1960s, 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 branches (for example, see Figure 13.5.1).

This section will summarise and extend your knowledge of the rules that you learnt in the previous sections for naming organic compounds. You will also learn how to name organic molecules that contain two different functional groups.

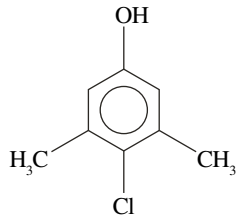


FIGURE 13.5.1 According to the IUPAC rules, the active ingredient in the antiseptic Dettol has the name 4-chloro-3,5-dimethylphenol.

IUPAC NOMENCLATURE

IUPAC nomenclature is the set of rules by which chemists can name a given compound. The rules can be used in reverse to derive a structure from the IUPAC name. IUPAC names of organic molecules can be simple or complex, but most IUPAC names follow the same basic pattern.

All 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 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 functional groups are indicated by numbers. As an example, the meaning of each part of the name butan-2-ol, an alcohol, is shown in Figure 13.5.2, along with its structural formula.

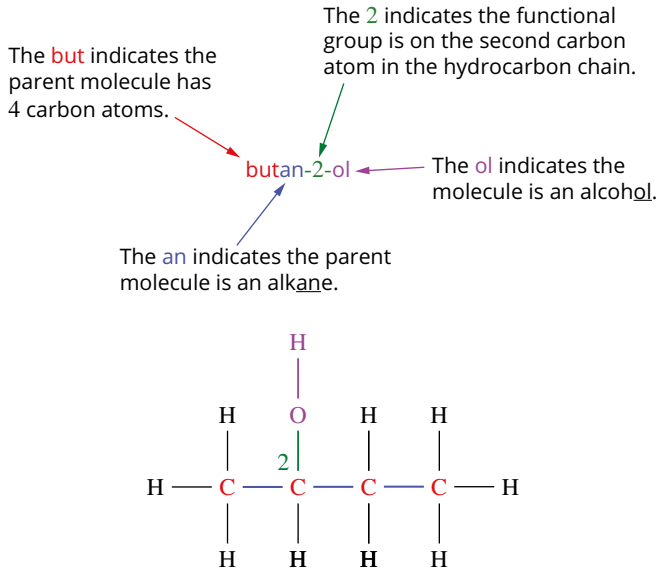


FIGURE 13.5.2 The name and structural formula of butan-2-ol. The colours of each part of the name correspond with the section of the structure that it represents.

SUMMARY OF IUPAC RULES FOR NOMENCLATURE

The following conventions are used for naming organic molecules.

- The longest carbon chain is used to derive the parent name. The longest chain must include the functional group for alkenes, alcohols, amines, carboxylic acids and esters.
- The names and locations of branches and additional functional groups are added to this parent name.
- Numbers are used to identify the carbon atom that groups are attached to.
- Numbers and letters are separated by hyphens.
- Numbers are separated from other numbers by commas.
- There are no spaces in a name, apart from the two-word names of acids and esters.
- The names of branching alkyl groups are added before the parent name.
- If there is more than one type of 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 13.5.1.

TABLE 13.5.1 The identity, functional groups and naming conventions of the homologous series

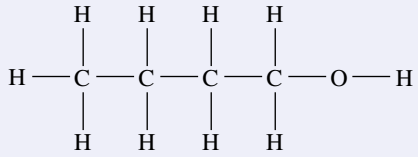
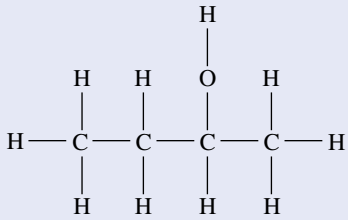
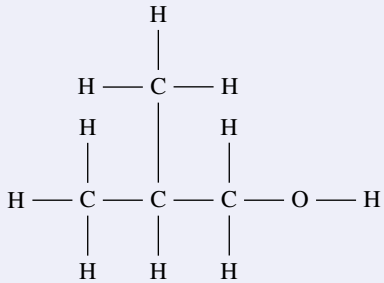
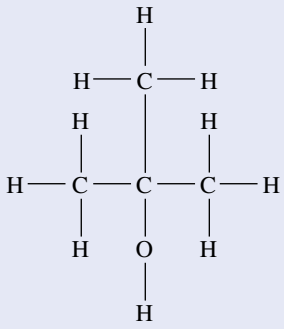
Homologous series	Functional group name	Condensed structural formula	Naming convention
Alkane	Not applicable	Not applicable	Suffix -ane
Alkene	Carbon–carbon double bond	–C=C–	Suffix -ene
Haloalkane	Halo	–F, –Cl, –Br, –I	Prefix fluoro-, chloro-, bromo- or iodo-
Alcohol	Hydroxyl	–OH	Suffix -ol Occasionally prefix hydroxy-
Amine	Amino	$-NH_2$	Suffix -amine Occasionally prefix amino-
Carboxylic acid	Carboxyl	–COOH	Suffix -oic acid
Ester	Ester	–COO–	Two-word name with suffixes -yl and -oate
Aldehyde	Carbonyl (end of carbon chain)	–CHO	Suffix -al
Ketone	Carbonyl (within carbon chain)	–CO–	Suffix -one
Amide	Amide	$-CONH_2$	Suffix -amide

Naming organic molecules with a functional group and alkyl side chain

Organic molecules with functional groups can also have alkyl side chains. The names of alkyl groups 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 13.5.2 with the naming of the structural isomers of an alcohol with the molecular formula $C_4H_{10}O$.

TABLE 13.5.2 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

EXTENSION

Naming organic molecules 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.) can be used. 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 13.5.3). In an organic molecule with two functional groups, the following naming conventions are used.

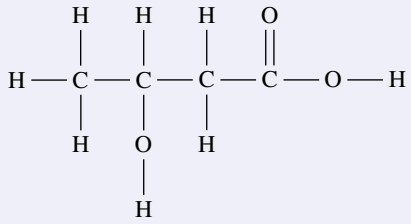
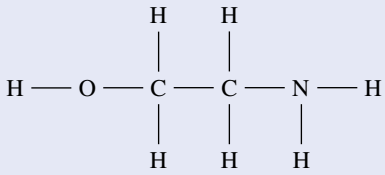
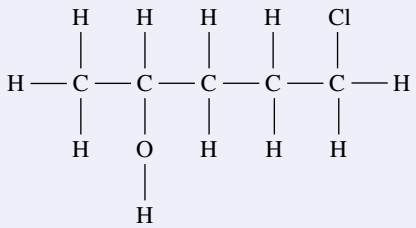
- The functional group with the highest priority is assigned the lowest possible number and the suffix for this functional group is used in the name.
- The lower priority functional group is indicated by a prefix or alternative name.

TABLE 13.5.3 IUPAC functional group priorities

	Functional group	Suffix	Alternative name (when needed)
Highest priority	Carboxyl	-oic acid	–
↓	Hydroxyl	-ol	hydroxy-
	Amino	-amine	amino-
	Alkene	-ene	-an- becomes -en-
Lowest priority	Halo	–	halo-

This priority system is illustrated in Table 13.5.4 with the naming of molecules with two functional groups.

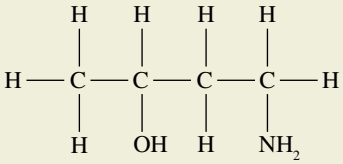
TABLE 13.5.4 Naming molecules with two functional groups

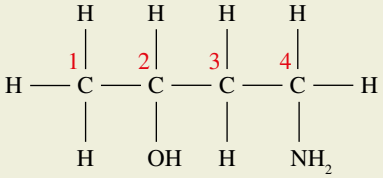
Structure	Name
	3-Hydroxybutanoic acid
	2-Aminoethanol
	5-Chloropentan-2-ol

Worked example 13.5.1

NAMING AN ORGANIC MOLECULE WITH TWO FUNCTIONAL GROUPS

Name this molecule according to IUPAC rules.

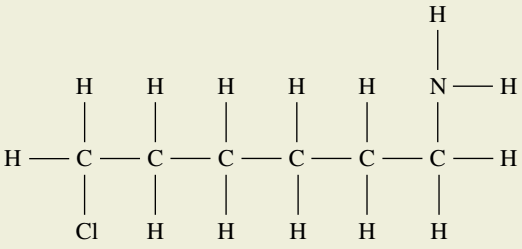


Thinking	Working
Identify the parent name by counting the longest continuous chain of carbon atoms.	There are four carbons in the longest chain, so the parent name is butane.
Identify the functional groups present.	The two functional groups present are hydroxyl and amino.
Determine which functional group has the higher priority and determine the prefixes and suffixes to use.	The hydroxyl group has the higher priority, so the molecule will end in -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.	
Determine the number of the carbon each functional group is attached to.	The –OH is attached to carbon 2 and $–NH_2$ is attached to carbon 4.
Use the functional group names and carbon numbers to construct the full name.	The name of the molecule is 4-aminobutan-2-ol.

Worked example: Try yourself 13.5.1

NAMING AN ORGANIC MOLECULE WITH TWO FUNCTIONAL GROUPS

Name this molecule according to IUPAC rules.



13.5 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.
  - Name functional groups by prefixes or suffixes.
  - Number the carbon chain so that the carbon attached to the highest priority functional group has the lowest number.
  - Insert numbers before each functional group.
  - When multiples of a functional group are present, use a multiplier (e.g. 'di-').

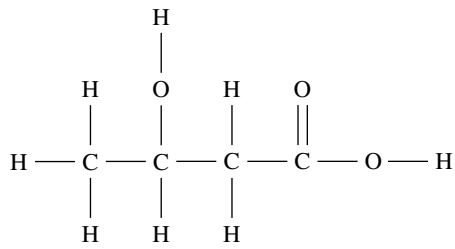
KEY QUESTIONS

1 Draw the structural formula of the functional group of each of the following homologous series.

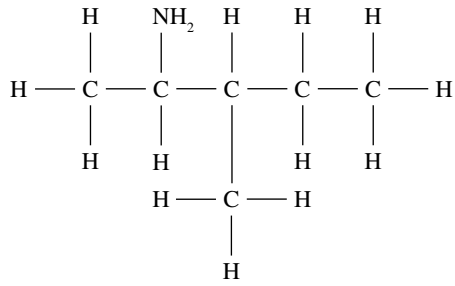
a carboxylic acid
b aldehyde
c amide
d alcohol
e ester

2 Write the systematic name for the following molecules.

a



b



3 Draw the structure of:

a 2-methylpropan-1-ol
b butan-2-ol
c 3,4-diethylhex-3-ene.

4 **a** Write the condensed formulae based on the following incorrect names.

i 3-aminopropane
ii 3-ethyl-hydroxy-2-butane

b Explain why each name is incorrect and give the correct name.

13.6 Determining formulae of organic compounds

When chemists determine the structure of a new compound, one of the most useful pieces of information is the chemical formula of the compound. Even large chemical compounds have a chemical formula. For example, Figure 13.6.1 shows the structure of the hormone insulin, which has a chemical formula of $C_{257}H_{383}N_{65}O_{77}S_6$.

Insulin is a hormone responsible for regulating sugar levels in the body. Determining the formula was a very important step in working out the structure of insulin. Once the formula of insulin was established, scientists were able to carry out research on chemical reactions that could influence the way in which it operates in the body.

In this section, you will learn about ways in which the chemical formulae of compounds can be determined.

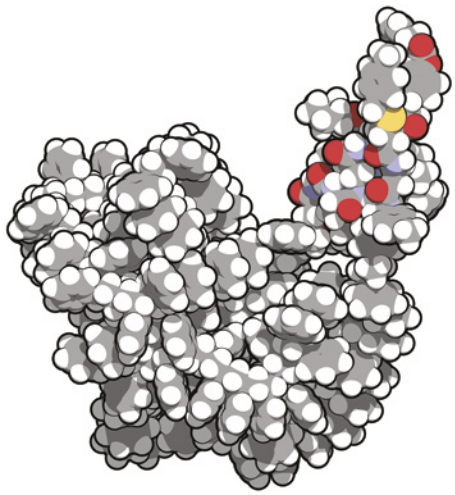


FIGURE 13.6.1 A representation of the chemical structure of the hormone insulin

CALCULATING PERCENTAGE COMPOSITION OF ORGANIC COMPOUNDS

The **percentage composition** of a compound tells you the proportion by mass of the different elements in that compound.

To determine the percentage composition by mass of a compound, divide the mass of each element present by the mass of the whole sample and express the result as a percentage.

$$\%\text{ by mass of an element in a compound} = \frac{\text{mass of the element present}}{\text{total mass of the compound}} \times 100$$

Worked example 13.6.1

CALCULATING PERCENTAGE COMPOSITION OF ORGANIC COMPOUNDS

2.85 g of an organic compound contains 1.52 g carbon, 0.45 g hydrogen and 0.88 g nitrogen. Determine the percentage composition of the compound.

Thinking	Working
Divide the mass of the first element by the total mass of the compound and multiply by 100.	$\%\text{ carbon} = \frac{\text{mass of carbon present}}{\text{total mass of the compound}} \times 100$ $= \frac{1.52}{2.85} \times 100$ $= 53.3\%$
Divide the mass of the second element by the total mass of the compound and multiply by 100.	$\%\text{ hydrogen} = \frac{\text{mass of hydrogen present}}{\text{total mass of the compound}} \times 100$ $= \frac{0.45}{2.85} \times 100$ $= 15.8\%$
Repeat the previous step for any further elements in the compound.	$\%\text{ nitrogen} = \frac{\text{mass of nitrogen present}}{\text{total mass of the compound}} \times 100$ $= \frac{0.88}{2.85} \times 100$ $= 30.9\%$
Add up all the elemental percentages to check that they equal 100%. (If they don't, then check your calculations and rounding off.)	If the calculations above are correct, then: total % elements = % carbon + % hydrogen + % nitrogen = 53.3 + 15.8 + 30.9 = 100%

Worked example: Try yourself 13.6.1

CALCULATING PERCENTAGE COMPOSITION OF ORGANIC COMPOUNDS

8.38 g of an organic compound contains 5.44 g carbon, 1.13 g hydrogen and 1.81 g oxygen. Determine the percentage composition of the compound. Give all answers to three significant figures.

USING PERCENTAGE COMPOSITION TO DETERMINE EMPIRICAL FORMULAE

Empirical formula

Atoms or ions are present in compounds in fixed whole number ratios. The **empirical formula** of a compound gives the simplest whole number ratio of elements in that compound. Table 13.6.1 contains some examples.

TABLE 13.6.1 Empirical formulae for some examples

Compound	Empirical formula	Simplest whole number ratio of elements in the compound
Water	H_2O	H : O 2 : 1
Ethene	CH_2	C : H 1 : 2
Calcium carbonate	$CaCO_3$	Ca : C : O 1 : 1 : 3

Determining empirical formulae

The empirical formula for a compound is determined from the mass of each element present in a given mass of the compound. These masses can be determined experimentally. Once the masses of elements in a compound are known, the steps in Figure 13.6.2 are followed to convert these masses to a mole ratio, that is, a ratio by number of atoms, and then to an empirical formula.

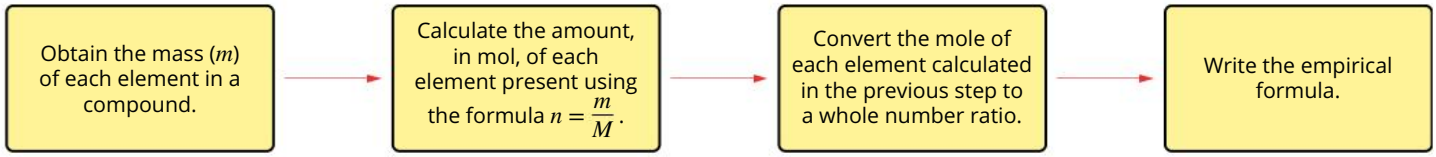


FIGURE 13.6.2 Follow these steps to calculate empirical formula.

Worked Example 13.6.2 shows how to calculate the empirical formula of an unknown organic compound.

Worked example 13.6.2

CALCULATING EMPIRICAL FORMULA FROM PERCENTAGE COMPOSITION

An organic compound is found to be composed of 52.2% carbon, 13.0% hydrogen and the remainder is oxygen. Calculate the empirical formula of the compound.

Thinking	Working
Assume there is 100 g of the compound, so percentages convert directly to masses. Write down the mass, in g, of all elements present in the compound.	C: 52.2 g H: 13.0 g O: 100 – 52.2 – 13.0 = 34.8 g
Calculate the amount, in mol, of each element in the compound using: $n = \frac{m}{M}$	$n(\text{C}) = \frac{52.2}{12.0}$ $= 4.35$ $n(\text{H}) = \frac{13.0}{1.0}$ $= 13.0$ $n(\text{O}) = \frac{34.8}{16.0}$ $= 2.18$
Simplify by dividing all of the numbers of moles by the smallest number of moles calculated above. This gives you a ratio of the elements by number of atoms.	$\text{C} = \frac{4.35}{2.18}$ $= 2.0$ $\text{H} = \frac{13.0}{2.18}$ $= 6.0$ $\text{O} = \frac{2.18}{2.18}$ $= 1.0$
Find the simplest whole number ratio.	C : H : O 2 : 6 : 1
Write the empirical formula.	C_2H_6O

Worked example: Try yourself 13.6.2

CALCULATING EMPIRICAL FORMULA FROM PERCENTAGE COMPOSITION

Chemical analysis of an organic compound present in the gaseous emissions from a factory shows that its percentage composition is 40.0% carbon, 6.7% hydrogen and the remainder is oxygen. Find its empirical formula.

ELEMENTAL ANALYSIS: MEASURING THE MASS OF EACH ELEMENT IN A COMPOUND

In the examples above, the mass of each element in the sample of the compound was provided. That information comes from an experiment called **elemental analysis**.

One way of performing an elemental analysis of an organic compound is to burn the compound in air. The combustion products (carbon dioxide and water) are absorbed by chemicals that have been previously weighed to determine the mass of the products produced.

- Carbon dioxide can be absorbed by sodium hydroxide solution.
- Water is absorbed in a drying agent such as magnesium perchlorate ($Mg(ClO_4)_2$).

The experimental apparatus is shown in Figure 13.6.3.

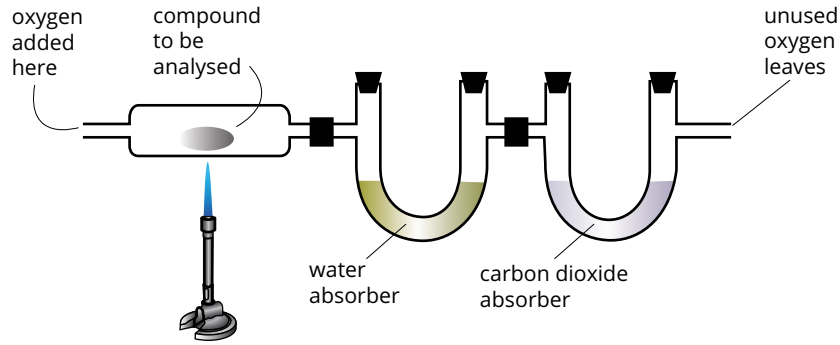


FIGURE 13.6.3 Experimental set-up for the elemental analysis of an organic compound.

The empirical formula of a hydrocarbon or a compound containing only carbon, hydrogen and oxygen can be calculated from the masses of carbon dioxide and water obtained by elemental analysis.

Determining the mass of carbon in the organic compound

Suppose an empirical formula calculation is being carried out on an organic compound containing only carbon, hydrogen and oxygen, using data from elemental analysis. From the mass of carbon dioxide produced, calculate the amount of carbon dioxide produced, in mol:

$$n(CO_2) = \frac{m}{M} = \frac{m}{44.01}$$

Since all the carbon in the organic compound ends up in the carbon dioxide produced, the amount of carbon dioxide produced, in mol, is equal to the amount of carbon in the organic compound, in mol:

$$n(C) = n(CO_2)$$

The mass of carbon in the organic compound can then be determined:

$$m(C) = n \times M = n \times 12.01$$

Determining the mass of hydrogen in the organic compound

From the mass of water produced, calculate the amount of water produced, in mol:

$$n(H_2O) = \frac{m}{M} = \frac{m}{18.016}$$

All the hydrogen in the organic compound ends up in the water produced. The amount of hydrogen in the organic compound, in mol, is twice the amount of water produced, in mol. This is because there are two hydrogen atoms in each molecule of water:

$$n(H) = 2 \times n(H_2O)$$

The mass of hydrogen in the organic compound can then be determined:

$$m(H) = n \times M = n \times 1.008$$

Determining the mass of oxygen in the organic compound

The amount of oxygen in the organic compound cannot simply be determined from the amount of oxygen present in both the carbon dioxide and water produced. This is because the oxygen present in the products comes from two sources—the organic compound and the oxygen gas that was added so that a combustion reaction could occur.

However, the mass of oxygen in the organic compound can be determined by subtracting the mass of carbon plus the mass of hydrogen from the original mass of the compound:

$$m(\text{O}) = m(\text{compound}) - m(\text{C}) - m(\text{H})$$

Once the mass of each element in the organic compound has been determined, the empirical formula can be determined using the steps outlined earlier in this section (Figure 13.6.4).

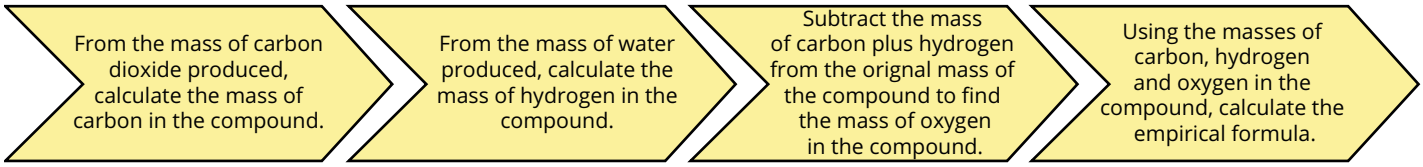


FIGURE 13.6.4 The steps taken to determine the empirical formula from data obtained by elemental analysis

Worked example 13.6.3

CALCULATING THE EMPIRICAL FORMULA OF A COMPOUND

A compound undergoes elemental analysis and was found to contain 24.0 g of carbon, 4.0 g of hydrogen and 32.0 g of oxygen. Determine the empirical formula of the compound.

Thinking	Working
Calculate the number of moles of carbon, hydrogen and oxygen using: $n = \frac{m}{M}$	$n(\text{C}) = \frac{24.0}{12.01} = 2.00\,\text{mol}$ $n(\text{H}) = \frac{4.0}{1.008} = 4.00\,\text{mol}$ $n(\text{O}) = \frac{32.0}{16.00} = 2.00\,\text{mol}$
Find the simplest whole number ratio.	C : H : O 1 : 2 : 1
Write the empirical formula.	CH_2O

Worked example: Try yourself 13.6.3

CALCULATING THE EMPIRICAL FORMULA OF A COMPOUND

A compound was found to contain 72 g of carbon and 18 g hydrogen. Determine the empirical formula of the compound.

Determining molecular formulae

The molecular formula of a compound can be determined if you know its empirical formula and its molar mass. Remember that the molar mass of a compound is the mass of one mole of the compound. For example, the molar mass of water (H_2O) is 18.016 g mol^{-1}. Figure 13.6.5 summarises the steps taken to determine the molecular formula from the empirical formula.

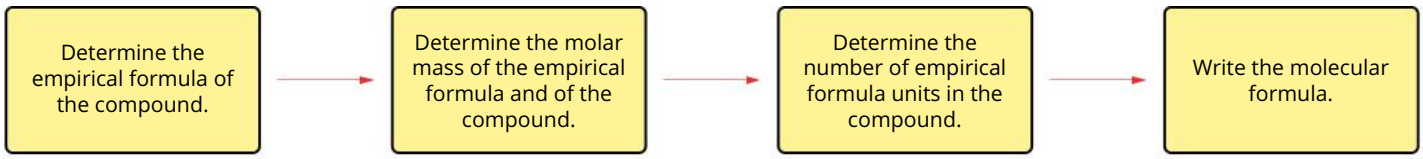


FIGURE 13.6.5 Follow these steps to calculate the molecular formula from the empirical formula.

Worked Example 13.6.4 shows how to calculate a molecular formula.

Worked example 13.6.4

CALCULATING THE MOLECULAR FORMULA OF A COMPOUND

A compound has the empirical formula CH_3. The molar mass of this compound is 30 g mol^{-1}. What is the molecular formula of the compound?

Thinking	Working
Calculate the molar mass, in g mol^{-1}, of one unit of the empirical formula.	$M(CH_3) = 12.01 + (3 \times 1.008)$ $= 15.03$
Determine the number of empirical formula units in the molecular formula.	Number of empirical formula units $= \dfrac{\text{molar mass}}{\text{molar mass of empirical formula unit}}$ $= \dfrac{30}{15.03}$ $= 2.0$
Multiply the empirical formula by this factor to determine the molecular formula of the compound.	The molecular formula is $2 \times CH_3$ i.e. C_2H_6

Worked example: Try yourself 13.6.4

CALCULATING THE MOLECULAR FORMULA OF A COMPOUND

A compound has the empirical formula CH. The molar mass of this compound is 78 g mol^{-1}. What is the molecular formula of the compound?

13.6 Review

SUMMARY

- Determining the chemical formula of an unknown compound is an important step in working out its chemical structure.
- The percentage composition of a compound is found by calculating:

$$\frac{\text{mass of the element present}}{\text{total mass of the compound}} \times 100$$

for each element in the compound.

- The empirical formula of a compound can be determined from the percentage composition of each element in the compound.
- The molecular formula of a compound can be determined from its empirical formula and its molar mass.

KEY QUESTIONS

1 If 6.84 g of an organic compound is found to contain 4.66 g of carbon, what is the percentage of carbon by mass in the compound?

A 31.8%
B 40.0%
C 60.0%
D 68.1 %

2 8.00 g of an organic compound is made up of 6.13 g carbon, 0.51 g hydrogen and the remainder is oxygen. Determine the percentage composition of the compound.

3 A clear liquid used for cleaning glass was found to consist of carbon, hydrogen and oxygen. Analysis showed it to be 60.0% carbon and 26.7% oxygen.

a Find the mass of each element in 100 g of the compound.
b Calculate the number of moles of each element from their masses.
c Calculate the simplest mole ratio of each element in the compound. Give your answer to three significant figures.
d Give the simplest mole ratio of carbon : oxygen : hydrogen as a whole number ratio.
e Write the empirical formula of the compound.

4 Mannitol is a sweet-tasting crystalline solid often found in lollies and chewing gum. Its empirical formula is $C_3H_7O_3$. It was determined that 0.8390 mol of mannitol has a mass of 152.7 g. Given this information, determine the molecular formula of mannitol.

5 Elemental analysis was conducted on a compound and it was found to contain 72.0 g of carbon, 18.0 g hydrogen and 48.0 g of oxygen. What is the empirical formula of the compound?

Chapter review

13

KEY TERMS

alcohol
aldehyde
alkane
alkene
alkyl group
amide
amide functional group
amine
carbonyl functional group
carboxyl functional group
carbonyl group
carboxylic acid
chain isomers
cis isomer
cis–trans isomers
combustion
condensation reaction
condensed formula
crude oil
dimer
dispersion force
electronegative
elemental analysis
empirical formula
ester
ester functional group
esterification reaction
functional group
geometric isomer
homologous series
hydrocarbon
hydrogen bonds
hydroxyl functional group
immiscible
isomer
IUPAC nomenclature
ketone
miscible
molecular formula
organic molecule
percentage composition
positional isomer
primary alcohol
primary amine
saturated
secondary alcohol
semistructural formula
stem name
structural formula
structural isomer
tertiary alcohol
tetrahedral
trans isomer
valence shell electron pair repulsion (VSEPR) theory

Diversity of carbon compounds

1 Why can carbon form so many compounds?

2 Which one of the following best describes a homologous series?

A compounds in which successive members differ by one carbon and two hydrogen atoms
B a series of compounds that exist in different physical forms
C compounds in which each member differs from the previous one by a $–CH_3$ group
D compounds with the same molecular formula but different arrangements of atoms

3 The formula of a hydrocarbon is $C_{16}H_{34}$.

a To which homologous series does it belong?
b What is the formula of the next hydrocarbon in the homologous series?
c What is the formula of the previous hydrocarbon in the same homologous series?
d What mass of carbon is present in 275 g of the hydrocarbon $C_{16}H_{34}$?

4 Draw the structural formulae and give the systematic names of:

a CH_3CH_3
b $CH_3CH(CH_3)_2$
c $CH_3CH_2CH(CH_3)CH_2CH_3$
d $CH_3(CH_2)_3CH_3$

5 Draw the structural formulae and give the systematic names of all the isomers of butene.

Functional groups

6 Choose the correct response to complete the following sentences to explain why alcohols dissolve in water.

An alcohol molecule contains the carboxyl/hydroxyl functional group. This group is non-polar/polar and can form covalent/hydrogen/ionic bonds with water molecules. These intramolecular/intermolecular bonds enable all/large/small alcohol molecules to dissolve in water.

7 Identify whether each statement is true or false.

a A functional group affects the chemical properties of a molecule.
b The name of the –OH group in an organic molecule is a hydroxyl functional group.
c Alcohols contain the carboxyl functional group.

8 Which one of the following is a correct condensed structural formula for a carboxylic acid?

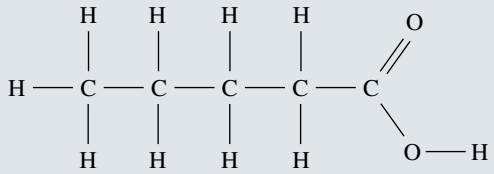
A $CH_3CH_2CH_2OH$
B CH_2CHCH_3
C CH_3COOCH_3
D CH_3CH_2COOH

9 Two carboxylic acid molecules can bond together to form a dimer. In this dimer, which one of the following is the strongest form of bonding between the two molecules?

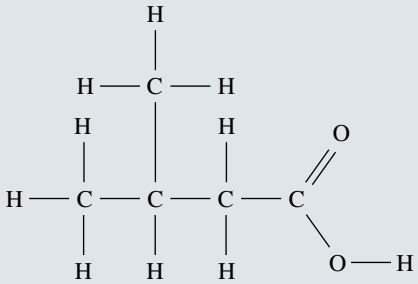
A hydrogen bonding
B dipole–dipole attraction
C dispersion forces
D carbon–oxygen bonding

10 Write the systematic names of these carboxylic acids, based on their structural formulae.

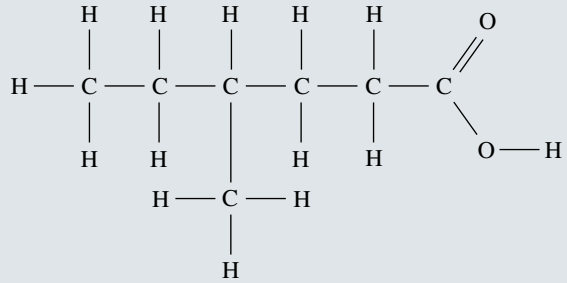
a



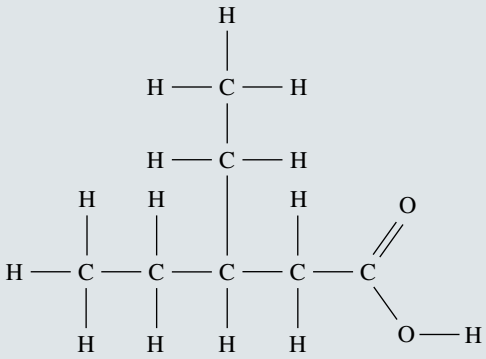
b



c



d



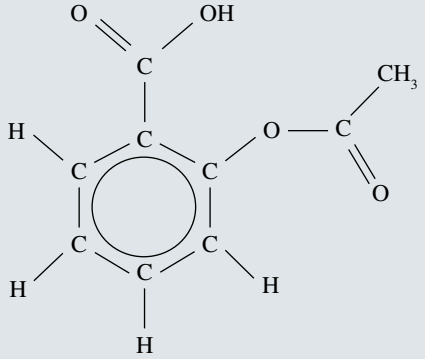
11 Draw the structural formulae of the following esters and then name them.

a CH_3COOCH_3

b $CH_3COOCH_2CH_3$

c $CH_3CH_2COOCH_2CH_3$

12 This is the structure of aspirin (acetylsalicylic acid).



a Identify the ester functional group in the structure of aspirin.

b Draw the structure of the alcohol and carboxylic acid that reacted together to produce aspirin.

13 What is the structural difference between an aldehyde, a ketone, a carboxylic acid and an amide?

Properties of organic compounds

14 The following table lists the boiling points of the first five alkanes and alcohols (hydroxyl group on carbon number 1).

Numbers of carbon atoms	Boiling point of alkane (°C)	Boiling point of alcohol (°C)
1	−162	65
2	−89	79
3	−42	97
4	0	117
5	36	138

Explain why the alcohols have a higher boiling point than their corresponding alkane.

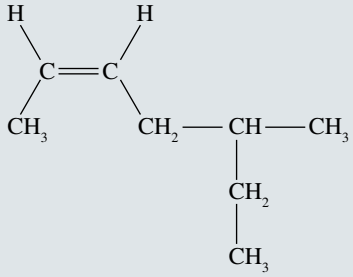
15 Explain why butan-1-ol has a higher boiling point than methanol.

16 Explain why the solubilities of carboxylic acids in water decrease as the length of their carbon chain increases.

Isomers overview

17 Draw the structure of *trans*-methylpent-2-ene.

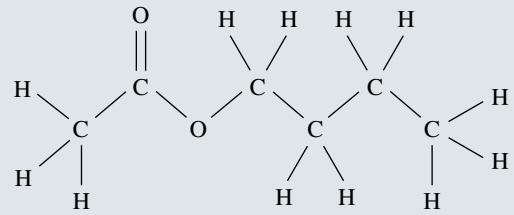
18 Write the name of this alkene.



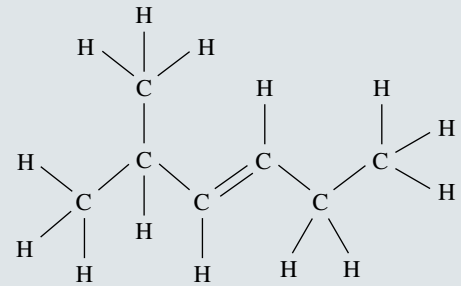
IUPAC nomenclature overview

19 Name each of the following molecules.

a



b



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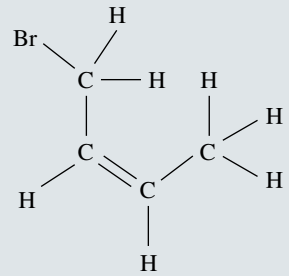


20 Draw the structure of:

a heptyl propanoate

b *cis*-4-iodo-3-methylpent-2-ene

c 3-methylbutan-1-amine.

Determining formulae of organic compounds

21 A sample of an unknown hydrocarbon was found to contain 92.3% carbon by mass. The mass of carbon in the sample was 1.15 g. Determine the mass of hydrogen in the sample.

22 Using the empirical formula and the relative molecular mass, determine the molecular formulae of the following compounds.

Empirical formula	Relative molecular mass ($g\,mol^{-1}$)	Molecular formula
CH	78.0	
CH_3	30.0	
CH_2O	90.0	
C_3H_6O	116.0	
CH_2	98.0	

23 A hydrocarbon contains 85.7% carbon and its molar mass is between 40 and 50 $g\,mol^{-1}$.

a Calculate the empirical formula of the hydrocarbon.

b Determine its molecular formula.

c To which homologous series does the compound belong?

24 An organic compound has the following percentage composition: 40.0% carbon, 6.7% hydrogen and 53.3% oxygen.

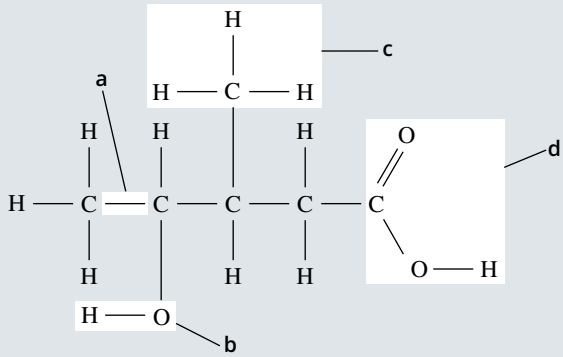
a Determine the empirical formula of the organic compound.

b 0.250 mol of this compound has a mass of 15.0 g. Using this information, determine the molecular formula of this organic compound.

25 A 1.50 g sample of a hydrocarbon undergoes complete combustion to produce 4.40 g of carbon dioxide and 2.70 g of water. What is the empirical formula of this compound?

Connecting the main ideas

26 Identify the structures or functional groups labelled a, b, c and d.



27 Prepare a poster that summarises the rules for the systematic naming of carbon compounds.

28 Explain the following.

a The first member of the alkene homologous series is ethene, not methene.

b Carbon compounds usually have four covalent bonds around each carbon atom.

29 Labels on margarine and oil often include one of the following terms: polyunsaturated, mono-unsaturated, saturated.

a What do you think each of these terms means?

b Check some food containers at home or in a supermarket and note the details on any labels that include these terms.

30 Explain why each of these names is incorrect, then determine its correct name.

a but-4-ene

b 2-chloro-3-ethylbutane

c 2,2-dimethylpent-3-ene

d 1-bromo-1,1-dipropylmethane

31 The condensed structural formulae of some organic compounds are given below. For each compound:

i identify the homologous series to which it belongs

ii give its systematic name.

a $CH_3(CH_2)_5CH_2OH$

b $CH_3(CH_2)_2CHCl(CH_2)_2CH_3$

c $CH_3CHOH(CH_2)_3CH_3$

d $CH_3(CH_2)_3COOH$

e $CH_3CH_2CHNH_2CH_3$

f $(CH_3)_2CH(CH_2)_5CH_3$

g $(CH_3)_2C{=}CH_2$

CHAPTER

14 Reactions of organic molecules

Life on Earth is carbon based. This is because the structures of living things on Earth are based mainly on organic compounds whose structures have a carbon skeleton. The growth and decay of living things involve a series of reactions in which these organic compounds are made, decomposed or changed from one form to another.

Organic reactions occur in life processes such as photosynthesis and respiration in plants, as well as in building muscle and other tissues, digesting food and the decay of dead organisms. The industrial manufacture of paints, plastics, pharmaceuticals and foods also involve organic reactions.

At the end of this chapter, you will be able to describe some specific chemical reactions involving organic compounds, including oxidation, addition and condensation reactions. You will learn that the functional groups of compounds are usually involved in chemical reactions and, thus, members of a homologous series usually undergo similar reactions because they have the same functional group.

Science as a human endeavour

Scientific knowledge can be used to design alternative chemical synthesis pathways, taking into account sustainability, local resources, economics and environmental impacts (green chemistry), including the production of ethanol and biodiesel.

Science understanding

- organic molecules have a hydrocarbon skeleton and can contain functional groups, including alkenes, alcohols, aldehydes, ketones, carboxylic acids, esters, amines and amides; functional groups are groups of atoms or bonds within molecules which are responsible for the molecule's characteristic chemical properties
- functional groups within organic compounds display characteristic chemical properties and undergo specific reactions; these reactions include addition reactions of alkenes, redox reactions of alcohols, and acid–base reactions of carboxylic acids; these reactions can be used to identify the functional group present within the organic compound
- all alcohols can undergo complete combustion; with oxidising agents, including acidified MnO_4^- or $Cr_2O_7^{2-}$, oxidation of primary alcohols produces aldehydes and carboxylic acids, while the oxidation of secondary alcohols produces ketones; these reactions have characteristic observations and can be represented with equations
- alcohols can react with carboxylic acids in a condensation reaction to produce esters and can be represented with equations
- chemical synthesis processes may involve the construction of reaction sequences with more than one chemical reaction, including the hydration of ethene to form ethanol and the subsequent reaction of ethanol with acetic (ethanoic) acid to produce ethyl ethanoate

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14.1 Chemical properties of alkenes

FIGURE 14.1.1 Vegetable oils are organic compounds that can be converted to margarine by reacting them with hydrogen gas.

The properties and reactions of an organic compound are largely determined by the functional groups in the compound. As all members of a homologous series have the same functional group, the members of that series typically undergo the same type of reactions.

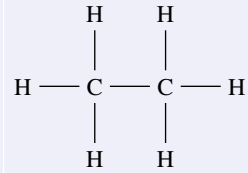
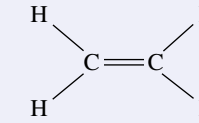
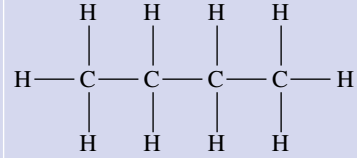
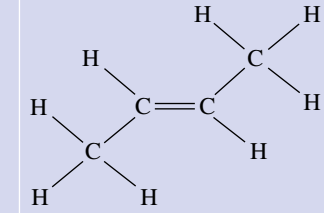
For example, alkenes are a homologous series of compounds that contain a carbon–carbon double bond. Vegetable oils are liquids that contain alkene molecules that have one or more carbon–carbon double bonds. Vegetable oils react with hydrogen gas to form semisolid substances that have a consistency suitable for spreading on bread. These semisolid products (for example, margarine) provide an alternative to **saturated** fats, such as those found in butter (Figure 14.1.1).

The production of margarine involves an addition reaction. In this section, you will learn about addition reactions and other typical reactions that alkenes undergo and the reaction conditions required.

REACTIONS OF ALKENES

Alkenes and alkanes are hydrocarbons. Hydrocarbons are molecules that contain only the elements hydrogen and carbon. Alkenes are described as **unsaturated** hydrocarbons because they contain a carbon–carbon double bond. You studied the structure and naming of alkanes and alkenes in Year 11 Chemistry and in Chapter 13. Some examples are listed in the Table 14.1.1.

TABLE 14.1.1 Nomenclature and structures for some simple straight chain alkanes and alkenes

Alkane name	Formula	Structure	Alkene name	Formula	Structure
ethane	C_2H_6		ethene	C_2H_4	
butane	C_4H_{10}		but-2-ene	C_4H_8	

Combustion in air

You have previously learnt that alkanes are rather unreactive, but burn in oxygen to produce carbon dioxide and water. This releases heat, thus making alkanes good fuels. Alkenes also burn in an excess of oxygen to produce carbon dioxide and water. The equation for the combustion of ethene is:

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

Note that in a limited supply of oxygen, incomplete combustion can occur and carbon monoxide is produced instead of carbon dioxide. The equation for the incomplete combustion of ethene is:

$$C_2H_4(g) + 2O_2(g) \rightarrow 2CO(g) + 2H_2O(g)$$

Addition reactions of alkenes

The carbon–carbon double bond in alkenes has a significant effect on the chemical properties of the homologous series. Alkenes are generally more reactive compounds than alkanes, which contain only single bonds. The reactions of alkenes usually involve the addition of a small molecule across the double bond. These reactions are called **addition reactions** because two reactants combine (or add) to give a single product.

During addition reactions:

- two reactant molecules combine to form one product molecule
- the carbon–carbon double bond of the alkene becomes a single bond
- an unsaturated compound becomes saturated
- the atoms of the small molecule adding to the alkene are 'added across the double bond'. The small molecule splits into two parts, which add to either end of the original double bond. This can be seen in the reaction of hydrogen bromide with ethene in Figure 14.1.2.

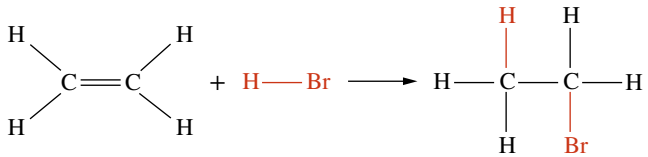


FIGURE 14.1.2 The reaction between ethene and hydrogen bromide. This is an example of an addition reaction between an alkene and a hydrogen halide.

When ethene reacts with hydrogen bromide, an addition reaction occurs and bromoethane is the only product. During this reaction, the hydrogen atom from the HBr molecule forms a covalent bond to one carbon atom in the double bond of ethene and the bromine atom forms a bond to the other carbon atom. Unlike substitution reactions (see Revision box), there is no **inorganic** product formed. All the atoms in the reactants end up in the final product.

REVISION

Substitution reactions

In Year 11 Chemistry, you learnt that alkanes undergo a type of reaction called substitution. A **substitution reaction** occurs when an atom or functional group in a molecule is replaced or 'substituted' by another atom or group.

Alkanes undergo substitution reactions with halogens, such as chlorine and bromine, to produce haloalkanes. 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 shown 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.

There are four different types of addition reactions of alkenes that you need to learn about. These were all introduced in Year 11 Chemistry and are explained in detail below.

Reactions of alkenes with hydrogen

Alkenes react with hydrogen gas in the presence of a metal catalyst, such as nickel, to form alkanes. This reaction is known as a hydrogenation reaction and forms a saturated alkane. The reaction shown in Figure 14.1.3 is the hydrogenation of ethene with hydrogen gas to produce ethane.

The activation energy for this reaction is too high for the reaction to proceed at room temperature without a catalyst.

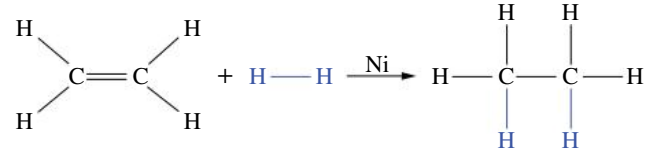


FIGURE 14.1.3 The addition reaction of ethene with hydrogen to form the saturated alkane, ethane. Note that nickel is used as a catalyst in this reaction.

Reactions of alkenes with halogens

Figure 14.1.4 shows the reaction of ethene with bromine to form 1,2-dibromoethane. The halogen adds across the double bond of the molecule, so in the product there is one bromine atom attached to each carbon atom.

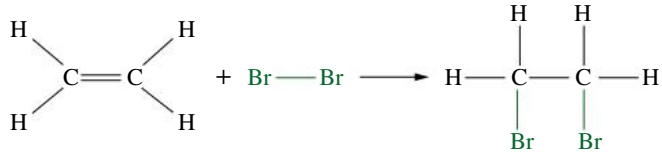


FIGURE 14.1.4 The addition reaction of ethene with bromine produces 1,2-dibromoethane.

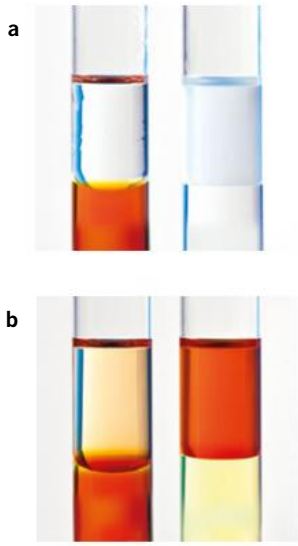


FIGURE 14.1.5 (a) When an alkene is added to aqueous bromine, the alkene reacts with the coloured bromine and the solution loses colour. (b) When an alkane is added to aqueous bromine, no addition reaction occurs and so the colour remains.

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 disubstituted haloalkanes.

Bromine is often used to test for the presence of a carbon–carbon double bond because of the ease and speed with which it reacts with an alkene. The orange colour of the bromine quickly disappears when it is mixed with an alkene (Figure 14.1.5).

Reactions of alkenes with hydrogen halides

Just as you saw with the reaction of ethene and hydrogen bromide, but-2-ene reacts with hydrogen chloride, a **hydrogen halide**, in an addition reaction. Figure 14.1.6 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.

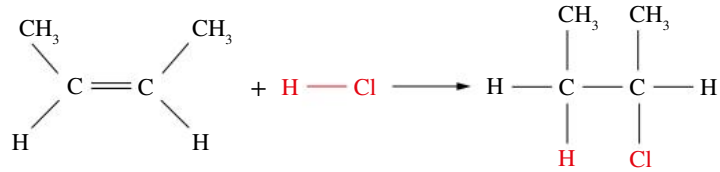


FIGURE 14.1.6 The addition reaction of but-2-ene with hydrogen chloride produces 2-chlorobutane.

However, as Figure 14.1.7 shows, when hydrogen chloride reacts with but-1-ene, two products are possible.

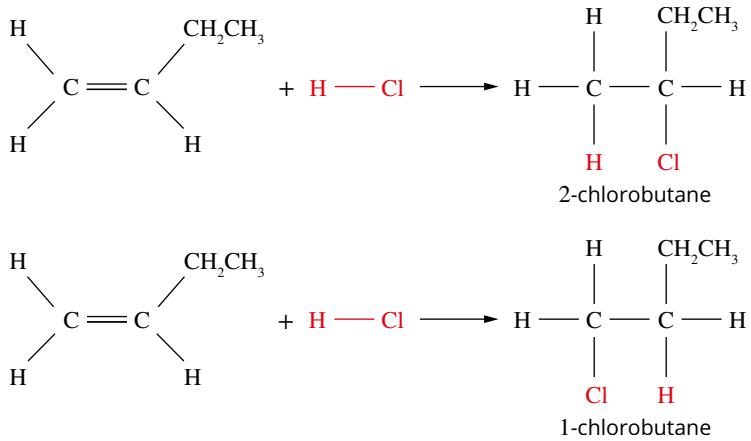


FIGURE 14.1.7 The addition reaction of but-1-ene with hydrogen chloride. Two isomers are possible as products.

The addition reaction can produce two isomers. In one product, the hydrogen atom from the hydrogen chloride molecule has been added to the carbon atom in the carbon–carbon double bond at the end of the but-1-ene molecule (C1). In the other product, the hydrogen atom has been added to a carbon atom at the other end of the carbon–carbon double bond (C2).

When you react an asymmetrical alkene with an asymmetrical reactant, as is the case in Figure 14.1.7, isomers are produced. More of one isomer is usually produced than the other because one of the reactions is more likely to occur than the other. The reasons for this depend on the 'mechanism' for the reaction, which is beyond the scope of Year 12 Chemistry.

Reactions of alkenes with water

Alkenes react with water under specific conditions to form the corresponding alcohol. For example, an addition reaction of ethene and water, using an inorganic acid catalyst, will produce ethanol. Figure 14.1.8 shows the addition reaction of steam and ethene, using a phosphoric acid catalyst. This reaction is used in industry for the production of ethanol.

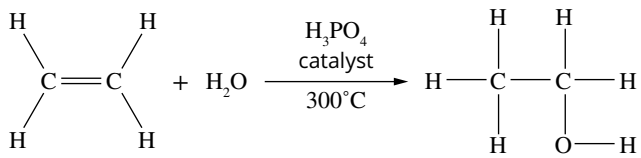


FIGURE 14.1.8 The addition reaction of ethene with water in the presence of a phosphoric acid catalyst produces ethanol.

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.

The reaction of ethene with steam is often described as a **hydration reaction**. Hydration reactions involve water as a reactant. 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 nature of the reaction system means it is easy for manufacturers to remove the product from the reaction mixture, leaving the catalyst intact.

Reactions that involve water as a reactant are referred to as hydration reactions.

Addition polymerisation

Alkenes can also react with each other in addition reactions to form **polymers** (meaning 'many units'). The reaction of ethene with itself to form polyethene, shown in Figure 14.1.9, is an example of an **addition polymerisation** process. The small molecule that undergoes the addition reaction (ethene) is called a **monomer** ('one unit'). Several thousand ethene monomers usually react to make one molecule of polyethene. (Polymerisation is covered in more detail in Chapter 15.)

Other alkenes react in a similar way. For example, propene forms polypropene and butene forms polybutene.

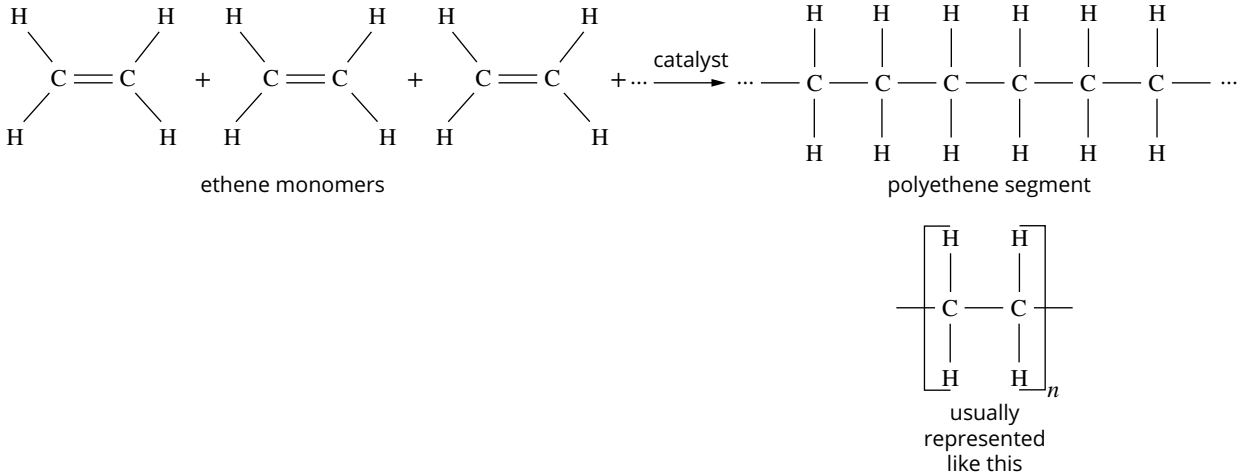


FIGURE 14.1.9 Thousands of ethene monomers join together in an addition reaction to make one chain of polyethene. The standard notation shown on the right simplifies the drawing of such a large chain.

CHEMFILE

Making margarine

The raw materials used to make many margarines include vegetable oils. Most vegetable oils are liquids and so cannot be spread on bread in the same way as butter.

Vegetable oils contain long hydrocarbon chains that are polyunsaturated; that is, they contain a number of carbon–carbon double bonds. If some of these double bonds are converted to single bonds, the molecules can pack more closely, resulting in stronger dispersion forces between the molecules and therefore higher melting points. The liquids become semisolids and the product is then suitable for spreading.

One of the steps in making margarine from a vegetable oil usually involves reacting vegetable oils with hydrogen gas, using a metal catalyst such as nickel. In this step, some of the carbon–carbon double bonds react with the hydrogen in an addition reaction, and are converted into single bonds, as shown in Figure 14.1.10.

Note that in this type of diagram the carbon and hydrogen atoms are not represented by letters. Each 'kink' in the long chains represents a carbon atom with two hydrogen atoms attached. Where a double bond is shown, each carbon atom in the double bond has only one hydrogen atom attached to it.

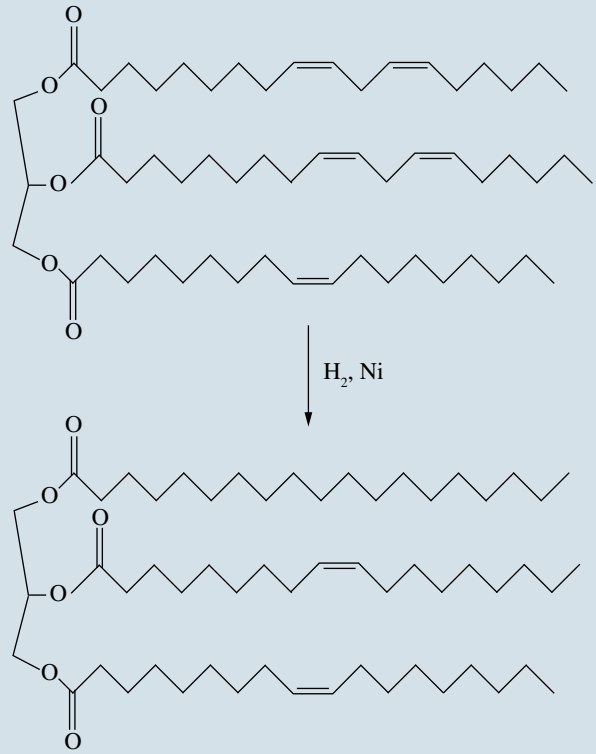


FIGURE 14.1.10 Hydrogenation of some of the carbon–carbon double bonds in a vegetable oil can convert it from a liquid into a 'spreadable' semisolid.

14.1 Review

SUMMARY

- Alkenes burn in the presence of oxygen to produce carbon dioxide and water.
- 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
  - halogens to produce dihaloalkanes
  - hydrogen halides to produce haloalkanes
  - water and an inorganic acid catalyst to produce alcohols.
- Alkenes undergo addition polymerisation reactions to form polymers containing only carbon–carbon single bonds.

KEY QUESTIONS

1 Name the products formed when ethene reacts with:
- **a** hydrogen chloride
- **b** chlorine
- **c** water
- **d** hydrogen.

2 Use structural formulae to write equations and name the products for the reactions of:
- **a** but-1-ene with chlorine
- **b** but-2-ene with hydrogen bromide.

3 Name the organic products formed when each of the following pairs of compounds react.
- **a** Ethene and water in the presence of sulfuric acid
- **b** Hex-3-ene and hydrogen chloride

4 Write equations for the production of:
- **a** propane from propene
- **b** 2,3-diiodobutane from but-2-ene
- **c** pentan-3-ol from pent-2-ene.

5 Write the structural formula (showing all atoms and bonds) of the alkene that could be used to produce:
- **a** 2,3-dibromohexane
- **b** 3-chloropentane.

14.2 Chemical properties of alcohols

FIGURE 14.2.1 Ethanol (*álcool*) is used as a fuel in Brazil and is cheaper than petrol (*gasolina*), although petrol delivers better fuel consumption.

As you learnt in section 14.1, alcohols can be produced by addition reactions of alkenes. Ethanol is the most widely used alcohol in society. You may have seen E10 fuel being sold at your local service station. The E10 classification indicates that the petrol contains 10% ethanol. In Brazil, ethanol fuels are widely used, with the percentage of ethanol being a minimum of 20–25% (Figure 14.2.1). Some cars have been developed to run on 100% ethanol. The ethanol in Brazil is considered a renewable biofuel because it is sourced from the fermentation of sugar cane. The combustion of bioethanol for fuel was studied in Year 11 Chemistry and you will study the synthesis of biodiesel as a further example of a biofuel in Chapter 16.

The presence of the hydroxyl functional group means ethanol has very different properties from ethene or chloroethane. These properties make ethanol useful in a wide variety of applications. Ethanol is a liquid at room temperature and is highly soluble in water because of its ability to form hydrogen bonds. It is widely used as a solvent in cosmetics and pharmaceuticals, as well as in alcoholic drinks such as wine, beer and spirits. When consumed, ethanol acts as a depressant on the human body, slowing reactions and responses. Excess ethanol consumption also blocks the production of antidiuretic hormones, increasing urination and resulting in dehydration.

In this section, you will examine some of the common reactions that alcohols undergo.

COMBUSTION OF ALCOHOLS

FIGURE 14.2.2 Burning brandy is sometimes poured over a Christmas pudding to add flavour. Brandy can contain as much as 40% ethanol.

Just like alkanes and alkenes, alcohols burn readily in air to form carbon dioxide and water as products. The equation for the combustion of ethanol is:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

This is a highly exothermic reaction, so ethanol is used as a fuel. On a smaller scale, methylated spirits, which contains about 95% ethanol mixed with other chemicals, is used as a fuel for camping stoves. Some cooking techniques make use of the burning of alcohol for effect and flavour. Figure 14.2.2 shows how the ethanol in brandy can burn as it is added to enhance the flavour of a Christmas pudding.

Oxidation of alcohols

The combustion of alcohols and other fuels can be classified as a type of oxidation–reduction (redox) reaction. Alcohols can also be oxidised by strong inorganic oxidising agents such as acidic solutions of potassium dichromate ($K_2Cr_2O_7$) and potassium permanganate ($KMnO_4$). The products of these oxidation reactions depend on the type of alcohol involved.

Alcohols can be classified (see Chapter 13) into three types—primary, secondary or tertiary—depending on the position of the hydroxyl group within the molecule.

- **Primary alcohols** have the –OH group bonded to a carbon that is attached to only one alkyl group. These alcohols first oxidise to form **aldehydes** and then further oxidation forms the corresponding carboxylic acids.
- **Secondary alcohols** have the –OH group bonded to a carbon that is attached to two alkyl groups. These alcohols oxidise to form **ketones**.
- **Tertiary alcohols** have the –OH group bonded to a carbon that is attached to three alkyl groups. These alcohols are not oxidised by the oxidising agents listed above.

You can see in Figure 14.2.3 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.

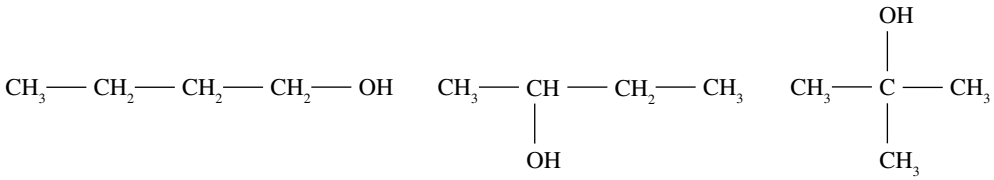


FIGURE 14.2.3 Structures of some primary, secondary and tertiary alcohols

Oxidation of primary alcohols

Figure 14.2.4 shows how a primary alcohol can be oxidised to a carboxylic acid in two stages.

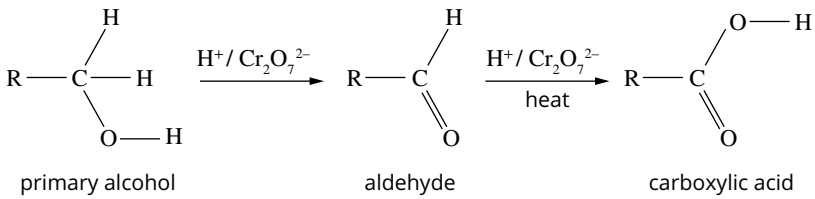


FIGURE 14.2.4 The general reaction for the oxidation of a primary alcohol

In the first stage, the primary alcohol is oxidised to an aldehyde. In the second stage, further heating of the reaction mixture in the presence of the oxidising agent oxidises the aldehyde to a carboxylic acid.

The example in Figure 14.2.5 shows that propan-1-ol is oxidised first to propanal (an aldehyde) and then to propanoic acid (a carboxylic acid).

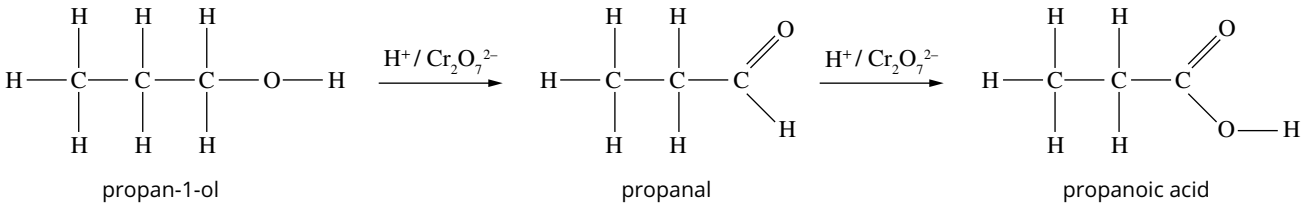


FIGURE 14.2.5 Reactions for the oxidation of the primary alcohol propan-1-ol

If the required product is an aldehyde, production must occur under milder conditions (lower temperatures and shorter reaction times), and the aldehyde can be distilled from the reaction mixture as it is formed so that it is not oxidised further. If the required product is the carboxylic acid, higher temperatures and longer reaction times are adhered to.

Aldehydes are produced as an intermediate in the oxidation of a primary alcohol to a carboxylic acid. If an aldehyde is the required product, it can be distilled off as it forms to prevent further oxidation.

Oxidation of secondary alcohols

When secondary alcohols are oxidised by strong oxidising agents, such as solutions of acidified potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$), the corresponding ketones are produced. Figure 14.2.6 gives the general reaction for the oxidation of secondary alcohols to ketones.

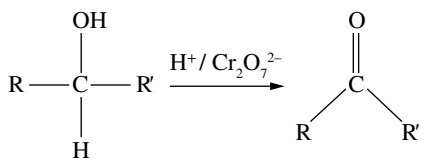


FIGURE 14.2.6 The general reaction for the oxidation of a secondary alcohol. The R groups in the structures represent different alkyl groups.

Figure 14.2.7 gives the equation to produce the ketone propanone by the oxidation of the secondary alcohol propan-2-ol. Propanone is commonly known as acetone and is a common solvent used in nail polish remover and glues.

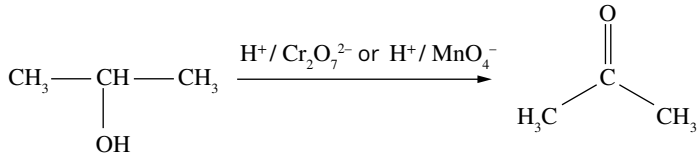


FIGURE 14.2.7 The secondary alcohol propan-2-ol can be oxidised to propanone.

Tertiary alcohols are not normally oxidised by heating in the presence of a strong oxidant such as acidified dichromate or acidified permanganate.

Tertiary alcohols and oxidising agents

Tertiary alcohols are resistant to reaction with solutions of acidified potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$).

During the oxidation of alcohols, there is an increase in the number of C–O bonds and a simultaneous decrease (at the same carbon atom) in the number of C–H bonds. In tertiary alcohols, the carbon attached to the hydroxyl group does not have a C–H bond to break, so oxidation cannot occur at that carbon atom.

Colour changes in oxidation reactions

The strong oxidising agents potassium dichromate and potassium permanganate are both highly coloured due to the presence of the transition metal elements chromium (Cr) and manganese (Mn).

A solution of dichromate ions in water is orange. When this acidified dichromate solution is used to oxidise a primary or secondary alcohol, the dichromate is reduced to the chromium ion (Cr^{3+}), which is green. 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 14.2.8.

The rate of reaction may also help to distinguish a primary alcohol from a secondary alcohol. A primary alcohol will usually react faster than a secondary alcohol of similar chain length.

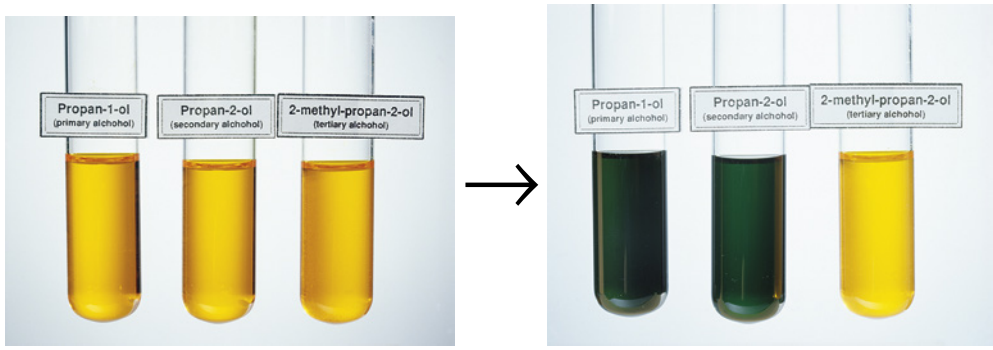


FIGURE 14.2.8 Solutions of the primary alcohol propan-1-ol and secondary alcohol propan-2-ol with acidified potassium dichromate change from orange to green on heating. Tertiary alcohols such as 2-methylpropan-2-ol will not react under these conditions, so no colour change is observed.

A solution of acidified potassium permanganate is a deep purple colour. When this solution reacts with primary or secondary alcohols, the manganese in the permanganate ion (MnO_4^-) is reduced to Mn^{2+}, which is a very, very pale pink and appears colourless. Tertiary alcohols do not react, so there is no change in the colour of the solution (Figure 14.2.9). As for the reaction with dichromate ions, the rate of reaction of primary alcohols with permanganate ions is usually greater than it is for secondary alcohols.

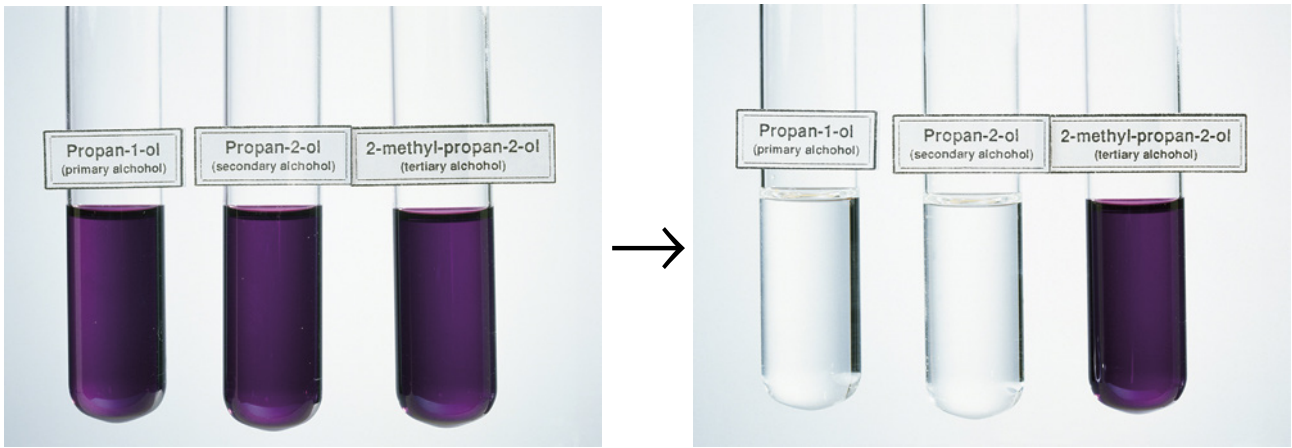


FIGURE 14.2.9 The strong oxidising agent potassium permanganate is deep purple in colour. On reaction with primary and secondary alcohols, the colour changes from purple to colourless. The tertiary alcohol is resistant to oxidation under these conditions and does not react, so the solution does not change colour.

Table 14.2.1 summarises the reactions of primary, secondary and tertiary alcohols with an acidified solution containing dichromate or permanganate ions.

These reactions, and the associated colour changes can be used to determine whether a given alcohol is a primary, secondary and tertiary alcohol.

TABLE 14.2.1 Summary of the oxidation reactions of primary, secondary and tertiary alcohols with acidified dichromate solution or acidified permanganate solution

Type of alcohol	Oxidising agent	Products
Primary (1°)	Acidified dichromate solution or acidified permanganate solution	Aldehydes (under mild conditions) Carboxylic acids (at higher temperatures and longer reaction times)
Secondary (2°)	Acidified dichromate solution or acidified permanganate solution	Ketones
Tertiary (3°)	Acidified dichromate solution or acidified permanganate solution	No products because tertiary alcohols are resistant to oxidation by these oxidising agents

Writing equations for oxidation of alcohols

The reactions that take place when alcohols react with oxidising agents, such as acidified dichromate or permanganate ions, are redox reactions. To write balanced equations for the reactions, you write oxidation and reduction half-equations and combine them to construct overall equations for these reactions, as you learnt in Chapter 8.

For example, the oxidation of ethanol with acidified potassium dichromate can be represented by the following equations.

Oxidation half-equation:

$$C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$$

Reduction half-equation:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

Overall equation:

$$3C_2H_5OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$$

Another example is the oxidation of propan-1-ol with acidified potassium permanganate under mild conditions to give the aldehyde.

Oxidation half-equation:

$$C_3H_7OH(aq) \rightarrow C_3H_6O(aq) + 2H^+(aq) + 2e^-$$

Reduction half-equation:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

Overall equation:

$$5C_3H_7OH(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5C_3H_6O(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$$

Worked example 14.2.1

WRITING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Propan-1-ol is oxidised to propanoic acid by acidified potassium permanganate.
Write the half-equations for the reaction and hence write the balanced overall equation.

Thinking	Working
Write the half-equation for the oxidation of the alcohol.	$C_3H_7OH(aq) + H_2O(l) \rightarrow C_3H_6O_2(aq) + 4H^+(aq) + 4e^-$
Write the half-equation for the reduction of the oxidising agent. (This can normally be found in your Chemistry Data Booklet.)	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
Multiply one equation or both equations by a suitable factor to ensure that the number of electrons is balanced.	$5C_3H_7OH(aq) + 5H_2O(l) \rightarrow 5C_3H_6O(aq) + 20H^+(aq) + 20e^-$ $4MnO_4^-(aq) + 32H^+(aq) + 20e^- \rightarrow 4Mn^{2+}(aq) + 16H_2O(l)$
Add the oxidation and the reduction half-equations together, cancelling out electrons so that none are in the final equation. Cancel out any species, such as H_2O or H^+, that appear on both sides of the equation.	$5C_3H_7OH(aq) + 4MnO_4^-(aq) + 12H^+(aq) \rightarrow 5C_3H_6O(aq) + 4Mn^{2+}(aq) + 11H_2O(l)$

Worked example: Try yourself 14.2.1

WRITING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Butan-1-ol is oxidised with acidified sodium dichromate under mild conditions to form butanal.

Write the half-equations for the reaction and hence write the balanced overall equation.

14.2 Review

SUMMARY

- Alcohols burn in the presence of oxygen to produce carbon dioxide and water.
- Alcohols react with oxidising agents, such as acidified solutions of dichromate ions and 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.
- Oxidation reactions can be used to identify the different types of alcohols.
- The different types of reactions you have studied in this module can be represented by chemical equations.

KEY QUESTIONS

1 Pentan-3-ol, 2-methylbutan-2-ol and pentan-1-ol are all isomers of $C_5H_{12}O$.

a Write an equation for the complete combustion of $C_5H_{12}O$.

b Identify each isomer as a primary, secondary or tertiary alcohol.

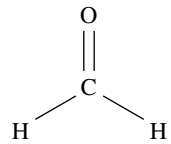
c For each isomer, show the reaction (using structural formulae—no balanced equations required) for all the reactions that would occur if the alcohol was heated with acidified potassium permanganate solution. Describe any colour changes that would be observed.

2 Give the name and structural formula for the alcohols that would produce the following products when oxidised with acidified dichromate.

a butanal

b 3-hexanone

c



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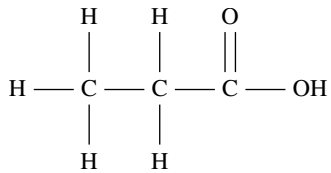


3 Show the oxidation and reduction half-equations and the balanced redox equation for any reaction that occurs when the following are mixed.

a Propan-2-ol is heated with acidified permanganate solution.

b Butan-1-ol is heated with acidified dichromate solution.

14.3 Chemical properties of carboxylic acids

FIGURE 14.3.1 The ripening of blackberries involves many chemical reactions, including the conversion of carboxylic acids to esters.

Molecules that contain the carboxylic acid functional group are common in the natural world and are present in most plants. The sour taste of vinegar, lemons, yoghurt, rhubarb and most unripe fruits is due to the presence of carboxylic acids.

When fruits and berries, such as the blackberries in Figure 14.3.1, ripen, complex reactions take place. These include the conversion of carboxylic acids to other compounds. In some of these reactions, carboxylic acids react with alcohol molecules to produce esters. Esters give many fruits their characteristic aromas and tastes.

IONISATION IN WATER

You will remember from Chapter 4 that ethanoic (acetic) acid is a weak acid and only ionises to a small extent in water to form hydronium ions. Most carboxylic acids are weak acids and react with water in a similar way (Table 14.3.1).

TABLE 14.3.1 Acid ionisation constants (equilibrium constants) for two common inorganic acids and two common carboxylic acids

Acid	Formula	K_a at 25°C
Nitric acid	HNO_3	2.4×10^{1}
Hydrochloric acid	HCl	1.3×10^{6}
Ethanoic acid	CH_3COOH	1.8×10^{-5}
Methanoic acid	HCOOH	1.8×10^{-4}

The reaction of a carboxylic acid with water is a reversible process, so the equation for ionisation is written using equilibrium arrows. The equation for the ionisation of ethanoic acid in water is:

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

The partial ionisation of carboxylic acids is because the equilibrium position of the reaction favours the reactants.

REACTIONS OF CARBOXYLIC ACIDS WITH METALS AND THEIR COMPOUNDS

Carboxylic acids undergo reactions typical of other acids, such as inorganic acids. Some examples are given below.

- Carboxylic acids react with metal oxides and hydroxides to give metal salts and water. For example, ethanoic (acetic) acid reacts with sodium hydroxide to produce sodium ethanoate (acetate) (the salt) and water. Note that when writing the formula of a salt of an organic acid, the formula of the metal ion is usually placed after the formula of the acid ion.

  $$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

  When writing these as ionic equations, the carboxylic acid is shown in its molecular form because most of the molecules are not ionised in the original solution:

  $$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

- Carboxylic acids react with metal carbonates and hydrogencarbonates to give a salt, water and carbon dioxide. For example, propanoic acid reacts with solid sodium carbonate:

  $Na_2CO_3(s) + 2CH_3CH_2COOH(aq) \rightarrow 2CH_3CH_2COONa(aq) + H_2O(l) + CO_2(g)$

  Or ionic equation:

  $Na_2CO_3(s) + 2CH_3CH_2COOH(aq) \rightarrow 2CH_3CH_2COO^-(aq) + 2Na^+(aq) + H_2O(l) + CO_2(g)$

- Carboxylic acids react with reactive metals, such as sodium and magnesium, to give a salt and hydrogen gas. For example, methanoic acid reacts with magnesium:

  $2HCOOH(aq) + Mg(s) \rightarrow (HCOO)_2Mg(aq) + H_2(g)$

  Or ionic equation:

  $2HCOOH(aq) + Mg(s) \rightarrow 2HCOO^-(aq) + Mg^{2+}(aq) + H_2(g)$

REACTIONS OF CARBOXYLIC ACIDS WITH ALCOHOLS

Reactions that involve the combination of two reactants and the elimination of a small molecule, such as water, are called **condensation reactions**. Esters are made by a condensation reaction between a carboxylic acid and an alcohol. A condensation reaction in which an ester is formed is also known as an **esterification reaction**.

For example, the ester ethyl ethanoate can be produced by gently heating a mixture of ethanol and pure ethanoic acid with a trace amount of sulfuric acid. The sulfuric acid acts as a catalyst. As well as the desired ester, water is produced.

The general equation for the esterification reaction involving a carboxylic acid and an alcohol is shown in Figure 14.3.3. Two examples of esterification reactions are also shown.

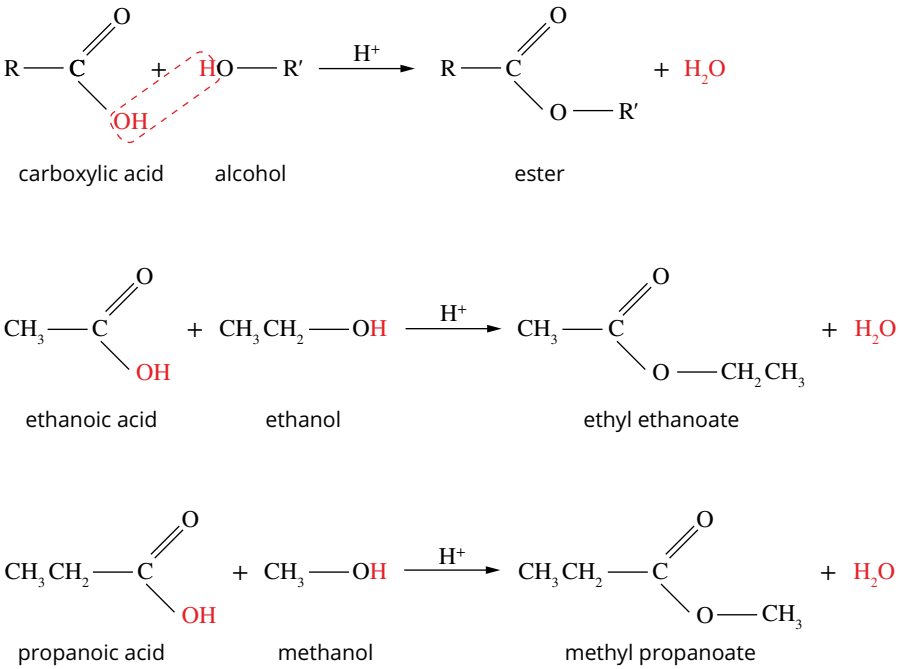


FIGURE 14.3.3 Esterification reactions occur when alcohols are heated with carboxylic acids and a small amount of sulfuric acid as a catalyst. The top reaction shows the general equation for esterification. Two specific examples are also shown: ethanoic acid with ethanol and propanoic acid with methanol.

CHEMFILE

Effervescence from a carboxylic acid reaction

The effervescence (bubbling) that occurs when some simple over-the-counter pain relievers or antacids are added to water is usually produced by the reaction of a carboxylic acid with a carbonate or hydrogencarbonate. Two common ingredients you may see listed on the packs of such medications are mineral salt 500 and food acid 334. Mineral salt 500 is the food additive code for sodium carbonate (or sodium hydrogencarbonate). Food acid 334 is the code for tartaric acid, commonly known as cream of tartar. Tartaric acid is a diprotic carboxylic acid (Figure 14.3.2). When placed in water, these ingredients react with each other to release carbon dioxide gas, which is observed as effervescence.

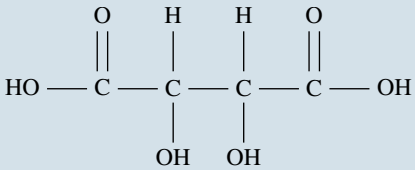


FIGURE 14.3.2 The structure of tartaric acid (IUPAC name 2,3-dihydroxybutanedioic acid). In water, tartaric acid ionises to produce hydronium ions, which can react with carbonates to produce carbon dioxide gas.

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.

As you learnt in Chapter 13, the first part of the name of an ester is derived from the name of the alcohol from which it was made. The second part of the name is derived from the name of the carboxylic acid from which it was made. Therefore, the name of the ester formed from methanol (an alcohol) and propanoic acid (a carboxylic acid) is methyl propananoate.

CHEMISTRY IN ACTION

Aspirin, an ester derived from a herbal remedy

Pharmaceutical products are often developed from substances found in plants that have been used as a traditional medicine. For example, the mild painkiller aspirin originated from a naturally occurring substance called salicin, which is found in the leaves and bark of willow trees and in the herb meadowsweet.

As long ago as 400 BCE, the Greek physician Hippocrates (Figure 14.3.4) recommended an infusion of willow leaves and bark to assist in childbirth and relieve other pains. It wasn't until 1829 that the active ingredient, salicin, was identified and isolated.

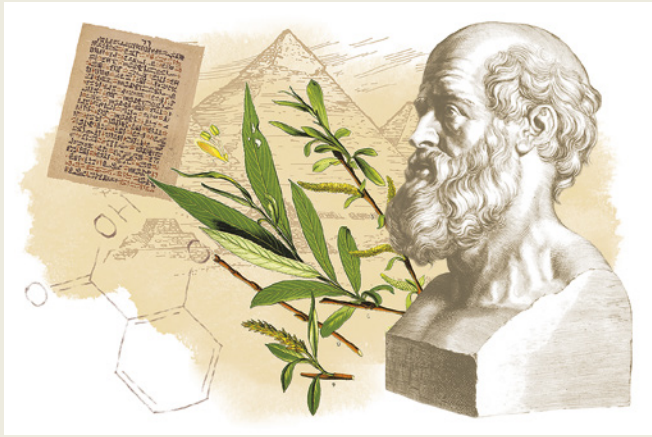


FIGURE 14.3.4 In 3000–1500 BCE, willow was used as a medicine by ancient civilisations, such as the Sumerians and Egyptians. In Greece, in about 400 BCE, Hippocrates administered willow leaf tea to people suffering pain.

It is now known that the body converts salicin to salicylic acid, which is the active substance that helps to reduce fever and acts as a painkiller. Pure salicylic acid is hard to ingest and causes stomach irritation.

In 1897, Felix Hoffmann replaced the hydroxyl functional group on salicylic acid with an ester functional group to form acetylsalicylic acid, later named aspirin, which was much gentler on the mouth and stomach than salicylic acid.

The preparation of aspirin is a relatively simple process, involving one main step in which the hydroxyl functional group of a salicylic acid molecule reacts with the carboxylic acid functional group of an ethanoic acid molecule in a condensation reaction (Figure 14.3.5). The product, aspirin, has properties that are quite different from those of either of the two reactant molecules.

Although this reaction can be easily carried out in a laboratory, the yield is quite low. A more complex reaction is used to produce aspirin on an industrial scale.

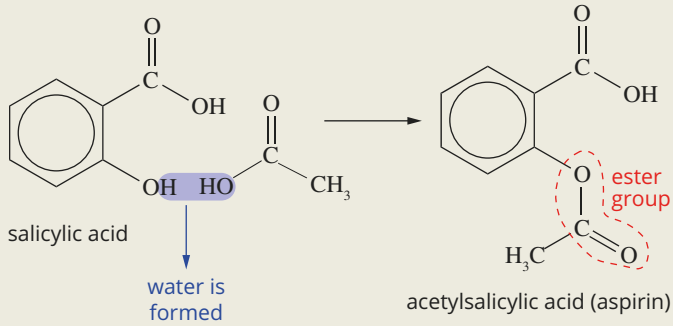


FIGURE 14.3.5 Aspirin can be made from salicylic acid and ethanoic acid. The process involves a reaction between hydroxyl and carboxyl functional groups to form an ester.

HYDROLYSIS OF ESTERS

The condensation reaction between carboxylic acids and alcohols is a reversible reaction. You can see in Figure 14.3.6 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**. In effect, hydrolysis can be seen as the reverse of the condensation reaction used to produce the ester molecule. This reaction is catalysed by an alkali or dilute acid.

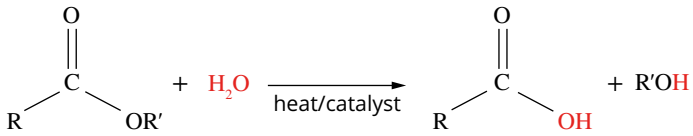


FIGURE 14.3.6 General equation for the hydrolysis of an ester: esters react with water to produce a carboxylic acid and an alcohol.

Figure 14.3.7 shows the equation for the hydrolysis of ethyl propanoate to form ethanol and propanoic acid using an acid catalyst.

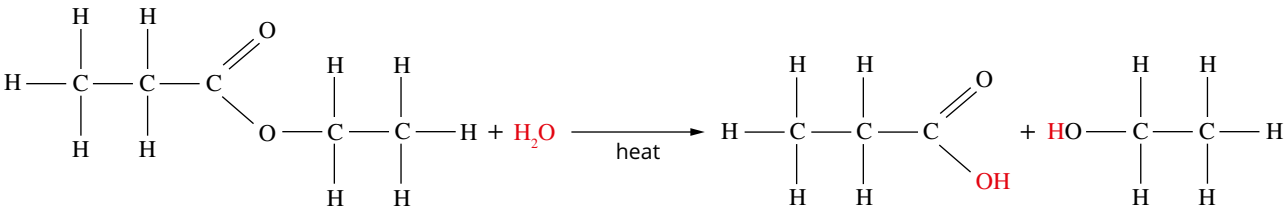


FIGURE 14.3.7 Equation for the acid-catalysed hydrolysis of ethyl propanoate to produce propanoic acid and ethanol.

When the hydrolysis of an ester is catalysed by an alkali such as sodium hydroxide, the products are an alcohol and the sodium salt of the carboxylic acid. The sodium salt can be easily converted to the carboxylic acid by adding dilute acid solution, such as hydrochloric acid.

The hydrolysis of esters by alkalis to produce soaps will be studied in Chapter 16.

i The hydrolysis of esters by metal hydroxides forms a salt of the carboxylic acid. Addition of excess acid regenerates the carboxylic acid.

14.3 Review

SUMMARY

- Carboxylic acids are weak acids that ionise in water to produce hydronium ions and carboxylate ions.
- Carboxylic acids, like other acids, will react with:
  - reactive metals to produce a salt and hydrogen gas
  - metal oxides and hydroxides to produce a salt and water
  - metal carbonates and hydrogencarbonates to produce a salt, water and carbon dioxide.
- Carboxylic acids undergo condensation reactions with alcohols in the presence of an acid catalyst to produce esters.
- The condensation reaction to form an ester is called an esterification reaction.
- Esters can be hydrolysed by acids or alkalis to produce alcohols and carboxylic acids or their sodium salts, respectively.
- Each of the different types of reactions you have studied in this section can be represented by chemical equations.

KEY QUESTIONS

1 **a** Write the equation for the reaction that occurs when butanoic acid is added to water.
b List the species (molecules and ions) present in the solution formed in part **a** from most to least abundant. Give a reason for the order of abundance.

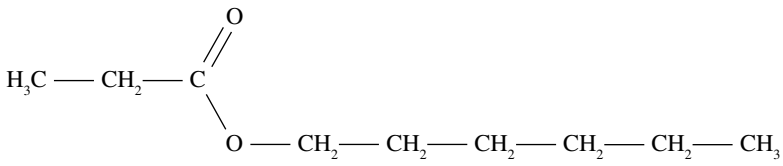
2 Give the formula and name for the conjugate base of propanoic acid.

3 Write the ionic equations for the reactions that occur when the following are mixed:
a aqueous solutions of ethanoic acid and potassium hydrogencarbonate
b sodium metal and aqueous propanoic acid.

4 Which one of the following combinations of reactants would not produce magnesium methanoate as a product?
A methanoic acid and magnesium chloride
B methanoic acid and magnesium hydroxide
C methanoic acid and magnesium metal
D methanoic acid and magnesium carbonate

5 Write the equation for the reaction that occurs when methanoic acid and propan-1-ol are mixed in the presence of a small amount of sulfuric acid. Name the organic product.

6 Name the reactants that would produce the following esters (assume no branching of carbon chains within the esters).
a pentyl ethanoate
b ethyl octanoate
c



d $CH_3CH_2CH_2COOCH_2CH_2CH_3$

14.4 Creating molecules: an introduction to organic synthesis

Organic chemists are highly skilled at developing compounds that have exactly the right properties needed for a particular purpose. These may be new pharmaceuticals, polymers or nano-materials. Once the desired compound has been identified, chemists must devise a way to make it. Chemists have to design an efficient method for converting readily available starting materials into the more complex product they want.

When selecting a chemical synthesis pathway, chemists need to consider the yield and purity of the products and should also minimise unwanted side-products and waste materials. Time and cost factors also need to be considered.

Modern chemists are also interested in devising environmentally sustainable synthetic routes. These pathways are designed to minimise waste, use 'greener' solvents, require less energy, and help to preserve the world's resources. This idea is discussed in more depth in Chapter 12.

In this section, 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 sections 14.2 and 14.3.

SIMPLE REACTION PATHWAYS

Figure 14.4.1 shows chemical reaction pathways that can be used to form some compounds from ethane or ethene. 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. The same inorganic reactants and reaction conditions can be applied to different hydrocarbon starting points to produce the same functional groups on the product molecules.

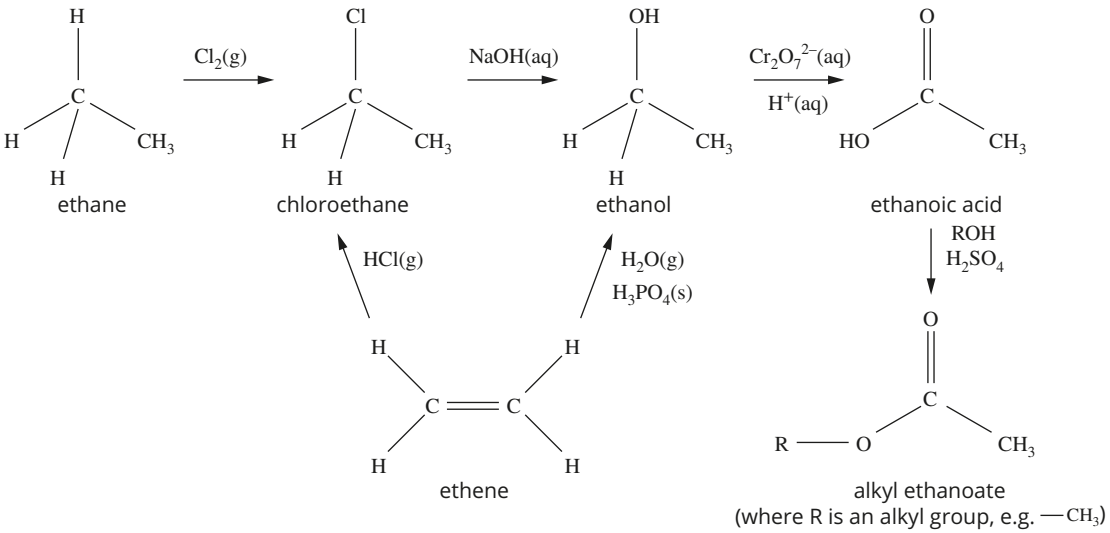


FIGURE 14.4.1 Some reaction pathways based on ethane and ethene. The same reaction conditions can be used to develop pathways for other members of the alkane and alkene homologous series.

CHEMFILE

Building the impossible

The chemist Robert Burns Woodward (Figure 14.4.2) was awarded the 1965 Nobel Prize in Chemistry for his synthesis of complex organic molecules. He devised procedures to synthesise complex natural products considered impossible to replicate in the laboratory. His approach resulted in the development of several rules still used by organic chemists to plan and predict how reactions will occur to devise sequential pathways to synthesise complex molecules.

When awarded the Nobel Prize, Woodward had synthesised large complex molecules such as quinine, cholesterol, cortisone, strychnine, reserpine and chlorophyll. His work on vitamin B_{12}, a large molecule (Figure 14.4.3), is considered to be the most complex. The synthesis took 69 steps and more than 12 years with the combined efforts of over 100 people from around the world.

The discoveries made during the synthesis of vitamin B_{12} have contributed greatly to organic chemistry and were recognised with another Nobel Prize, in 1981. The prize was awarded to Roald Hoffmann, who worked with Woodward on the synthesis, and Kenichi Fukui, who had devised an alternative approach with a similar result to Hoffman and Woodward. Woodward died in 1979, and because Nobel Prizes are not awarded posthumously (after death), he was not named on the 1981 Nobel Prize.

FIGURE 14.4.2 Professor Robert Burns Woodward (1917–1979) synthesised complex organic molecules.

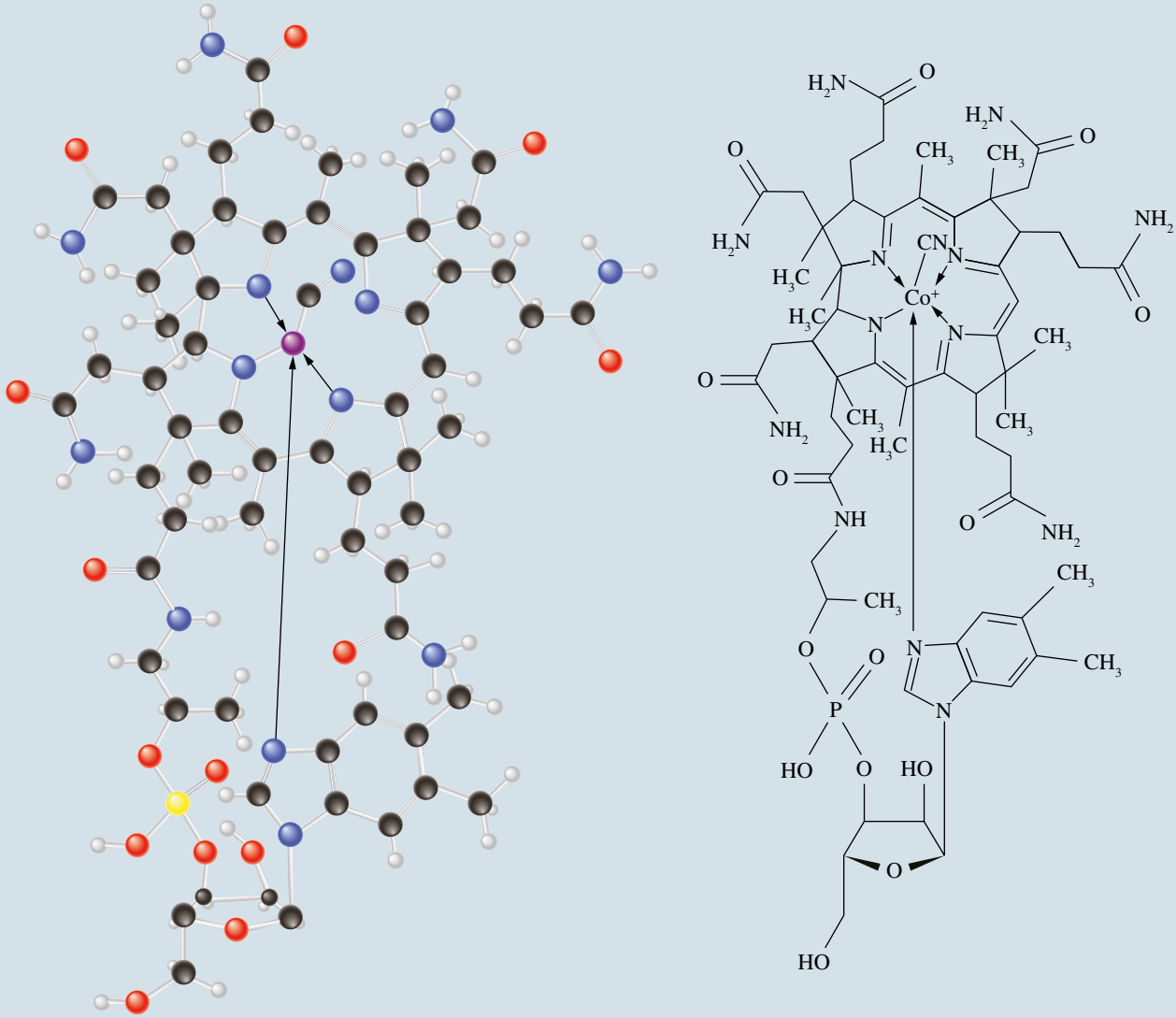


FIGURE 14.4.3 The structure of vitamin B_{12}. The manipulation of the functional groups and reaction conditions required to synthesise this large molecule from small starting materials takes 69 steps.

REACTION SEQUENCES: PRODUCTION OF ETHYL ETHANOATE

Ethyl ethanoate is an ester that has a wide range of uses. It is used as artificial fruit essences and flavours, and as a solvent in the decaffeination of tea and coffee. It is also used in the manufacture of printing inks and perfumes.

A close look at the structure of ethyl ethanoate (Figure 14.4.4) indicates that it is an ester and so can be produced by the condensation reaction between the appropriate carboxylic acid and alcohol—in this case, ethanoic acid and ethanol. Therefore, to synthesise ethyl ethanoate, you must first obtain ethanoic acid and ethanol.

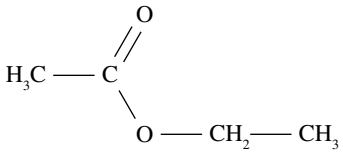


FIGURE 14.4.4 The ester ethyl ethanoate can be made by condensation of ethanoic acid with ethanol.

Ethanol is an alcohol containing two carbon atoms. Ethanol can be synthesised from ethene by an addition reaction with water or by fermentation of sugars by yeasts. Ethene is a good choice for a starting material because it is readily available through the cracking of hydrocarbon fractions obtained from the distillation of natural gas and oil. The annual world production of ethene is 156 million tonnes.

Ethanoic acid can then be made by oxidising some of the ethanol.

The manufacture of ethyl ethanoate is achieved in three steps.

Step 1: Ethanol is synthesised directly by the hydration of ethene in the presence of the catalyst phosphoric acid:

$$CH_2{=}CH_2(g) \xrightarrow{H_2O(g),\ H_3PO_4} CH_3CH_2OH(l)$$

Step 2: Ethanoic acid is synthesised by oxidising some of the ethanol produced in Step 1:

$$CH_3CH_2OH(l) \xrightarrow{Cr_2O_7^{2-},\ H^+} CH_3COOH(l)$$

Step 3: Ethyl ethanoate is produced by the condensation reaction between ethanoic acid and ethanol in the presence of sulfuric acid catalyst:

$$CH_3CH_2OH(l) + CH_3COOH(l) \xrightarrow{H_2SO_4} CH_3COOCH_2CH_3(l)$$

Figure 14.4.5 shows this chemical reaction pathway using structural formulae.

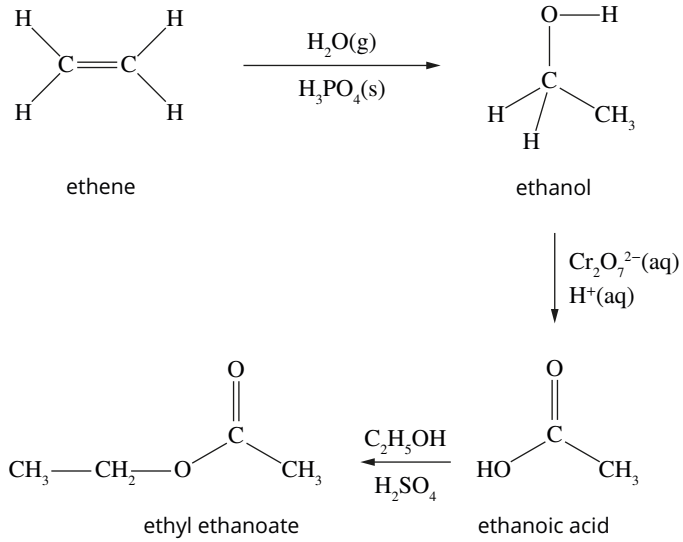


FIGURE 14.4.5 Synthetic pathway for the formation of ethyl ethanoate from ethene.

Considerations in devising a synthesis

As you saw in the synthesis of ethyl ethanoate, chemical synthesis pathways may require the preparation of several intermediate compounds. Some desired products can be synthesised by a number of routes, so different possible pathways may also need to be considered. Chemists also consider issues such as yield, rate, cost, safety and sustainability when deciding on the preferred pathway.

The methods of separation of the intermediate and final product from by-products must also be determined. The final product then needs to be purified and the purity evaluated.

Chemists must consider the yield of the product because not all of the reactants are necessarily converted to the product. For example, in the reaction:

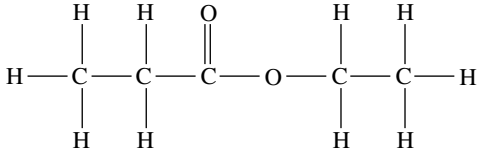
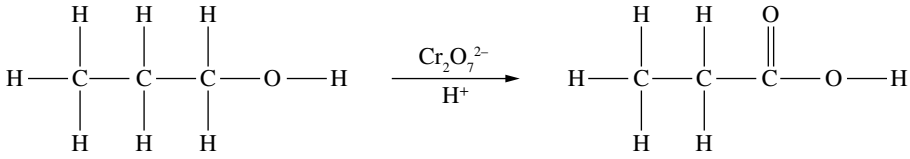
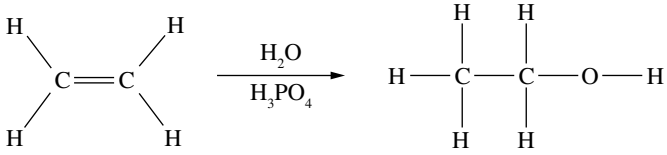
$$C_2H_4(g) \xrightarrow{H_2O(g),\ H_3PO_4} CH_3CH_2OH(l)$$

you would expect 100 kg of ethene to produce, 164 kg of ethanol if all the ethene was converted to ethanol. If only 82 kg of ethanol was obtained, then the reaction yield would be 50%. Yields were discussed in more detail in Chapters 2 and 11.

Worked example 14.4.1

DESIGNING A CHEMICAL SYNTHESIS PATHWAY FOR AN ESTER

Design a reaction pathway for the synthesis of ethyl propanoate, starting with propan-1-ol and ethene.

Thinking	Working
Write the structure of the ester to help determine which carboxylic acid and alcohol are required.	 The name ethyl propanoate indicates this is an ester. It is formed by a condensation reaction between an alcohol and a carboxylic acid. The first part of the name, 'ethyl', indicates the alcohol that reacted (ethanol) and the second part of the name, 'propanoate', indicates the carboxylic acid (propanoic acid).
Write an equation for the reaction that forms the ester from the alcohol and carboxylic acid identified above.	$CH_3CH_2COOH + CH_3CH_2OH \xrightarrow{H_2SO_4} CH_3CH_2COOCH_2CH_3 + H_2O$
Identify the reactions that will produce each of the two reactants in the step above. (Continue these steps if necessary until all the chemicals required have been made from the starting compounds.)	Propanoic acid is made by the oxidation of propan-1-ol:  Ethanol is made by the hydration of ethene: 

Worked example: Try yourself 14.4.1

DESIGNING A CHEMICAL SYNTHESIS PATHWAY FOR AN ESTER

Design a reaction pathway for the synthesis of methyl ethanoate, starting with ethene and methanol.

CHEMISTRY IN ACTION

Keeping it moving forward

When chemical engineers design a synthesis, one of their aims is to maximise the yield of the desired product. For a synthesis where the reaction is reversible, an equilibrium may form and so limit yield. An equilibrium can only establish in a closed system, so chemical engineers design processes that do not occur in closed vessels. One approach is to continuously feed reactants into the reaction vessel in order to keep their concentrations high and so favour the forward reaction. Another approach is to remove products as they form to prevent the reverse reaction from occurring. Ideally, both these approaches are used at the same time.

The reaction of ethanoic acid with ethanol to form ethyl ethanoate is reversible. To maximise the yield of ethyl ethanoate, chemical engineers take advantage of the differences in boiling points of the substances involved.

The reaction mixture contains ethanoic acid, ethanol, ethyl ethanoate and water, which boil at 118°C, 78°C, 77.1°C and 100°C, respectively. As the reaction proceeds, ethyl ethanoate is removed from the reaction vessel by distillation (studied in Year 11 Chemistry). Although ethyl ethanoate has the lowest boiling point, distillation does not remove only ethyl ethanoate. At about 70°C, a mixture containing about 83% ethyl ethanoate, 8% water and 9% ethanol distills from the reaction mixture. Because about 10 times more ethyl ethanoate than ethanol is removed, the forward reaction is still favoured. Ethanoic acid has a higher boiling point (because it has dipole–dipole and hydrogen bonding in addition to dispersion forces), so it does not distill over.

As well, to further favour the forward reaction, the ratio of ethanoic acid to ethanol is kept high. This results in more ethanol reacting and less being available to distill over with the ethyl ethanoate and water. Figure 14.4.6 shows the laboratory apparatus for a fractional distillation of a mixture of liquids.

FIGURE 14.4.6 Fractional distillation using a Liebig condenser (diagonal, centre) to separate a liquid into its component parts

14.4 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 from the organic reactions studied in this chapter.
- Reaction pathways indicate the reaction conditions and reagents required for each step.
- For maximum efficiency and profit, the production of an industrial chemical should occur at a fast rate with a high equilibrium yield.

KEY QUESTIONS

1 Design reaction pathways for the following reactions.
- **a** butanoic acid from butan-1-ol
- **b** pentan-2-one from pent-1-ene

2 Propose the shortest reaction pathway that will synthesise:
- **a** ethanol from ethene.
- **b** propyl methanoate from propan-1-ol and methanol.

3 Describe a reaction pathway to synthesise ethyl ethanoate from ethene.

4 In the production of ethanol by the addition reaction between ethene and water (in the form of steam), the ethene and steam are continuously fed into the reaction vessel. Explain how this improves the yield of ethanol.

Chapter review

14

KEY TERMS

addition polymerisation
addition reaction
aldehyde
condensation reaction
esterification reaction
hydration reaction
hydrogen halide
hydrolysis
hydrolytic reaction
inorganic
ketone
monomer
polymer
primary alcohol
reaction pathway
saturated
secondary alcohol
substitution reaction
tertiary alcohol
unsaturated

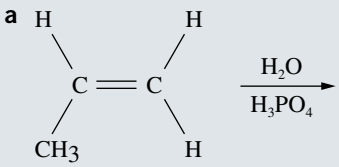
Chemical properties of alkenes

1 Complete this table about the different types of reactions of alkenes.

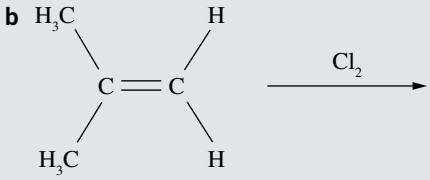
Reactants	Type of reaction	Product(s)
Alkene and hydrogen		
Alkene and hydrogen bromide		
Alkene and water (with a catalyst and heat)		
Alkene and bromine		
Alkene in the presence of a catalyst		

2 Write the structural formulae of the products of the following reactions.

a



b



3 Give the names of the chemicals, including any catalysts, that would be used to achieve the following conversions.

a $C_3H_6 \rightarrow C_3H_7Br$
b but-1-ene → 2-chlorobutane
c propene → 1,2-dichloropropane
d $CH_3CHCH_2 \rightarrow$ propane

4 Alkanes, alkenes and alcohols all burn in air to form carbon dioxide and water. Equations for such a reaction are shown below. For each reaction, determine the formula of X, give its name and identify if it is an alkane, alkene or alcohol.

a $X(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
b $X(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

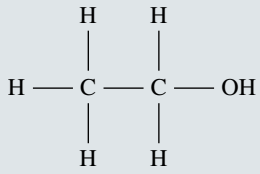
Chemical properties of alcohols

5 State the name of the functional group that will be formed in reactions of the following types of alcohols with potassium permanganate solution. If there is more than one possible product, state both names.

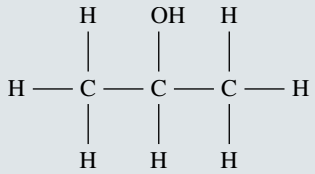
a primary alcohol
b secondary alcohol
c tertiary alcohol

6 Write the structural formulae of all the possible products from the oxidation of the following alcohols.

a

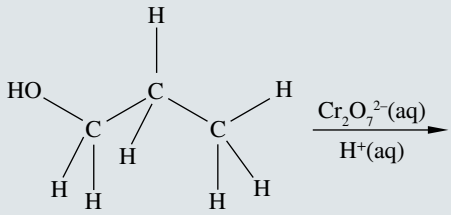


b

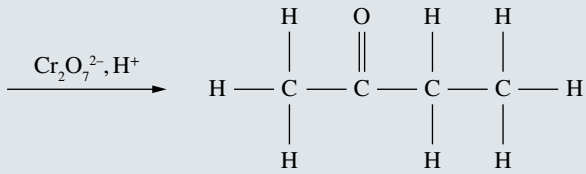


7 Write the structural formulae of the organic reactants or products for the following reactions.

a



b



c Pentan-3-ol heated with $H^+/Cr_2O_7^{2-}$ solution

d Butan-1-ol with $H^+/Cr_2O_7^{2-}$ solution, mild heat; the product is distilled off as it forms.

8 Write a balanced redox equation for the reaction that occurs when propan-1-ol is heated with a solution of acidified potassium permanganate. Show the half-equations.

9 When using acidified potassium permanganate solution to determine if an unknown alcohol is primary, secondary or tertiary, the laboratory instructions state that the permanganate solution must be added dropwise to an excess of the alcohol. Explain why it is important that the permanganate solution is added dropwise to an excess of alcohol for this test to be successful.

Chemical properties of carboxylic acids

10 Write an ionic equation to show propanoic acid behaving as an acid in aqueous solution. Label the conjugate acid–base pairs. Comment on the relative concentrations you would expect for the reactants and products for this acid.

11 Give the names of the products when ethanoic acid is reacted with:

a zinc hydrogencarbonate

b zinc oxide

c zinc metal

d zinc hydroxide.

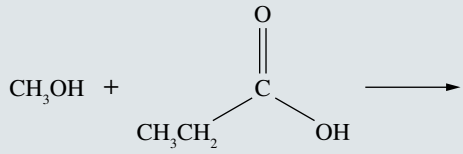
12 Write balanced equations for the reaction of:

a methanoic acid and solid sodium carbonate

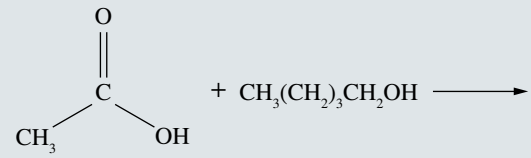
b $CH_3CH_2COOH + Mg(OH)_2$

13 Complete the following reactions by writing semistructural formulae for the missing organic compounds.

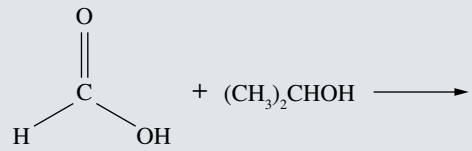
a



b



c



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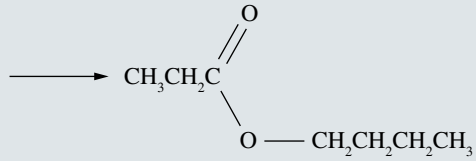
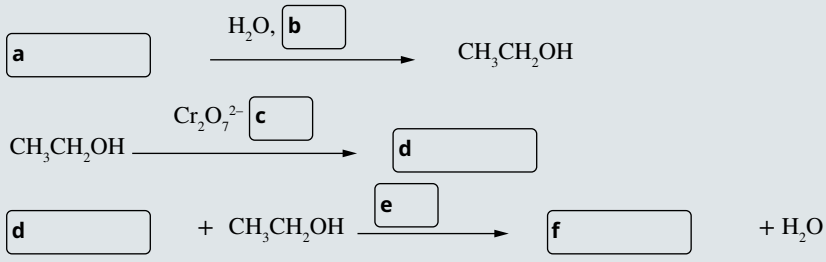


Creating molecules: an introduction to organic synthesis

14 Complete the following reaction pathway for the formation of ethyl ethanoate by giving the formulae for the missing compounds.



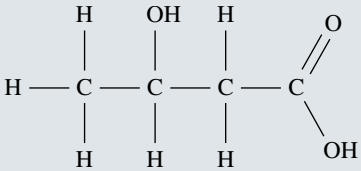
15 Consider the reaction pathway in which ethyl ethanoate is formed from ethene. List the reaction types in their correct order for this reaction pathway.

16 Ethyl propanoate can be manufactured from ethene as the only organic starting material. The ethene is converted to ethanol by hydration. Reaction of ethene with water and carbon monoxide gives propanoic acid as the only product. Write a balanced equation for the three steps in the conversion of ethene to ethyl propanoate.

Connecting the main ideas

17 In the redox reactions of alcohols with permanganate and dichromate, the permanganate and dichromate solutions are acidified with sulfuric acid. In the condensation reaction of an alcohol with a carboxylic acid, sulfuric acid is also used. Explain the role of sulfuric acid in each of these reactions.

18 Organic compounds can contain more than one functional group. 3-Hydroxybutanoic acid (shown below) has a carboxylic acid functional group and a hydroxy (alcohol) functional group. When this compound is heated with acidified dichromate solution, the hydroxy group is oxidised but the carboxylic acid group is not.



a Write the structural formula and give the name of the functional group for the product of the oxidation.

b Explain why the carboxylic acid group is not oxidised.

19 The reaction for the production of ethanol from ethene is shown below.

$CH_2CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$

$\Delta H = -45$ kJ mol^{-1}

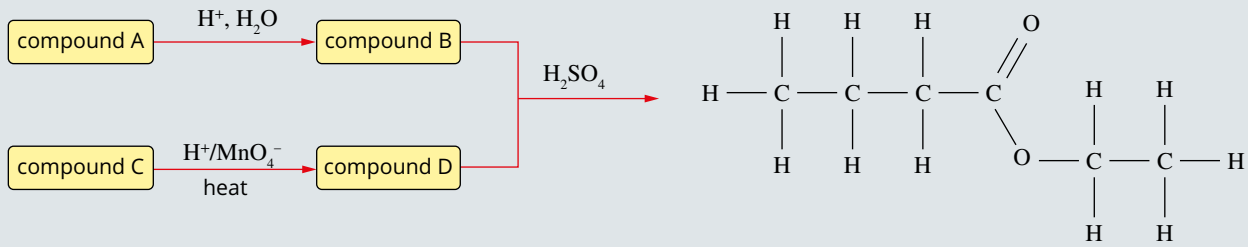
a Use equilibrium principles to suggest the conditions of temperature and pressure that will favour a high yield of ethanol. Explain your reasoning.

b The yield for the reaction is about 5%, but can be increased by cooling the gases to condense the ethanol and removing it from the equilibrium mixture. The ethene gas is then recycled. This is continually repeated and in this way an overall yield of about 95% is achieved. Explain, with reference to appropriate chemistry principles, why cooling the equilibrium mixture will condense the ethanol but not the ethene.

20 The ester ethyl butanoate is used as a synthetic fruit flavouring and as a solvent in perfumes. The reaction pathway shown below leads to ethyl butanoate.

a Complete the pathway by writing the structural formulae for compounds A–D.

b Which compound would be expected to have greater water solubility: B or C? Explain your answer.



CHAPTER

15 From monomers to polymers

Polymers offer an almost limitless variety of properties, enabling them to be used for many different purposes. Synthetic, carbon-based polymers are often called plastics.

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.

Using several common polymers as examples, you will also learn how the properties of polymers can be modified for different applications.

Science understanding

- addition reactions can be used to produce polymers, including polyethene and polytetrafluoroethene
- the structure of an addition polymer can be predicted from its monomer and the structure of an addition polymer can be used to predict the monomer from which it was derived
- condensation reactions can be used to produce polymers, including polyamides and polyesters
- the structure of a condensation polymer can be predicted from its monomer(s) and the structure of a condensation polymer can be used to predict the monomer(s) from which it was derived
- industry produces a vast range of plastics, including addition polymers (polyethene, polytetrafluoroethene) and condensation polymers (nylon and polyethylene terephthalate (PET)), which have different properties and uses

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15.1 Polymers: a diverse class of materials

FIGURE 15.1.1 (a) The polymer used to make the toy soccer players in this game was selected for its strength and because it is easy to mould. (b) The polymer bank notes used in Australia are strong and flexible. (c) The polymers in the helmet, gloves and bottle are similar, but structural differences have given them very different properties.

FIGURE 15.1.3 Darwin's bark spider (*Caerostris darwini*) is an orb-weaving spider whose web is made of one of the toughest natural polymers ever studied.

Polymers are an incredibly diverse range of materials. Natural polymers, such as proteins, starch, cellulose and DNA, play essential roles within living systems and have also been used and modified by humans for many other applications. In the last century, many wholly synthetic polymers have been developed and are one of the most successful and useful classes of materials. Synthetic polymers are used for everyday plastic bags, containers and clothing fibres, and in advanced medical applications such as drug delivery systems. In Figure 15.1.1, you can see a range of familiar polymers. The polymers that make up these objects were selected for their strength or flexibility. In this chapter, you will examine a range of polymers and learn how their properties are related to their structure.

POLYMER STRUCTURE

Polymers are covalent molecular substances composed of many small molecules joined together to form a long chain of atoms. The word 'polymer' comes from the Greek *poly*, meaning 'many', and *mer*, meaning 'part'. Polymers are formed by joining together thousands of smaller molecules, called **monomers** (*mono* means 'one') through a process called **polymerisation**, as shown in Figure 15.1.2. Polymer chains are made up of identical segments that are repeated along the length of the molecule. Each of these segments is called a repeating unit.

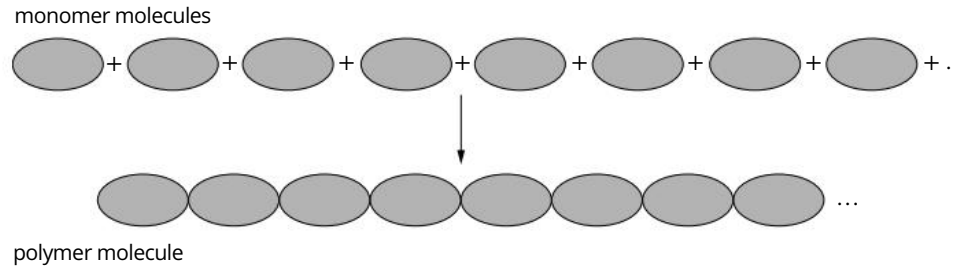


FIGURE 15.1.2 Monomers join to each other to form polymers.

NATURAL POLYMERS

Many polymers are found in nature. For example, carbohydrates are polymers made from sugar monomers, principally glucose and fructose. Proteins, as discussed in Chapters 17 and 18, are also polymers made from amino acid monomers. Many natural polymers are used in a range of applications. For example, silk and cotton are natural fibres used in the textile industry. Silk is a protein produced by the mulberry silkworm (*Bombyx mori*). Cotton is the seed hair of plants of the genus *Gossypium* and is primarily composed of the carbohydrate cellulose. Latex, used to make rubber, is also a polymer harvested from rubber trees.

The web of a Darwin's bark spider (*Caerostris darwini*) is the toughest natural polymer ever studied (Figure 15.1.3). The web is composed of proteins and amino acids that polymerise upon contact with air. The web has a similar tensile strength to high-grade steel and is of similar strength to Kevlar—the polymer used to make bulletproof jackets.

SYNTHETIC POLYMERS

The first synthetic polymer, Bakelite, was created in 1907 by Leo Baekeland, who called it 'the material of a thousand uses'. Bakelite is a hard, brittle plastic used to make cases for items such as telephones and electric guitars. Bakelite is not widely used any more, but other synthetic polymers are used for hundreds of thousands of different purposes (Figure 15.1.4).

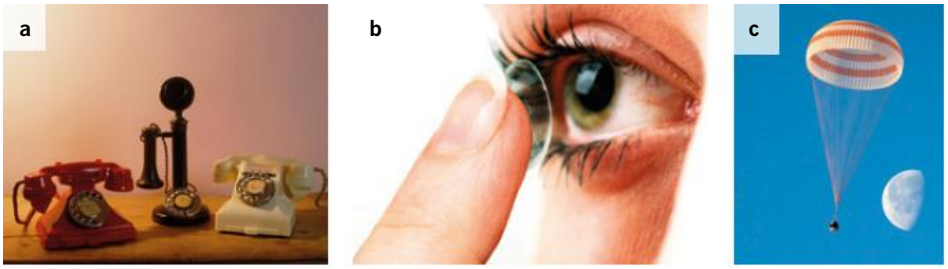


FIGURE 15.1.4 (a) The first synthetic polymer Bakelite was used to make telephone and radio casings. (b) Contact lenses are made of a flexible oxygen-permeable polymer. (c) A space shuttle falling back to Earth. The parachute is made of the synthetic polymers nylon and Kevlar. Many other synthetic polymers are used in the construction of the space shuttle itself, particularly its heat-resistant coatings.

Synthetic polymers can have very different properties from those of materials found in nature, such as metals or wood. These properties can be tailored to meet specific applications. As a result, polymers are used widely. Polymers can be made stronger, harder or more flexible than wood and are resistant to moisture and insects. Like metals, polymers can be hard, strong, malleable and ductile. However, polymers are much lighter than metals and are insulators of heat and electricity. Synthetic polymers can also be cheap to produce in large quantities because they can be produced from chemicals that are readily available.

CHEMISTRY IN ACTION

Synthetic polymers in medicine

Biological polymers, such as silk, horn, hair and cellulose, have been used by humans for hundreds of years for a range of different purposes, including in medicine. The use of sutures (stitches used to heal wounds) made from plant material or animal intestines can be traced back to the Ancient Egyptians and the process of mummification. The use of synthetic polymers has also recently become widespread in medicine because their properties are tailored to specific applications. Synthetic polymers are used in contact lenses, drug delivery systems, dentistry, joint replacements, dressings and grafts, as well as in a range of containers and tubings for storing and delivering fluids and drugs.

Some medicinal polymers are materials also commonly used outside the body. For example, polytetrafluoroethene (Teflon) and polyethene terephthalate (PET) are non-biodegradable and are widely used to make synthetic veins for bypass operations as alternatives to using transplanted veins from other parts of the body. Similarly, joint replacements and prosthetic limbs often consist of a metal such as titanium paired with ultra-high molecular weight polyethene (Figure 15.1.1a). Often antioxidants such as vitamin E are added to the polyethene to prevent oxidative damage caused by the biological environment.

An exciting emerging application for synthetic polymers in medicine is as drug delivery agents (Figure 15.1.5b). Drugs or other particles are coated in polymers and form small microspheres or nanospheres. These polymers can be designed to degrade under specific environmental conditions, such as particular pH, enzyme concentrations or light irradiation, only releasing the drugs at the desired destination within the body. A common polymer used in these applications is poly lactic glycolic acid, a biodegradable copolymer that breaks down to produce two naturally occurring molecules.

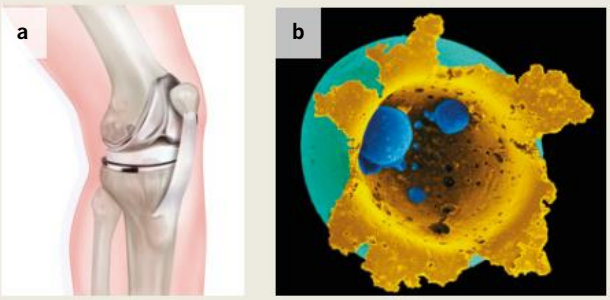


FIGURE 15.1.5 (a) A knee prosthesis consisting of titanium and polyethene. The prosthesis is designed so that the titanium is always bordered with the polyethene, to allow smoother movement. (b) A coloured scanning electron micrograph of a polymer-coated drug-delivery capsule. Some drugs work best when delivered to a specific site in the body. The polymer capsule is designed to burst in a particular biological environment, releasing the molecules held inside.

STRUCTURAL PROPERTIES OF POLYMERS

The properties of a polymer are determined primarily by the type of monomers used to produce it. However, other structural features also affect the properties of the polymer. These factors affect the strength of the intermolecular forces between the polymer chains and include:

- the length of the polymer molecules
- branching of the polymer chains
- cross-linking between polymer chains.

Length

As a polymer chain get longer, the strength of the dispersion forces between neighbouring polymer chains increases. This means that the resulting polymer is a harder and more rigid material. For example, ultra-high molecular weight polyethene (UHMWPE) consists of extremely long polymer molecules. This makes UHMWPE such a tough polymer that it can be used to make artificial hip joints, safety helmets and even bulletproof vests.

Branching

When polymers are formed, monomers can join together in a linear fashion or with a degree of branching. Branched polymers are formed when some monomers react with sites on the side of the polymer chain instead of at the end of the polymer chain. When a monomer joins to the side of the polymer chain, it begins a new chain growing in a different direction. The difference between straight-chain and branched-polymers is illustrated in Figure 15.1.6.

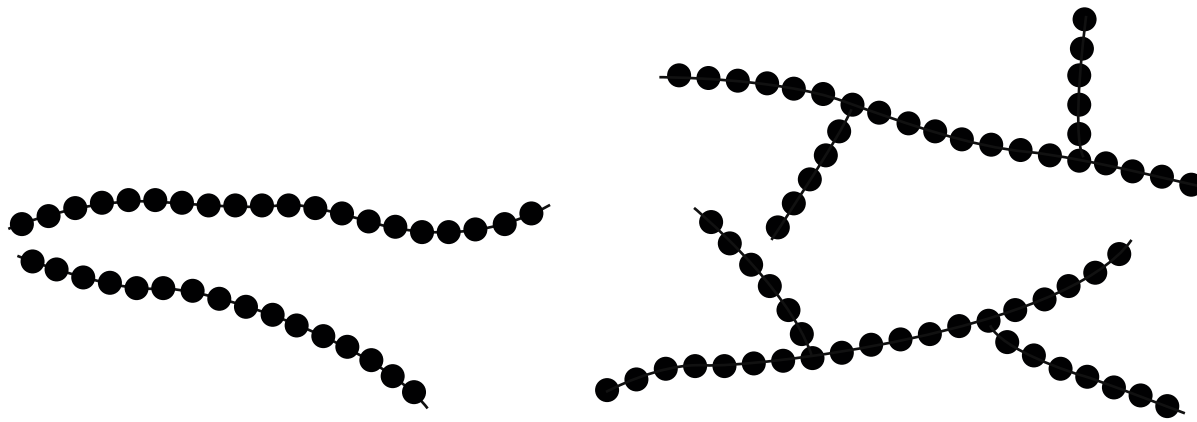


FIGURE 15.1.6 Straight-chain polymers have linear molecules. Branched-chain polymers have shorter polymer chains branching off in different directions from the main polymer.

Polymer branching changes the properties of the polymer significantly, depending on the nature and extent of the branching. Branching can cause the polymer molecules to be spaced further apart, resulting in a less dense material. With a greater distance between the polymer chains, the intermolecular attraction between neighbouring chains is weakened, increasing the flexibility of the material. The effect of branching on the properties of polyethene is discussed in greater depth in section 15.2.

Both straight-chain and branched-chain polymers exist as **thermoplastic** polymers, as long as there are no covalent **cross-links** between polymer chains. For chemists, the term '**plastic**' describes a property of a material, rather than the material itself. A substance is described as plastic if it can be easily moulded. Thermoplastic polymers soften when heated, which means they can be remoulded or recycled. Polymers are only thermoplastic if the bonds between the long polymer chains are hydrogen bonds, dipole–dipole bonds or weak dispersion forces, rather than covalent bonds. When heated, the molecules in thermoplastic materials have enough energy to overcome the intermolecular forces and become free to move and slip past one another (Figure 15.1.7). If the polymer can be remoulded, then it can probably be recycled easily—a desirable property.

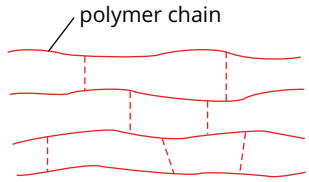


FIGURE 15.1.7 A thermoplastic polymer has weak bonds between the chains.

Cross-linking

In cross-linked polymers, the polymer branches are covalently bonded to neighbouring polymer chains. This bonding creates a polymer network as shown in Figure 15.1.8. Polymers of this type cannot be liquids because the polymer chains are held in place by the cross-linking and are unable to flow.

Cross-linked polymers typically exist as thermosetting polymers. **Thermosetting** polymers decompose or burn when heated, rather than melting, and are hard and rigid. They do not soften because the bonds between the chains are very strong. If the temperature is high enough to break the covalent bonds, the bonds may break at any point, causing the polymer to decompose. They are used to make items such as saucepan handles, bowling balls and shatterproof crockery. It is difficult to recycle thermosetting polymers as they cannot be remoulded into new shapes.

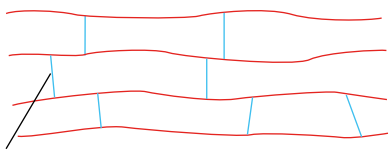


FIGURE 15.1.8 A thermosetting polymer has strong covalent bonds between the chains.

Elastomers

Elastomers 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 makes recycling difficult. For example, the sulfur cross-links in the polymer used for car tyres (Figure 15.1.9) make the tyres non-recyclable.

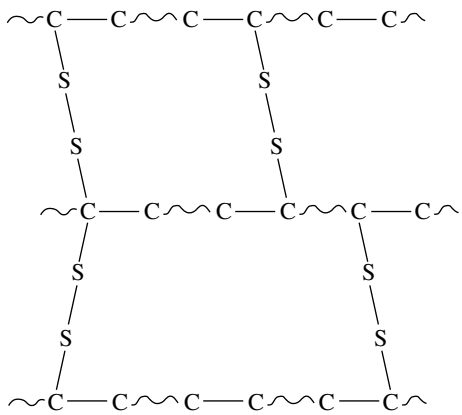


FIGURE 15.1.9 The elastomer chains in rubber car tyres are cross-linked by sulfur atoms.

15.1 Review

SUMMARY

- Polymers are a class of natural and synthetic materials with a wide range of properties and uses.
- Polymers are synthesised by forming covalent bonds between smaller molecules (monomers), which form a long chain.
- There are three main types of polymer structures: straight-chain polymers, branched polymers and cross-linked polymers.
- Straight-chain and branched polymers without covalent cross-links are known as thermoplastic polymers. They will soften when heated and can be reshaped.
- Polymers with covalent bonds, or cross-links, between chains are hard and rigid and are known as thermosetting polymers. They do not melt and instead either burn or decompose when heated.
- Elastomers are polymers with occasional cross-links that allow them to stretch and return to their original position.

KEY QUESTIONS

1 Define:
- **a** polymer
- **b** monomer
- **c** repeating unit.

2 Explain the difference between a thermosetting and thermoplastic polymer.

3 Two polymers A and B are composed of the same monomers, but polymer B has a much higher degree of branching. Which material, A or B, would you expect to have stronger dispersion forces between polymer chains? Explain your answer.

4 To what degree would you expect the polymer chains in natural rubber to be cross-linked? Suggest a reason for your answer.

15.2 Addition polymerisation

As you learnt in Year 11, addition reactions can involve the reaction of an alkene with another molecule. All of the atoms of both molecules are present in the final product. Under some conditions, alkenes undergo an addition reaction with themselves to produce long chains, known as **addition polymers**. The reaction of the monomer ethene with itself to form polyethene, shown in Figure 15.2.1, is the simplest example of the **addition polymerisation** process. Several thousand ethene monomers usually react to make one molecule of polyethene.

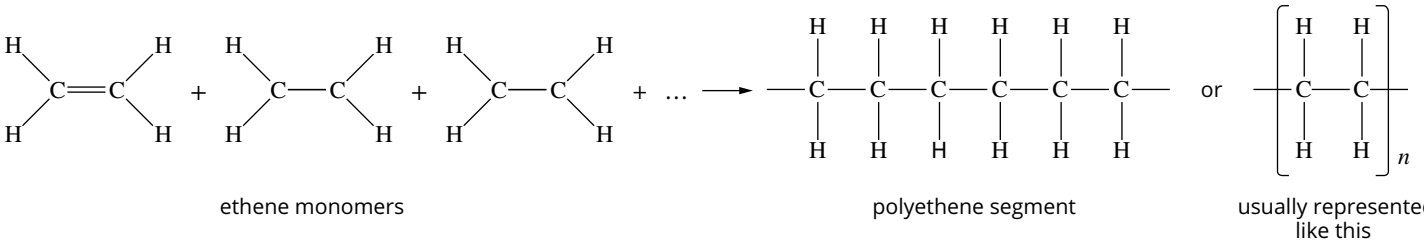


FIGURE 15.2.1 Thousands of ethene monomers join together to make one chain of polyethene. The standard notation shown simplifies the drawing of such a large chain.

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!

Because 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 15.2.2 provides an alternative representation of a polyethene chain segment, called a ball-and-stick model.

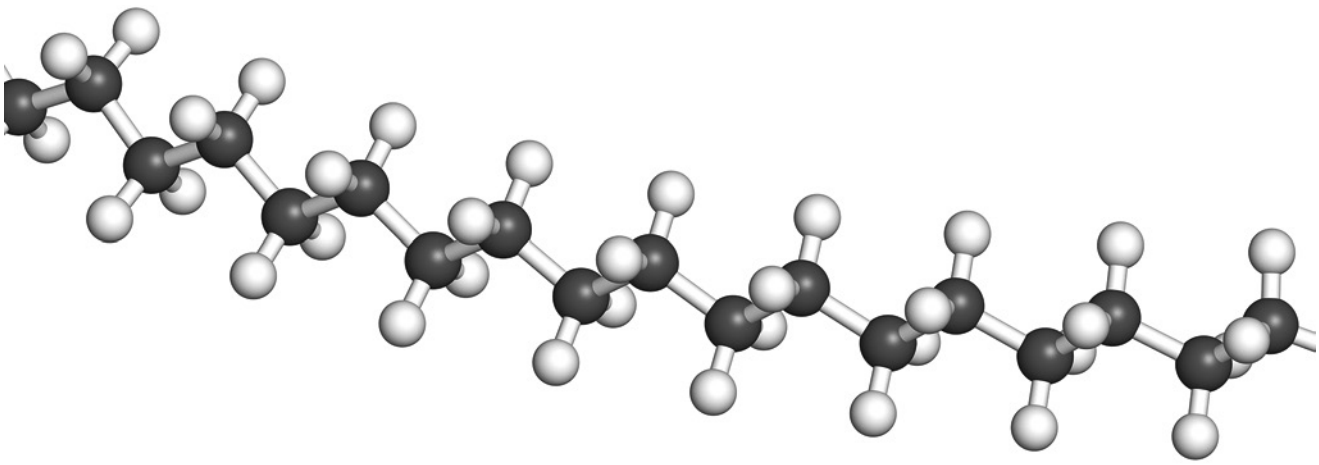


FIGURE 15.2.2 A ball-and-stick representation of a segment of polyethene

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. The polyethene formed does not contain any double bonds and is therefore a saturated molecule.

Addition polymerisation requires monomers that are unsaturated (contain a double or triple carbon–carbon covalent bond). During the polymerisation process, the double or triple bond is broken and single C–C bonds are formed between monomers.

The name of a polymer formed through addition polymerisation often includes the monomer that was used to make it. The names of four common addition polymers and their monomers are listed in Table 15.2.1.

TABLE 15.2.1 Monomer and polymer names

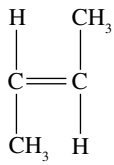
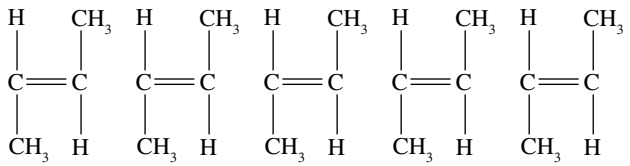
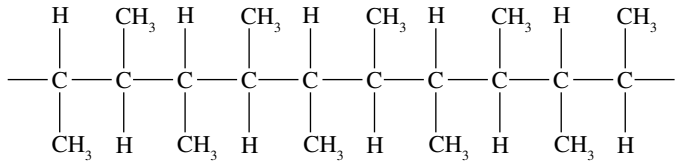
Monomer	Polymer
Ethene	Polyethene
Propene	Polypropene
Tetrafluoroethene	Polytetrafluoroethene (PTFE)
Chloroethene (vinyl chloride)	Polychloroethene, or polyvinylchloride (PVC)

It is possible to predict the structure of an addition polymer from the monomers. Read through the steps in Worked Example 15.2.1 to predict the structure of an addition polymer.

Worked example 15.2.1

ADDITION POLYMERS: FORMING POLYMERS

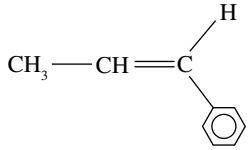
Draw the addition polymer that has $CH_3–CH=CH–CH_3$ as its monomer.

Thinking	Working
Write the chemical formula for the monomer so that the double bond is horizontal and the bonds to all other groups are perpendicular to the carbon centres.	
Repeat this several times so that the C=C double bonds of neighbouring monomers are adjacent to one another.	
Remove the double bonds and connect all carbon centres with single bonds. This gives you the structure of the polymer.	

Worked example: Try yourself 15.2.1

ADDITION POLYMERS: FORMING POLYMERS

Draw the addition polymer produced from the following monomer. Include at least three repeating units.

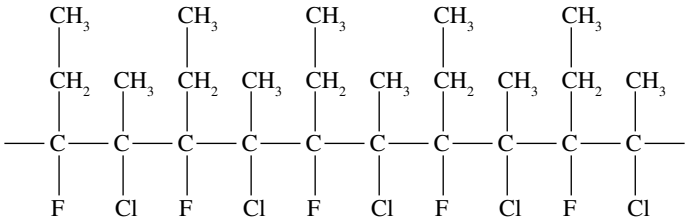


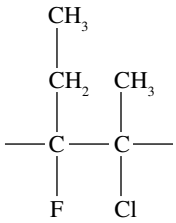
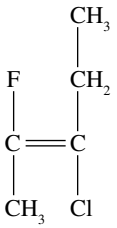
It is also possible to identify the monomers of an addition polymer from the polymer molecule. Read through the steps in Worked Example 15.2.2 to see how to identify the monomers of an addition polymer.

Worked example 15.2.2

ADDITION POLYMERS: DETERMINING THE MONOMER UNIT

Draw the structure of the monomer that produces the following polymer.

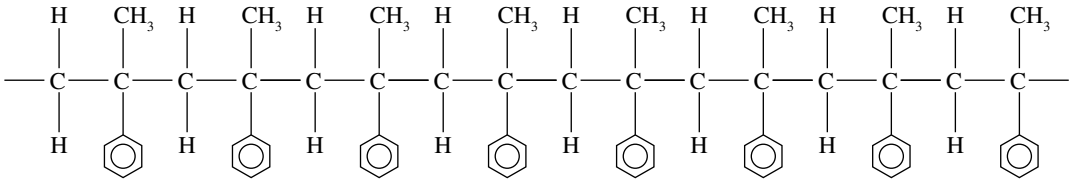


Thinking	Working
Identify the repeating unit of the polymer. It will contain just two adjacent carbon atoms from the polymer backbone.	
Remove every second single bond along the length of the chain and form the double bond between the two carbon atoms of the monomer. This gives you the structure of the monomer.	

Worked example: Try yourself 15.2.2

ADDITION POLYMERS: DETERMINING THE MONOMER UNIT

Draw the structure of the monomer that produces the following polymer.



POLYETHENE

As described above, polyethene is the simplest example of an addition polymer, consisting of a long C–C chain. It is better known by its common names, polythene or polyethylene. Because it is essentially an extremely long alkane, it is a non-polar molecule and exhibits only dispersion forces between adjacent long polymer chains (Figure 15.2.3). These dispersion forces are sufficiently strong to cause polyethene to be a solid at room temperature.

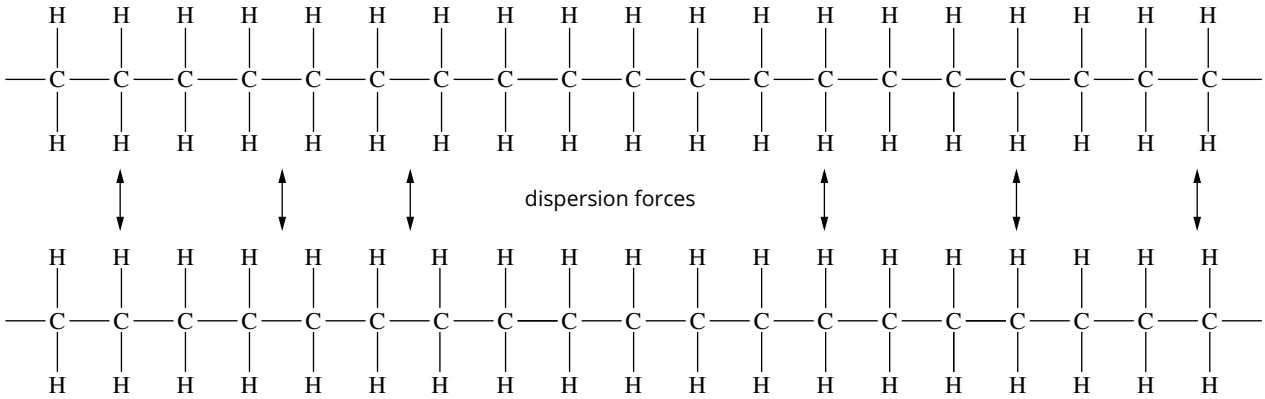


FIGURE 15.2.3 Dispersion forces between polyethene molecules are strong enough to make polyethene a solid at room temperature.

Polyethene can exist in two different structural forms depending on how it is manufactured. The manufacturing process affects the degree of branching on the polyethene chain and hence the strength of the dispersion forces between neighbouring chains. This makes the polymer suitable for different uses.

Low-density polyethene (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 rapidly by a process called free-radical polymerisation. Free radicals are highly reactive atoms, molecules or ions with an unpaired electron. The free radicals break the double bonds in the ethane monomers to start the polymerisation reaction. However, the free radicals also attack the sides of the polymer chain, resulting in significant branching. Figure 15.2.4 shows that the product contains many small branches off the main polymer.

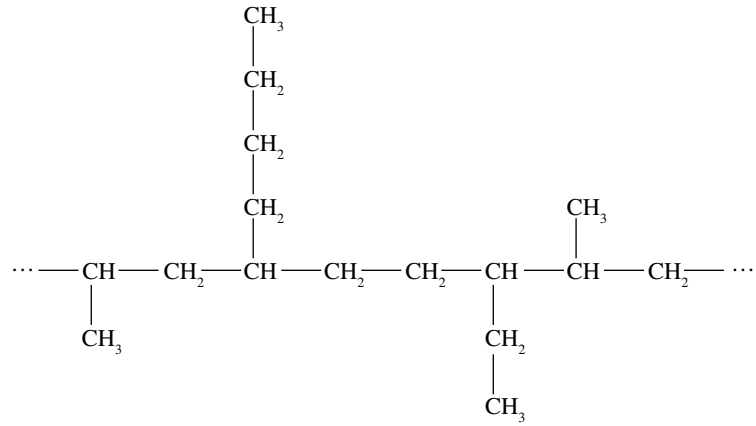
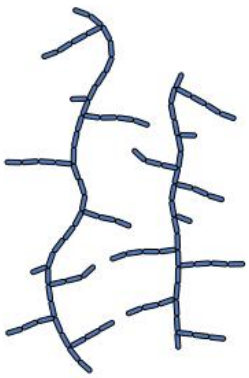


FIGURE 15.2.4 Polyethene made under high pressure and at high temperatures has short branches off the main chain.

The presence of these branches affects the properties of the polymer because 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, a low-density material that is soft and flexible. Its structure and properties are described in Figure 15.2.5. LDPE is used in plastic bags, flexible containers and the waterproof layer in juice and milk cartons.

b



Properties
- low density
- relatively soft
- low melting point
- non-crystalline
- non-conductor of electricity

FIGURE 15.2.5 Properties and structure of low-density polyethene: (a) a plastic bag made from LDPE; (b) LDPE has a branched structure.

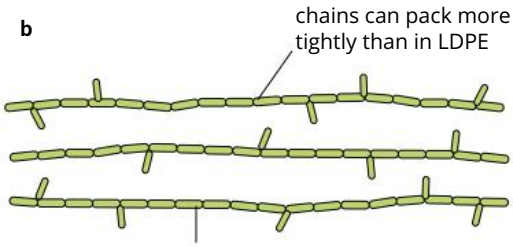
High-density polyethene (HDPE)

A low-pressure method of producing polyethene was developed by Union Carbide in the late 1960s. Highly specialised transition metal catalysts are used to avoid the need for high pressures. The polymer molecules are produced under much milder conditions and have 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 properties are summarised in Figure 15.2.6. HDPE is used in plastic bottles, food storage containers, water pipes and fuel tanks.

a

b



Properties
- High density
- Hard
- Relatively high melting point
- Crystalline sections
- Non-conductor of electricity

FIGURE 15.2.6 Properties and structure of high-density polyethene: (a) a bottle made from HDPE; (b) HDPE structure

CHEMFILE

The discovery of polyethene

The first practical method for the synthesis of polyethene was discovered by accident in 1933 in the laboratory of Imperial Chemical Industries (ICI) in Cheshire, England, when some oxygen was accidently added to a container of ethene. The oxygen initiated the polymerisation reaction between the ethene molecules.

'When it first happened, it was a fluke', recalled Frank Bebbington, a young laboratory assistant who was involved in the discovery. He assembled a reaction vessel to produce the polymer, only to watch the pressure slowly fall. 'We thought there was a small leak in the system. I felt embarrassed', he said.

Frank's colleagues went to lunch and he continued to top up the reaction vessel with more ethene. After his colleagues returned, the vessel was opened and they found that they had indeed made the new plastic. It took until 1938 for ICI to develop the industrial process that allowed them to produce their first commercial batch of polyethene.

Commercial use of the polymer flourished during World War II, when it was used to replace much heavier components in planes and ships.

POLYTETRAFLUOROETHENE (PTFE)

Many applications require polymers with more specialised properties than polyethene. Polytetrafluorethene (PTFE) has the structure $[-CF_2-CF_2-]_n$ and is formed from the monomer tetrafluoroethene $CF_2=CF_2$ (Figure 15.2.7). It is more commonly known by the brand name Teflon. Its many properties are summarised in Table 15.2.2 and have led to its use in a wide range of applications, including plumber's tape, non-stick cookware, artificial hips and vocal cords, and machinery parts that require lubrication, and pipes or containers designed to hold reactive or corrosive liquids.

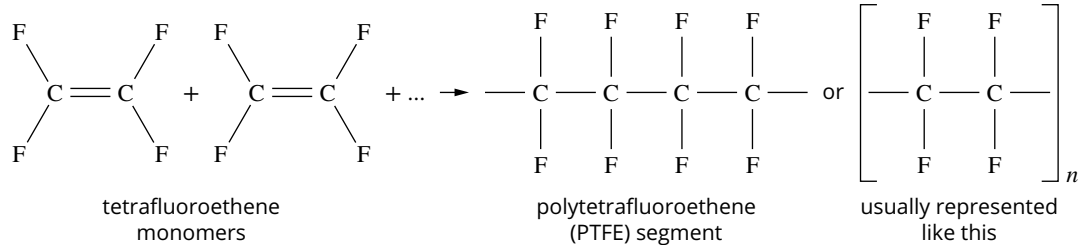


FIGURE 15.2.7 Tetrafluoroethene monomers react together to form polytetrafluoroethene (PTFE), also known as Teflon.

TABLE 15.2.2 The properties of Polytetrafluoroethene (PTFE), also known as Teflon

Property	Applications
Non-stick	Teflon repels all other substances, both hydrophobic (oil, fat) and hydrophilic (water and aqueous solutions).
Heat resistance	The melting point of Teflon is 335°C and its upper operating temperature is 260°C.
Chemical resistance	Because of the strength of the C–F bonds, Teflon is extremely resistant to all known chemicals. It is not attacked by strong acids and alkalis and is inert to all organic solvents.
Good mechanical properties	Teflon is strong and durable.
Low friction coefficient	Teflon is slippery to the touch. The friction coefficient between two pieces of Teflon is very low.
Flame resistance	Teflon is non-flammable.

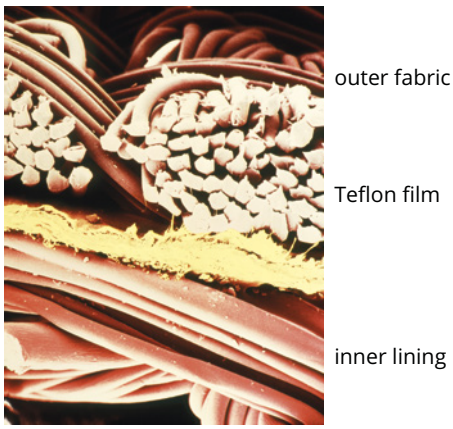


FIGURE 15.2.8 Scanning electron micrograph of Gore-Tex fabric. The small yellow and white particles are Teflon. The small holes between these particles allow vapour to pass through the fabric but not liquid.

Another innovative application of Teflon is in Gore-Tex® (Figure 15.2.8). Gore-Tex is a fabric that 'breathes'. Liquid water from 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.

POLYVINYLCHLORIDE (PVC)

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 15.2.9.

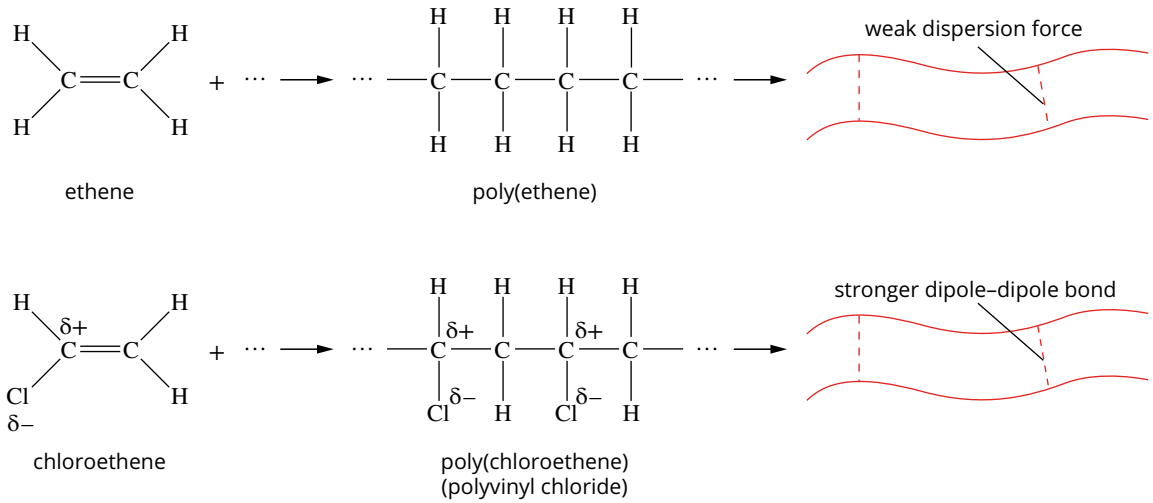


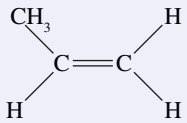
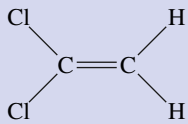
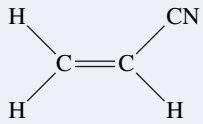
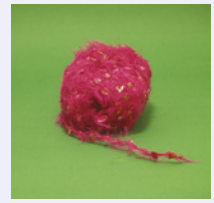
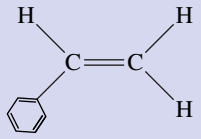
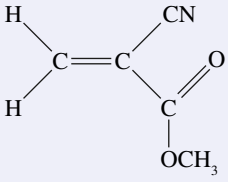
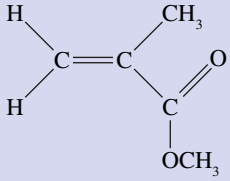
FIGURE 15.2.9 Polyvinyl chloride is formed from polymerisation of polar chloroethene monomers, and has dipole–dipole attractions between chains.

The carbon–chlorine bonds in a PVC molecule are polar and allow dipole–dipole attractions to form 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 such as plasticisers, as discussed in section 15.4, allows even more widespread use of PVC.

OTHER ADDITION POLYMERS

There are many examples of commercial addition polymers. Table 15.2.3 on page 412 shows polymers that may be familiar to you. Each of these polymers offers a unique property or properties that make them of commercial interest.

TABLE 15.2.3 Commercial addition polymers

Monomer	Polymer	Properties	Examples	Application
Propene 	Polypropene (polypropylene)	Durable, cheap	Artificial grass, dishwasher-safe plastic, ice-cream containers, rope	polypropene
Dichloroethene 	Polyvinylidene chloride (PVDC)	Sticks to self, transparent, stretchy	Food wrap	polyvinylidene chloride (PVDC)
Propenenitrile 	Polypropenenitrile (acrylic)	Strong, able to form fibres	Acrylic fibres, fabrics	polypropenenitrile (acrylic) 
Phenylethene (styrene) 	Polyphenylethene (polystyrene)	Hard, brittle, low melting point	Toys, packaging, expanded foams	polyphenylethene (polystyrene)
Methyl cyanoacrylate 	Polymethylcyanoacrylate	Polymerises on contact with water	Super glue	polymethyl cyanoacrylate (superglue
Methyl 2-methylpropenoate 	Polymethyl methacrylate (Perspex)	Transparent, strong	Perspex (a glass substitute)	polymethyl methacrylate (Perspex)

15.2 Review

SUMMARY

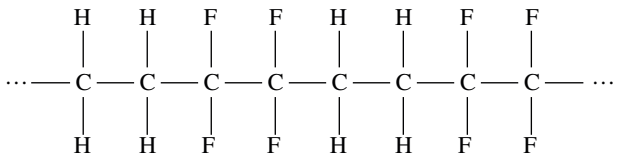
- Addition polymers are formed from the reactions of monomers containing carbon–carbon double (or triple) bonds.
- During addition polymerisation, the double (or triple) carbon–carbon bond is broken and new single bonds are formed between the monomers.
- The most common polymer used is polyethene ($–CH_2–CH_2–$), formed from the addition polymerisation of ethene monomers ($CH_2=CH_2$). It can be manufactured in two different ways to make two different products: high-density polyethene (HDPE) and low-density polyethene (LDPE).
- High-density polyethene (HDPE) has a low degree of branching and hence has relatively strong dispersion forces between polymer chains. This makes it harder, denser and more rigid than LDPE.
- Low-density polyethene (LDPE) has a high degree of branching and hence has weaker dispersion forces between polymer chains. This makes it less dense than HDPE and more flexible.
- Polytetrafluoroethene (PTFE), also known as Teflon and used in Gore-Tex, is a polymer with the formula ($–CF_2–CF_2–$), formed by the addition polymerisation of tetrafluoroethene monomers ($CF_2=CF_2$).
- The polarity and size of side groups in the polymer affect the strength of the attractions between polymer chains.

KEY QUESTIONS

1 Which one of the following is an important feature of a monomer if it is to undergo addition polymerisation?

A single carbon–carbon bonds
B functional groups on the end of each molecule
C a C=O double bond
D a carbon–carbon double bond

2 How many repeating monomer units does the following polymer segment contain?

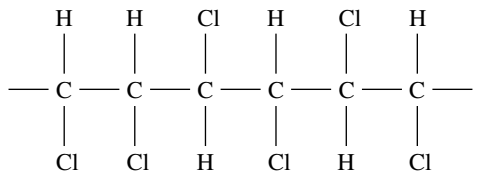


3 Draw a section of the addition polymers formed from the following monomers. For each, draw at least two repeating units.

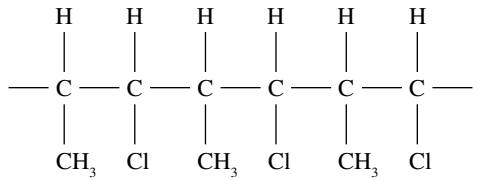
a bromoethene ($CH_2=CHBr$)
b propene ($CH_2=CHCH_3$)
c acrylonitrile ($CH_2=CHCN$)

4 Identify and draw the structural formulas of the monomers used to form the following polymers.

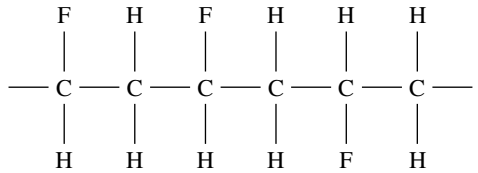
a



b



c



5 **a** In terms of their structures, explain the difference in properties between HDPE and LDPE.

b Which of these two forms would be a suitable material for:

i a soft, flexible plastic wrap?
ii a 2-litre drink container?
iii wrapping material for frozen food?

15.3 Condensation polymerisation

Addition polymerisation is limited to the use of unsaturated monomers. To obtain an even broader range of polymers, chemists use a second technique, known as **condensation polymerisation**. For condensation polymerisation to occur, the monomers must have two functional groups, one on each end of the monomer. These functional groups react chemically with the functional groups on neighbouring monomers. The reaction links the monomers into long polymer chains, as shown in Figure 15.3.1.

Another feature of condensation reactions is that small molecules are also produced during the reaction. In the two **condensation polymers** we will examine in detail, polyamides and polyesters, a molecule of water (H_2O) is produced during each reaction between the two functional groups.

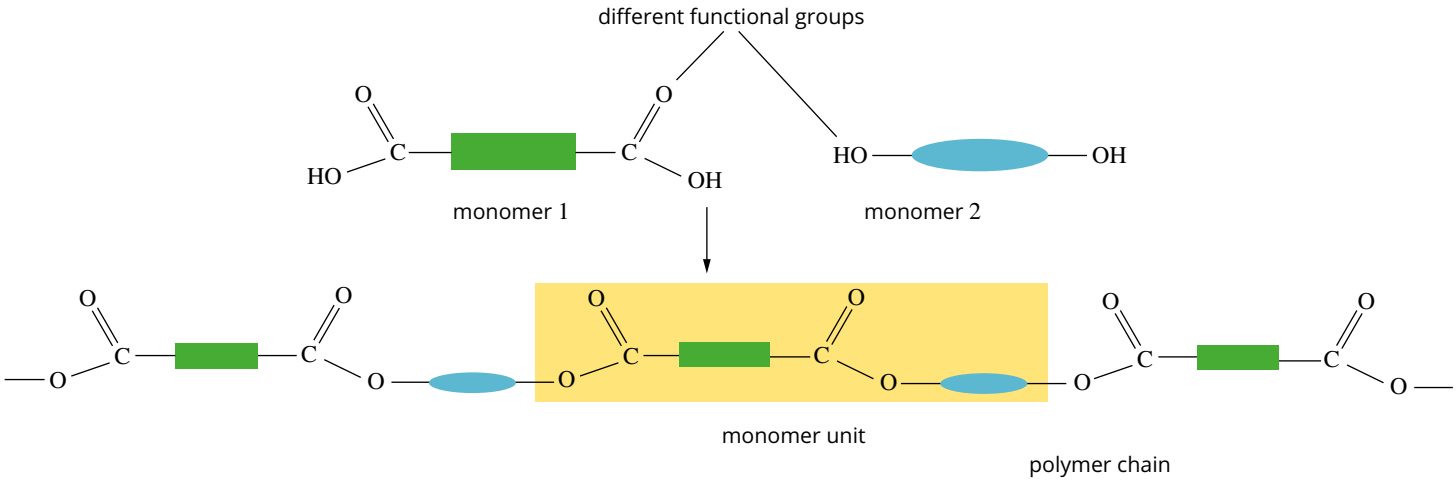


FIGURE 15.3.1 Condensation reactions require that the monomers have functional groups at each end of the molecule. These functional groups react together to form the polymer chain. As a result, an additional product is formed. In this case, the alcohol and carboxylic acid groups react to form an ester and water is produced.

The differences between addition and condensation polymers are summarised in Table 15.3.1.

TABLE 15.3.1 Comparision of addition and condensation polymers

Addition polymers	Condensation polymers
Monomers must be unsaturated, containing a double or triple carbon–carbon bond.	Monomers must contain two functional groups that can react with those on neighbouring molecules.
No by-products are produced during the reaction.	Small molecules, often water, are produced during the reaction.
The polymer backbone is a long C–C chain.	The polymer backbone contains functional groups; for example, amides or esters.

POLYESTERS

The term 'polyester' is commonly used to refer to a synthetic clothing material. However, in chemistry, **polyesters** are a class of polymers that are formed through the process of condensation polymerisation. Polyesters are formed by combining monomers that contain carboxyl and hydroxyl functional groups. Typically, they are formed by reacting a dicarboxylic acid monomer with a diol monomer (Figure 15.3.2). However, they can also be formed between monomers that contain both a carboxyl and a hydroxyl functional group within the same monomer.

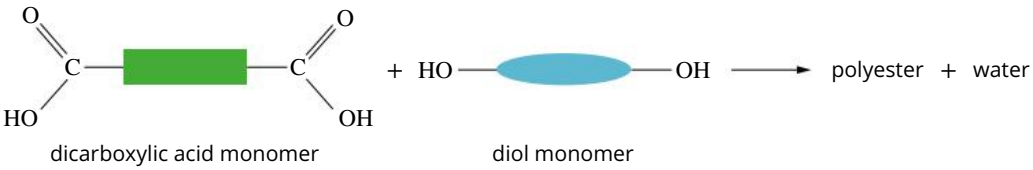


FIGURE 15.3.2 Dicarboxylic acid and diol monomers undergo condensation polymerisation to produce a polyester monomer and water.

Polyesters are typically formed by combining a dicarboxylic acid monomer with a diol monomer in a condensation polymerisation reaction. Water molecules are also produced during the polymerisation reaction.

Polyethylene teraphthalate (PET)

The polymer most often used to make polyester fabric is polyethylene terephthalate, or PET (or sometimes PETE). In addition to being used in fabrics, it has a range of uses, including recyclable drink bottles and food packaging (Figure 15.3.3). PET is synthesised by reacting 1,4-benzenedicarboxylic acid monomers with ethane-1,2-diol monomers, as shown in Figure 15.3.4. PET is a strong material because the ester groups are polar and therefore PET exhibits dipole-dipole attractions between polymer chains.

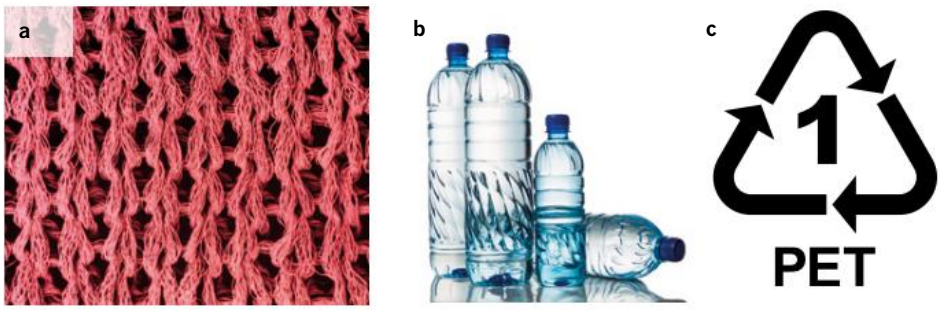


FIGURE 15.3.3 Polyethylene terephthalate (PET) has many uses. (a) A scanning electron micrograph showing knitted polyester fibres used in clothing. (b) PET is commonly used to make plastic bottles. (c) Bottles made of PET have the recycling code 01.

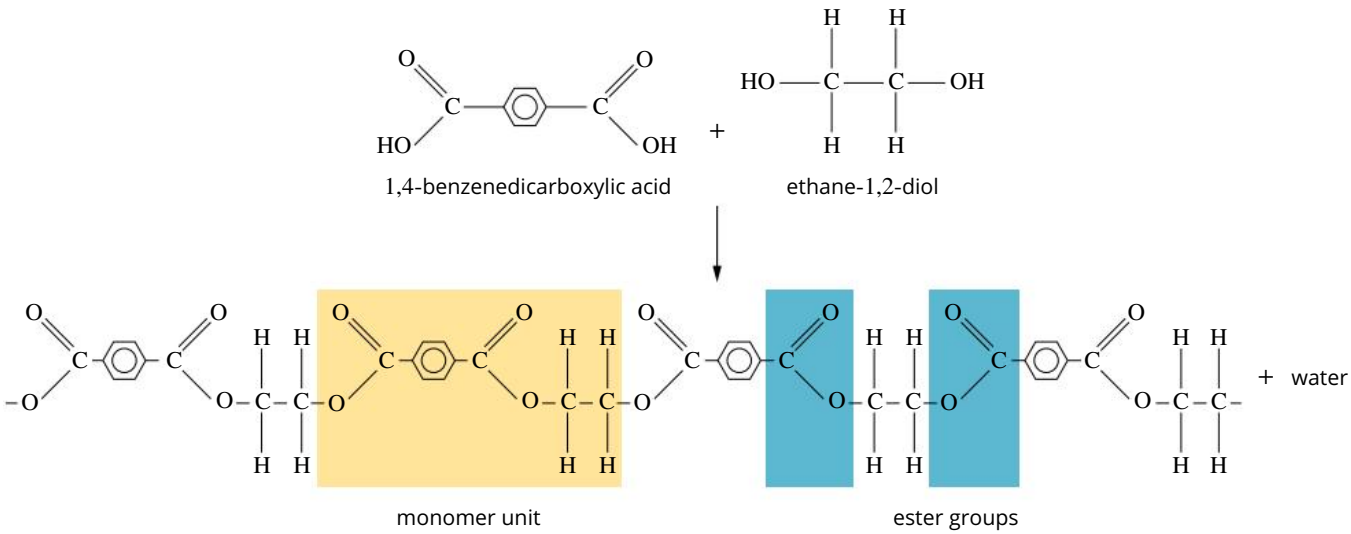


FIGURE 15.3.4 Polyethylene terephthalate (PET) is formed when 1,4-benzenedicarboxylic acid reacts with ethane-1,2-diol. Water is also produced. The PET is linked by ester groups, which is why it is part of the polyester family of polymers.

CHEMFILE

Bisphenol A (BPA)

Bisphenol A (BPA) is an organic compound containing two hydroxyl functional groups, as shown in Figure 15.3.5.

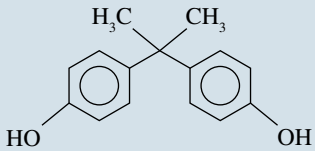


FIGURE 15.3.5 Bisphenol A (BPA) undergoes condensation polymerisation.

BPA is often used to produce condensation polymers. It can be combined with a dicarboxylic acid molecule to produce a polyester. More commonly, it is combined with phosgene ($COCl_2$) to produce polycarbonate plastic. In this condensation reaction, HCl is released rather than H_2O. Polycarbonate plastic is used to produce water bottles, sports equipment, medical devices, CDs and DVDs and the lining of water pipes.

There have been health concerns about the use of BPA in recent years. In particular, its use in baby bottles is of concern because BPA has been shown to mimic the action of the hormone oestrogen. Governments and health regulatory bodies have responded in various ways. In recent years, both the US Food and Drug Administration and European Food Safety Authority have concluded that BPA poses no risk to consumers of any age. Regardless, many products in the food industry are now advertised as 'BPA free'.

POLYAMIDES

Polyamides are another class of condensation polymer. Polyamides typically form when dicarboxylic acid molecules react with diamine molecules, as shown in Figure 15.3.6. They can also form between monomers that contain both a carboxyl and amino functional group within the same molecule. Polyamides tend to be stronger than polyesters of similar structure. This is because hydrogen bonds can form between the amide groups on neighbouring polymer chains. In polyesters, ester groups can only form dipole–dipole interactions with each other.

Nylon and Kevlar are two examples of commonly used synthetic polyamides. Proteins, as discussed in Chapter 17 and 18, are examples of biological polyamides.

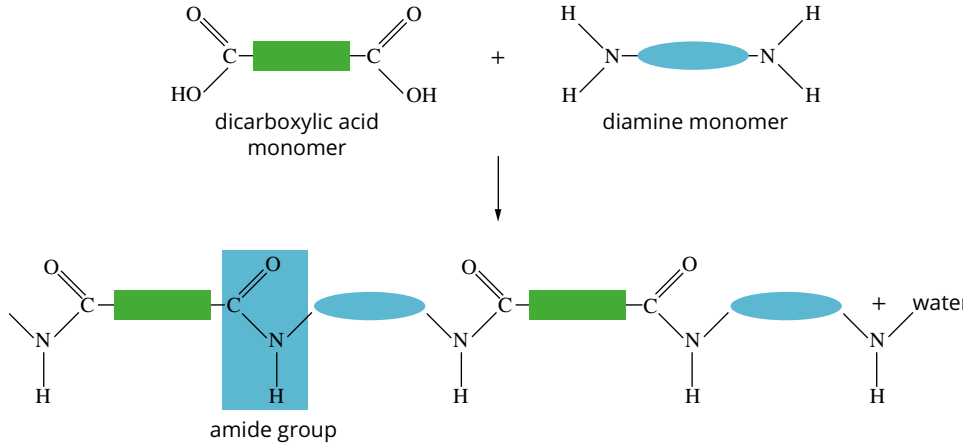


FIGURE 15.3.6 Dicarboxylic acid and diamine monomers undergo a condensation polymerisation reaction to produce a polyamide and water.

Polyamides are typically formed by combining a dicarboxylic acid monomer with a diamine monomer in a condensation polymerisation reaction. Water is also produced during the condensation reaction.

Nylon

Nylon is a common example of a polyamide. It can be easily drawn into fibres with a high tensile strength. These fibres are often used to produce strong, lightweight materials for clothes, parachutes, ropes, fishing line and even guitar strings. However, nylon can also be used to make hard, rigid plastics that can be used in pipes and machinery.

The term 'nylon' refers to a group of polyamides in which the monomers contain linear carbon chains. A common example is nylon-6,6, which is so-named because the dicarboxylic acid monomer has a chain of six carbons and the diamine monomer also has a chain of six carbon atoms, as shown in Figure 15.3.7.

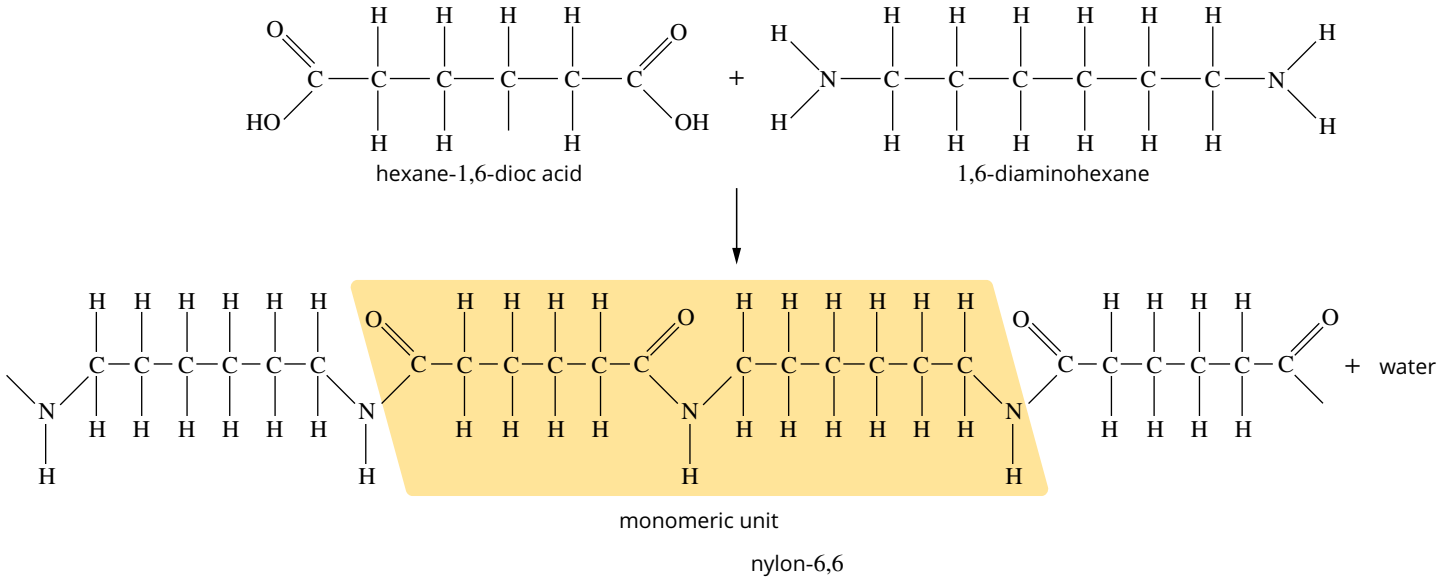


FIGURE 15.3.7 Nylon-6,6 is a polyamide formed when 1,6-hexanedioic acid reacts with 1,6-diaminohexane. Water is also produced.

Kevlar

Replacing the carbon chains in nylon with benzene rings produces the polymer known as Kevlar (Figure 15.3.8). Kevlar is an extremely strong material, which is also very lightweight. This makes Kevlar particularly useful in a range of applications where extreme strength is required, such as bulletproof vests and anchor cables.

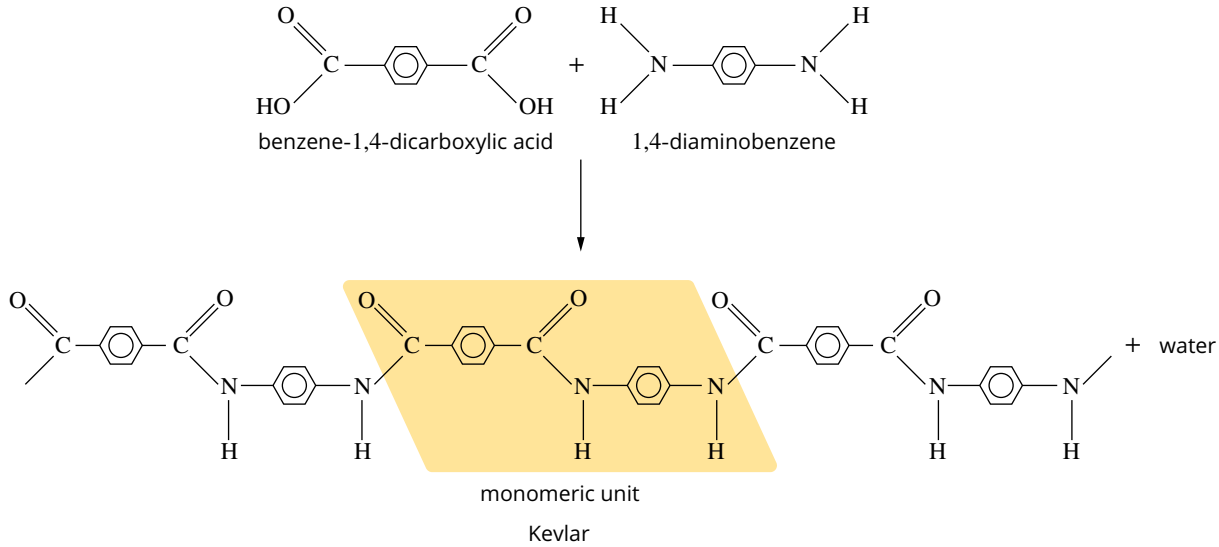


FIGURE 15.3.8 Kevlar is a polyamide molecule formed when benzene-1,4-dicarboxylic acid reacts with 1,4-diaminobenzene. Water is also produced.

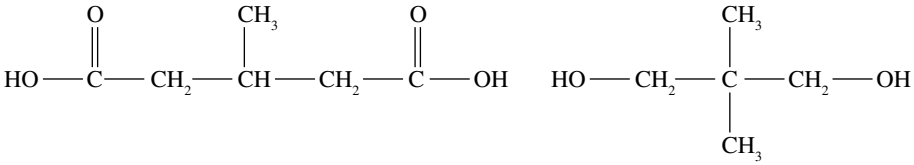
The unique strength of Kevlar is due to its molecular structure. The benzene rings make the polymer chains rigid. It also allows the molecules to align closely together. As a result, there is strong hydrogen bonding between the amide groups in these molecules.

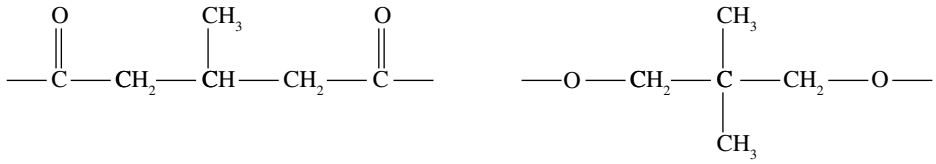
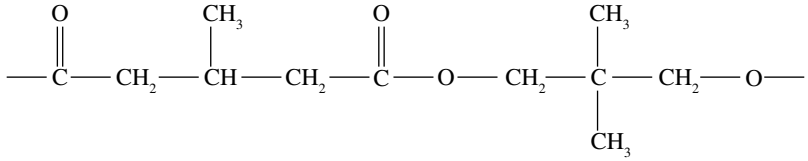
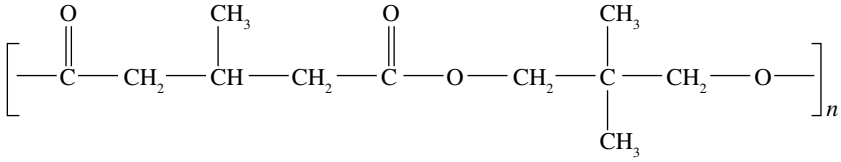
It is possible to predict the structure of a condensation polymer from the monomers. Read through the steps in Worked Example 15.3.1 to predict the structure of a condensation polymer.

Worked example 15.3.1

CONDENSATION POLYMERISATION: FORMING POLYMERS

Draw the condensation polymer produced from the following monomers.

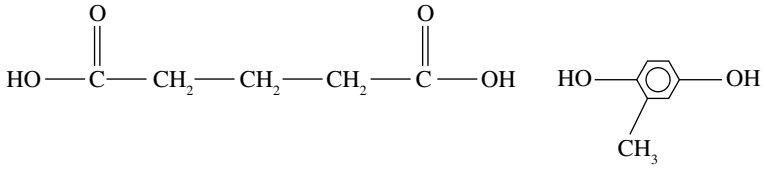


Thinking	Working
Examine the functional groups on the monomer(s) and determine whether a polyamide or polyester will be formed. Remember an alcohol and carboxylic acid condense to form an ester, and an amine and carboxylic acid condense to form an amide.	The monomers are a diol and a dicarboxylic acid. Therefore, they will react to form a polyester.
To form the ester group in the polymer, remove the hydroxyl groups from the dicarboxylic acid and the hydrogen atoms from the hydroxyl groups of the diol.	
Construct the repeating unit by joining the two halves.	
Write the repeating unit inside square brackets with a subscript *n* to indicate it is a polymer.	

Worked example: Try yourself 15.3.1

CONDENSATION POLYMERISATION: FORMING POLYMERS

Draw the condensation polymer produced from the following monomers. Include at least two repeating units.

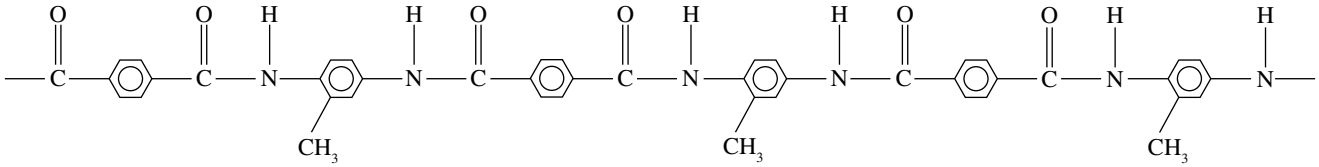


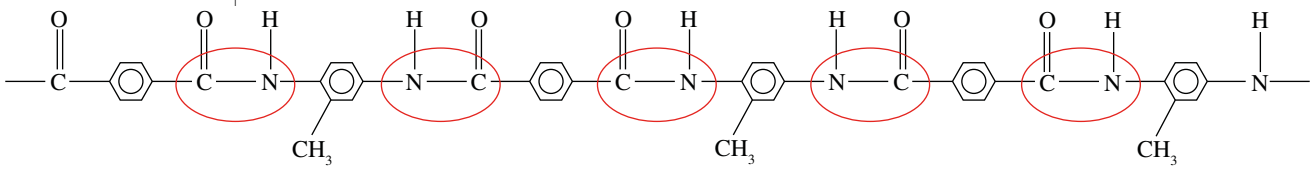
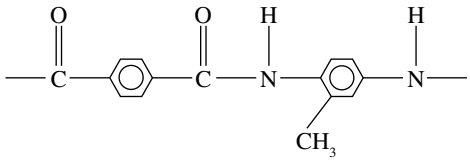
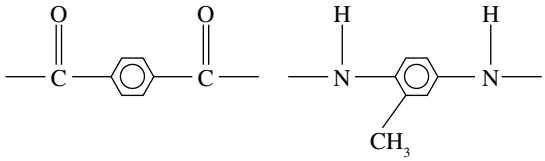
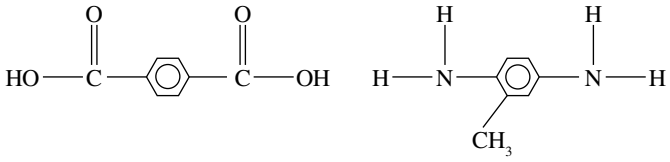
It is also possible to identify the monomers of a condensation polymer from the polymer molecule. Read through the steps in Worked Example 15.3.2 to see how to identify the monomers of a condensation polymer.

Worked example 15.3.2

CONDENSATION POLYMERISATION: DETERMINING THE MONOMER UNITS

Draw the structure of the monomer(s) used to produce the following polymer.

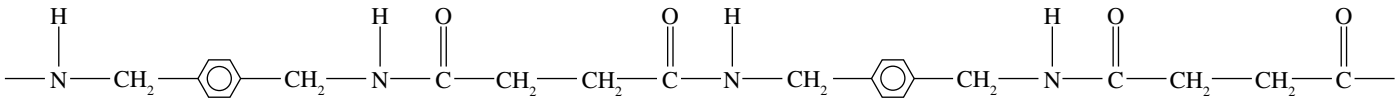


Thinking	Working
Determine whether the polymer is a polyamide or a polyester and circle the amide or ester linkages.	The polymer is a polyamide, due to the presence of the amide (–CONH–) groups. 
Identify the repeating unit. Note that this may be composed of 1 or 2 separate monomers.	
Within the repeating unit, split the amide group at the C–N bond.	
Draw the two monomers individually, adding the H and OH groups to re-form the hydroxyl, carboxyl or amino functional group on the monomer(s).	

Worked example: Try yourself 15.3.2

CONDENSATION POLYMERISATION: DETERMINING THE MONOMER UNITS

Draw the structure of the monomer(s) used to produce the following polymer.



15.3 Review

SUMMARY

- Condensation polymerisation is a method for synthesising polymers.
- In condensation polymerisation, the monomers are joined via a covalent bond, which is created by reacting two functional groups on each of the molecules.
- During a condensation reaction, smaller molecules are also produced. These are usually water molecules, but can also be other small molecules, such as hydrogen chloride (HCl), depending on the functional groups.
- Polyesters are formed by condensation polymerisation of dicarboxylic acid monomers and diol monomers.
- Polyethylene terephthalate (PET) is an example of a polyester.
- Polyamide polymers are formed by the condensation polymerisation of dicarboxylic acid monomers and diamine monomers.
- Nylon, Kevlar and proteins are examples of polyamides.
- Polyamides have hydrogen bonding between the amide groups on neighbouring chains, making polyamides tougher polymers than similar polyesters.
- The structure of condensation polymers can be predicted from their monomers. Likewise, the monomers can be derived from the structure of a condensation polymer.

KEY QUESTIONS

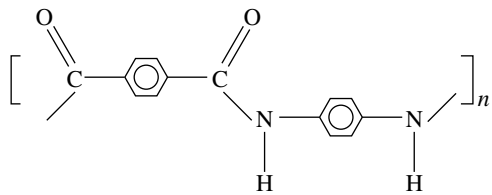
1 Which one of the following pairs of compounds could form a condensation polymer?

A ethene and a dicarboxylic acid
B two diol molecules
C a diamine and a dicarboxylic acid
D a diol and a diamine

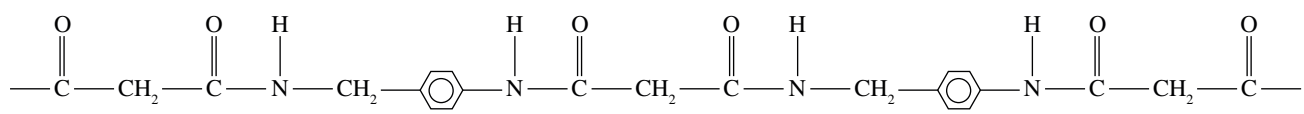
2 When a condensation reaction is used to create a polyester molecule, name the other substance that is also produced.

3 Classify the following polymers as polyesters or polyamides.

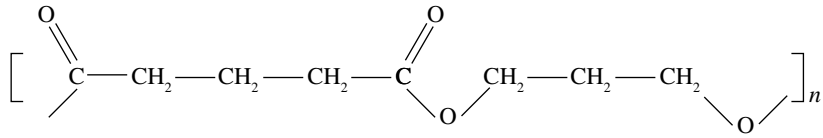
a



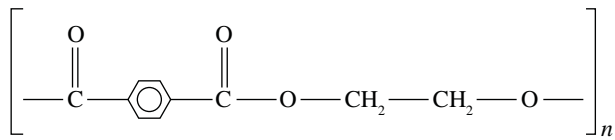
b



c

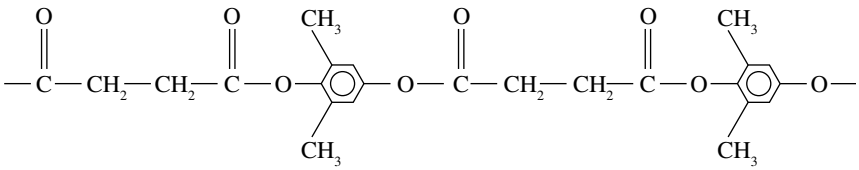


d

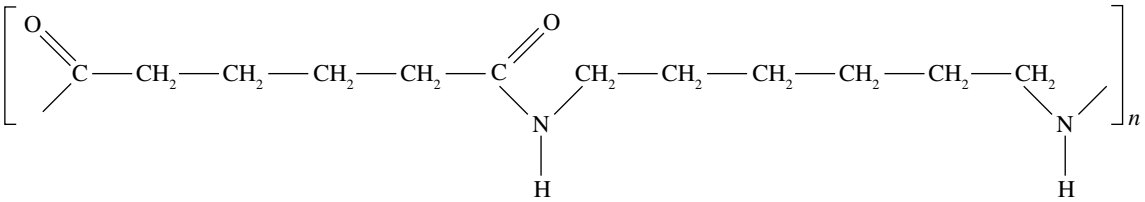


4 Draw the monomers that make up the following polymers.

a

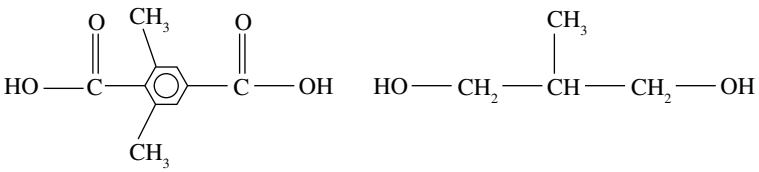


b

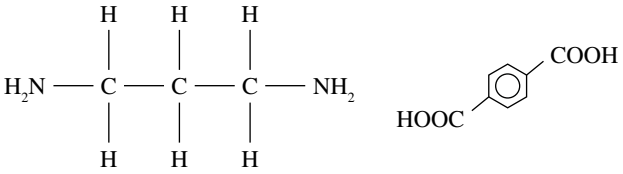


5 Draw the polymer that would be formed from the following two reactants.

a



b



6 In the name of nylon-6,6, the first 6 refers to the number of carbons in the diamine. The second 6 refers to the number of carbons in the dicarboxylic chain. Given this, deduce the structure of nylon-4,6.

15.4 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. An important issue is reducing polymer waste, through either **biodegradable** polymers or recyclable polymers. In section 15.1, you learnt how the length of polymer chains and the amount of branching can affect polymer properties. In this section you will explore how changes in monomer structure, and the addition of other substances to the polymer, can modify polymer properties.

COPOLYMERS

In recent years a new generation of versatile materials has been developed by combining two or more monomers into one polymer. A **copolymer** is a polymer made from at least two different monomers. Both addition and condensation polymers can be copolymers.

The Water Cube Stadium built for the 2008 Beijing Olympic Games (Figure 15.4.1) 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 15.4.1 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 15.4.2) is formed from styrene (CH_2=CH(C_6H_5)) and buta-1,3-diene (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.

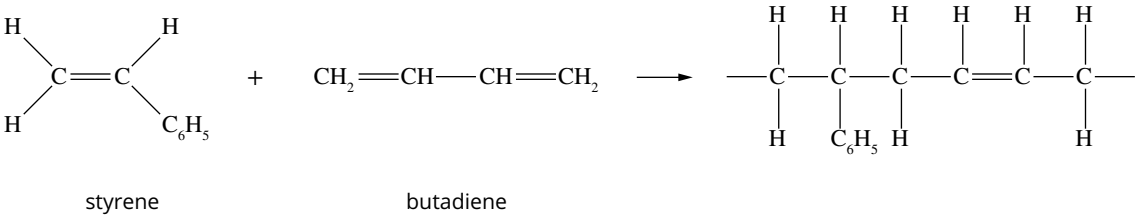


FIGURE 15.4.2 Formation of the SBR copolymer chain from two monomers.

A variety of polymers with different properties can be produced simply by altering the ratio of the monomers in styrene–butadiene rubber. For example, an elastomer similar to natural rubber is produced when the two monomers are present in close to equal amounts. Increasing the concentration of styrene monomers increases the abrasion resistance of the polymer and makes it suited for use in car tyres, its main application.

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 15.4.3, 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 solid object.

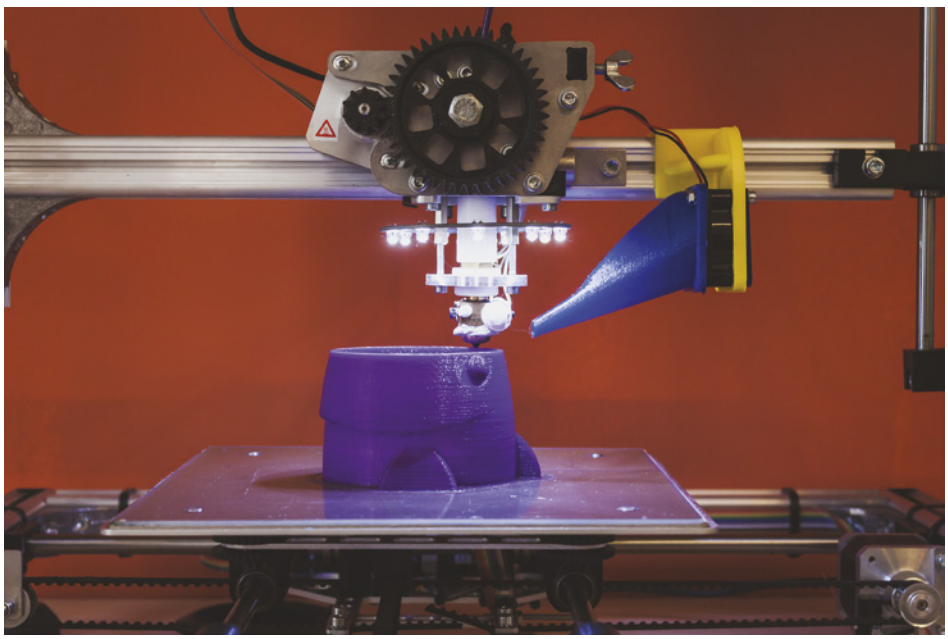


FIGURE 15.4.3 This 3D printer uses an ABS copolymer filament to make an object.

CHEMFILE

Conducting 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 Heegar (USA) for the discovery of electrically conducting polymers. These groundbreaking conductive polymers have opened the way to lighter, polymer-based circuits, which are now being used in biosensors.

The way in which a polymer can become electrically conducting is beyond the scope of this course, although the starting point is polymers with alternating double and single bonds, such as polyethyne (Figure 15.4.4). When ethyne (CH≡CH) polymerises, one of the carbon–carbon bonds is rearranged to bond to neighbouring monomers. Each repeating monomer unit in polyethyne retains a carbon–carbon double bond.

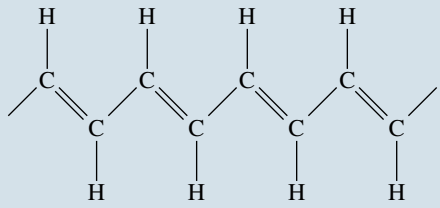


FIGURE 15.4.4 Polyethyne is a polymer that becomes conductive under some conditions.

The alternating double and single bonds in the polymer chain is called a conjugated system. Two of the electrons in the double bond are delocalised and able to move within the polymer chain.

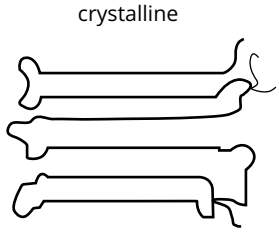


FIGURE 15.4.5 A crystalline region of a polymer material forms where the polymer chains are arranged in an ordered fashion.

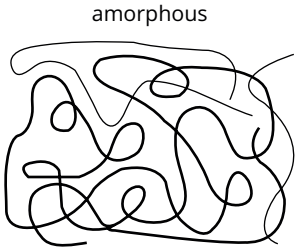


FIGURE 15.4.6 An amorphous region forms when polymer chains are disordered.

CRYSTALLINITY

Materials made from polymers consist of many long chains that twist around each other, with intermolecular forces from one chain to 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 15.4.5.

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).

An amorphous region is where the polymer chains are randomly tangled and unable to pack very closely. The polymer chains shown in Figure 15.4.6 are amorphous because they have no orderly arrangement.

In some polymer materials, the entire solid is amorphous. Amorphous polymers are usually less rigid and weaker and are 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 because the crystalline regions scatter light.

BRANCHING

As discussed in section 15.1, the degree of branching in a polymer chain has a large effect upon the density of the polymer material and strength of the intermolecular forces that exist between polymer chains. When extensive branching is present, polymer chains are unable to pack together as closely when solid, resulting in a less dense and more flexible material with far fewer crystalline regions. As discussed in section 15.2, HDPE can have a percentage crystallinity of up to 95%, whereas LDPE is more amorphous with a percentage crystallinity as low as 65%.

ADDITIVES

Very few polymers are used in their pure form. Most include additives that improve or extend the properties of the polymer. These additives 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.

EXTENSION

Arrangement of side chains

The way that side chains are arranged within the polymer chain also has a significant effect upon the properties of a polymer material, such as polypropene (PP).

PP is an addition polymer made from the monomer propene (CH_2=$CHCH_3$), as shown in Figure 15.4.7.

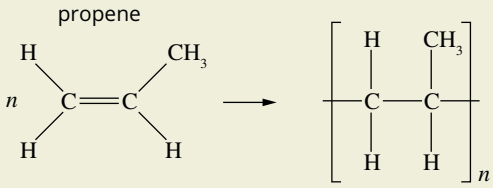


FIGURE 15.4.7 Propene undergoes addition polymerisation to form polypropene.

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 15.4.8 shows the three different structural forms of PP.

- Isotactic PP has all the side groups on one side of the polymer chain and syndiotactic PP has the side groups on regularly alternating sides of the polymer chain. These two arrangements allow crystalline regions to form, and significant attractive forces exist between the chains. Isotactic PP 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 fleece jackets.
- Atactic PP has the side groups randomly distributed. This prevents the chains from stacking together well and forming crystalline regions. Atactic PP is very soft and has limited usefulness.

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 had traditionally been used.

Polystyrene is an example of an addition polymer that is formed from a polar monomer called styrene or phenylethene (Figure 15.4.9). The styrene molecule contains a benzene ring as a bulky side chain.

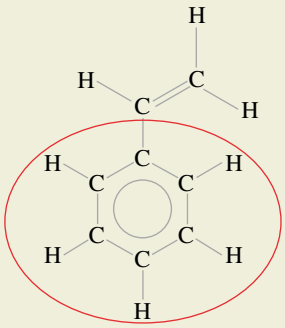


FIGURE 15.4.9 The styrene monomer contains a bulky benzene ring side group (circled in red).

In polystyrene, benzene rings are covalently bonded to every second carbon atom in the polymer chain. The bulky benzene side chain makes it quite difficult for the chains to slide over each other or to stack closely together. This causes polystyrene to be a hard but quite brittle plastic with a low density. It is used to make food containers, picnic sets, refrigerator parts and CD and DVD cases.

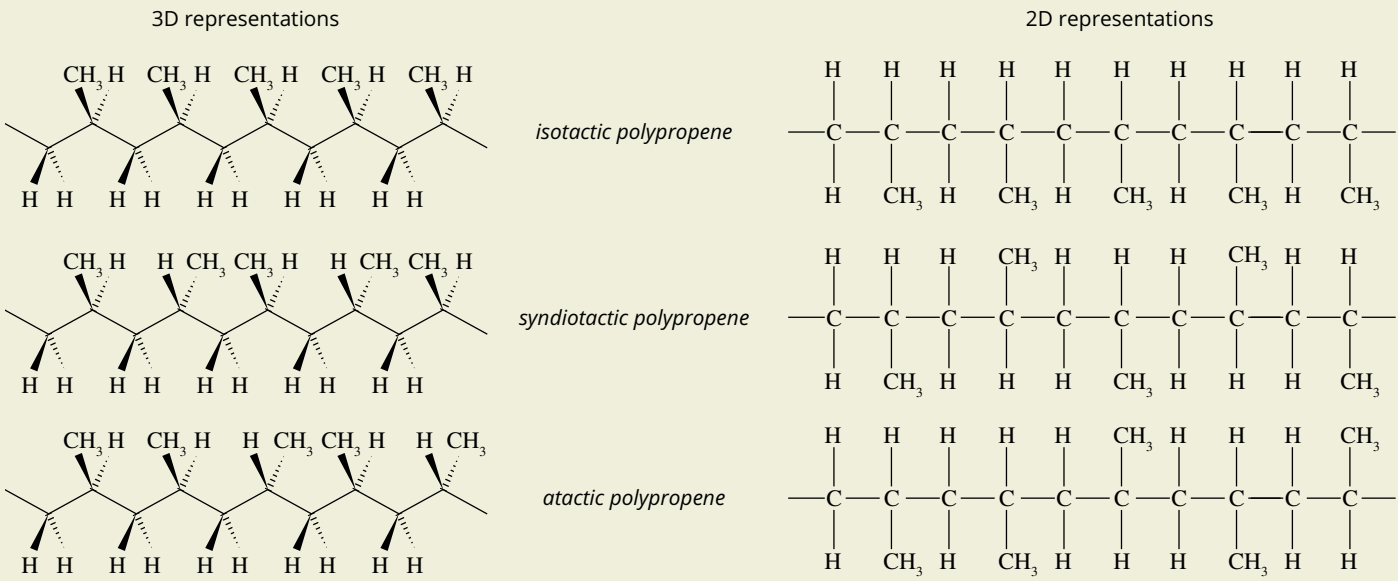


FIGURE 15.4.8 Sections of three different structural forms of polypropene

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, they 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 without and with plasticiser in Figure 15.4.10. Diisononyl phthalate is a plasticiser that is used to make PVC into vinyl floor coverings.

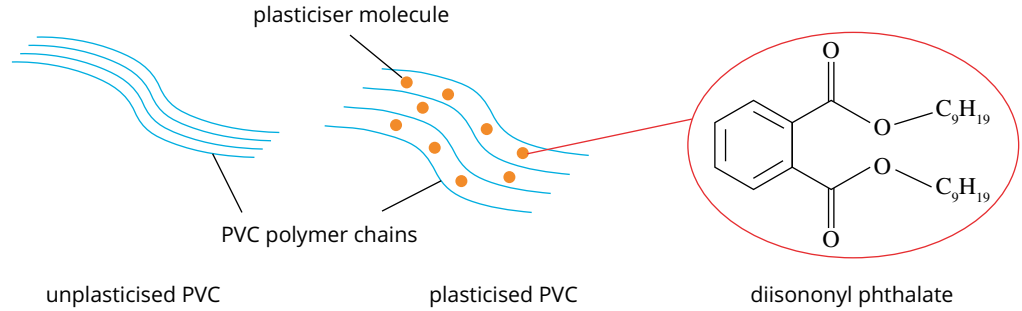


FIGURE 15.4.10 The presence of a plasticiser between the polymer chains weakens the attractive forces.

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 15.4.12. 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 take-away hot drink containers, bean bag beans and packaging materials.

FIGURE 15.4.12 A model plane made of rigid polystyrene sitting on a block of foamed polystyrene.

CHEMFILE

Hydrogels

Hydrogels are networks of polar polymer chains that are highly absorbent, containing up to 90% water (Figure 15.2.11). Hydrogels can be both natural and synthetic and are used in a range of applications. Because of their high water content, most hydrogel structures are biocompatible, and they are used in biomedical applications, such as contact lenses, breast implants, dressings for burns and scaffolds for tissue engineering. Hydrogels are also commonly used outside the body in disposable nappies and as water-saving granules for the garden. They are also used to plug leaks in dams and ponds, and to control water flow in the mining industry. For example, if suitable hydrogels are added to a leaky dam, they will absorb water and be forced down into the cracks and holes in the dam floor by the water pressure. The hydrogels will continue to expand, sealing the surface.

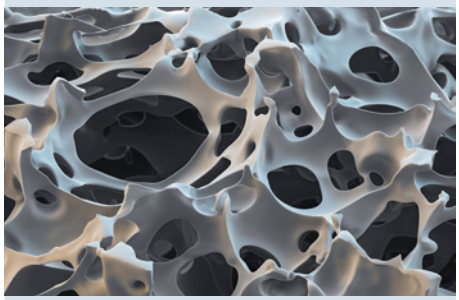


FIGURE 15.4.11 A scanning electron micrograph of a polymer hydrogel formed from the polymerisation of acrylic acid. It can hold many times its own weight in water.

RECYCLING PLASTICS

Australians consume more than 1.5 million tonnes (1.5 billion kilograms) of polymer materials every year, which includes many different plastics. Many polymers are derived from petroleum, a non-renewable resource, which increases the environmental impact associated with their production. Therefore, the disposal of the waste polymer material is a serious issue.

Plastics are durable, chemically resistant and lightweight. These properties make them very useful, but they also mean that plastics biodegrade very slowly. 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. Waste plastics occupy the limited space available in landfills and litter the environment. Burning plastics raises concerns about pollution from harmful combustion by-products. For example, hydrogen chloride is formed by the combustion of waste containing PVC.

The problems related to disposal have resulted in more waste plastic being collected from users to be recycled. There are two ways of recycling plastics. Reprocessing involves shredding, melting and reshaping used plastic into new, clean products, as shown in Figure 15.4.13. This method can be used only with thermoplastic polymers. For example, reprocessed polyethene can be used for manufacturing carry bags, rubbish bins and liners and bottle crates. One of the issues with recycling polymers in this way is that the different types of plastic need to be completely separated before they are melted. If not, the different polymers do not usually mix and instead form different layers, reducing the usefulness of the recycled polymer. A numbering scale is used to identify plastics for recycling (Figure 15.4.14).

FIGURE 15.4.13 This plastic is being reprocessed by shredding and blow-moulding new products.

PET	HDPE	PVC	LDPE	PP	PS	OTHER
Polyethene terephthalate	High-density polyethene	Polyvinyl chloride	Low-density polyethene	Polypropene	Polystyrene	Includes polycarbonates, ABS, Teflon, various copolymers, nylon & other condensation polymers
drink bottles, shampoo bottles, etc. take-away 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 15.4.14 International number codes are used to identify recyclable plastics.

The other method of plastic recycling involves depolymerisation, in which polymers are broken down into monomers, usually by heat. These monomers are then either used to produce new polymers or as fuel sources. Figure 15.4.15 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.

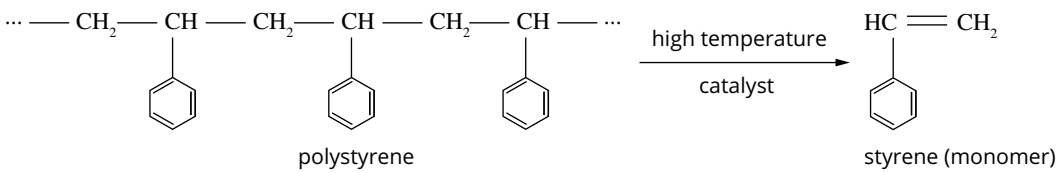


FIGURE 15.4.15 Depolymerisation of polystyrene at high temperature with a catalyst re-forms styrene monomers.

EXTENSION

Biodegradable polymers

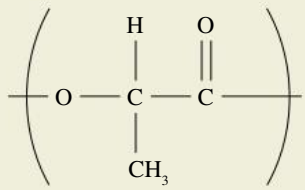
Biodegradable materials break down naturally by the action of microorganisms. Most polymers and plastics are non-biodegradable, which is a major environmental problem. However, biodegradable polymers are being developed and used more widely. Most biodegradable polymers are condensation polymers that are made from renewable plant materials, such as corn and starch. Their structure is often similar to those of biological macrolecules, such as carbohydrates and proteins, which is why they can be broken down.

Polylactic acid is one such material (Figure 15.4.16). It is a polyester that is commonly used as a packaging material or in bags and cups, as well as in medical applications. It is broken down by microorganisms into its lactic acid monomers, which occur naturally and pose no environmental or biological risk.

A second approach to form biodegradable polymers involves including additives 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.

Another approach to biodegradable polymers involves finding and investigating microorganisms that can break down common plastics. In recent years, scientists have identified several microorganisms capable of digesting oils and common plastics such as polyethylene terephthalate or polyurethane. For example, the fungus *Petalotiopsis microspore* can survive on a diet of polyurethane. The fungus was found in the Amazon jungle by a research team from Yale University in 2011. Scientists are now focusing on isolating the specific processes and enzymes involved within these very useful microorganisms.

a



b

FIGURE 15.4.16 (a) Polylactic acid is a biodegradable polymer produced from corn starch. (b) One of its applications is as a barrier to protect young plants from the ravages of frost. By the time the plastic degrades, the plants are big enough to survive on their own.

15.4 Review

SUMMARY

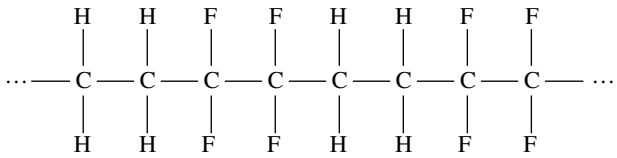
- Materials composed of polymers offer an almost limitless variety of properties, enabling them to be used for many different purposes.
- No polymer is entirely crystalline. Some are entirely amorphous; most consist of both structures.
- Polymers can be designed for a particular purpose by selecting 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
  - 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.
- Because most polymers are made from non-renewable resources and are not biodegradable they pose an environmental risk.

KEY QUESTIONS

1 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 ($CH_2=CHCN$)

2 The following polymer is a copolymer formed from an addition polymerisation reaction. Name the corresponding monomers used to form the chain.



3 The following side groups are found in different polymers. Sort the groups from smallest to bulkiest. –F (in Teflon), $–NC_{12}H_8$ (in polyvinyl carbazole), –H (in polyethene), $–C_6H_5$ (in polystyrene), –Cl (in polyvinyl chloride)

4 Identify whether the following features of a polymer chain will increase or decrease the crystallinity of the polymer material.

a regular (non-random) arrangement of side groups
b less branching
c larger side groups

5 Identify the desired outcome of the following modification techniques used by polymer chemists.

a inclusion of a plasticiser
b foaming
c using a catalyst to prevent branching of polymer chains

Chapter review

15

KEY TERMS

addition polymer
addition polymerisation
amorphous region
biodegradable
condensation polymer
condensation polymerisation
copolymer
cross-link
crystalline region
elastomer
high-density polyethene
low-density polyethene
monomer
plastic
plasticiser
polyamide
polyester
polymer
polymerisation
thermoplastic
thermosetting

Polymers: a diverse class of materials

1 Define:
- **a** monomer
- **b** thermoplastic
- **c** thermosetting
- **d** cross-link
- **e** plasticiser.

2 Are the following statements about polymers true or false?
- **a** Each chain in a polymer is the same length.
- **b** The chains in thermosetting polymers are held together by dipole–dipole bonds.
- **c** HDPE has no branches
- **d** The properties of a polymer are different from the properties of the monomer.

3 The polymer chains of a certain material can be cross-linked to varying extents.
- **a** Sketch 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 Use a diagram to explain how an elastomer is able to stretch and return to its original shape.

5 How does the strength of the inter-chain bonding differ between thermosetting and thermoplastic polymers?

6 Why do thermosetting polymers decompose rather than melt when heated to a high temperature?

7 Would a thermoplastic or thermosetting polymer be the most suitable material for the following purposes?
- **a** handle of a kettle
- **b** 'squeeze' container for shampoo
- **c** knob of a saucepan lid
- **d** shopping bag
- **e** rope

8 Elastic bands, golf balls and saucepan handles are made from polymers with some cross-linking.
- **a** Which of these objects requires a material with the greatest degree of cross-linking?
- **b** Describe the properties of the material you chose in part **a** to support your answer.

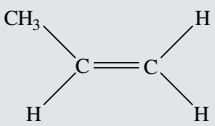
Addition polymerisation

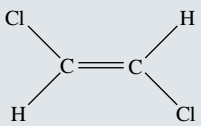
9 Which of the following molecules can act as monomers in addition polymerisation?
- **A** propene
- **B** propane
- **C** chloroethene
- **D** CH_2=CHF

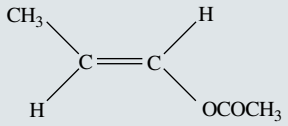
10 Ethene (C_2H_4) is the smallest alkene.
- **a** Why is it described as unsaturated?
- **b** Draw the structural formula of ethene.
- **c** Could ethane (C_2H_6) act as a monomer? Explain.

11 Using polyethene as an example, explain the following terms.
- **a** addition polymerisation
- **b** unsaturated and saturated
- **c** empirical formula

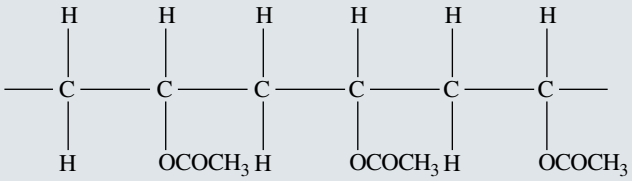
12 Draw a section of the polymer made from each of these monomers in an addition polymerisation process.

a


b


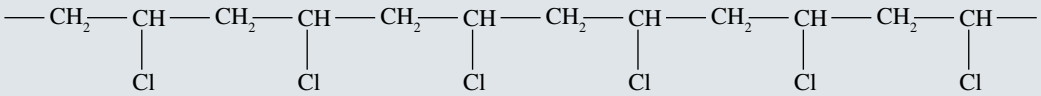
c


13 PVA (or white) adhesive contains polyvinyl acetate in water. A section of the polymer is shown below.



Give the structural formula for its monomer, vinyl acetate.

14 A segment of a PVC polymer is shown here.



a Draw the structure of the monomer used to make PVC.

b How many repeating monomer units are shown in the section of polymer?

c What is the strongest type of bonding between PVC polymer chains?

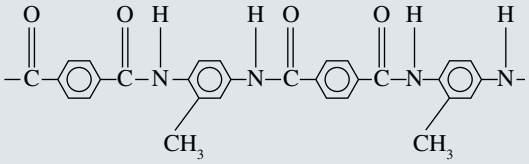
15 **a** What properties make plasticised PVC a suitable material for the covering of electrical cables?

b Explain how the structure of PVC chains give rise to these properties.

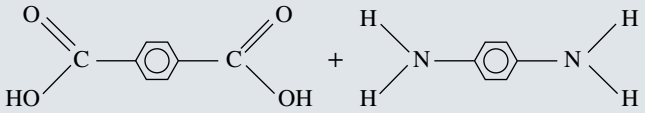
16 Polytetrafluorethene has a higher melting point than polyethene. Explain why.

Condensation polymerisation

17 The structure of a polyamide is shown below. Draw the structure of the two monomers.

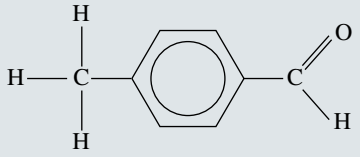


18 Draw the structure of the polymer formed when the following two monomers react.



19 Identify the two molecules below that could react with each other to form a condensation polymer.

a



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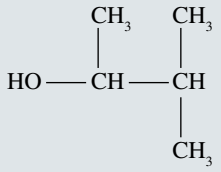
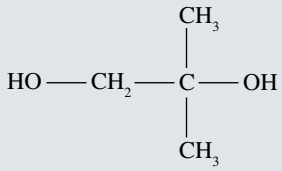
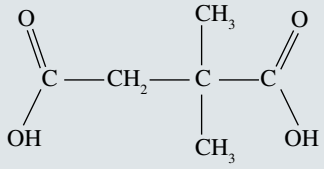


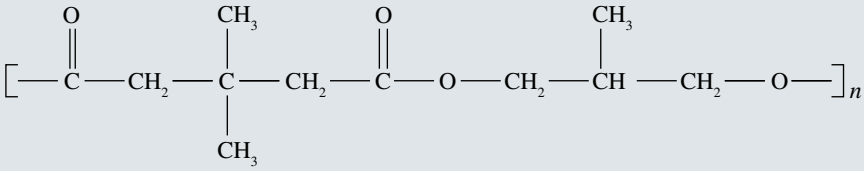
c



d



20 The structure of a polyester is shown below. Draw the structure of the two monomers.



21 In this chapter, you learnt about two different types of condensation polymers. In the case of polyesters, the polymer is generally formed by the reaction between two monomers, dicarboxylic acids and diols. However, condensation polymerisation does not always have to occur between two different monomers. It is possible to have a condensation polymerisation reaction with just one molecule.

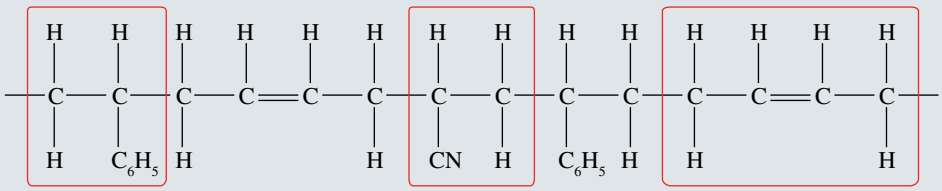
Use what you know about polyesters to construct the structural formula of a single monomer that can undergo condensation polymerisation.

Designing polymers for a purpose

22 Plasticisers can be added to polymers to change their properties. What effect does the addition of a plasticiser have on the hardness and softening temperature of a polymer?

23 What properties are most likely to cause a polymer to contain crystalline regions?

24 Part of the copolymer acrylonitrile–butadiene–styrene (ABS) that Lego® is made from is shown here. Identify the chemical formula of the monomers responsible for the sections in each box.



25 Explain how the following polymer production techniques will affect the properties of a polymer.

a production conditions that favour longer polymer molecules

b oncorporation of side groups with benzene rings ($-C_6H_5$)

26 Is a plastic that can be recycled more likely to be thermoplastic or thermosetting?

Connecting the main ideas

27 Describe two differences between addition and condensation polymerisation.

28 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 inter-chain forces and electrical conductivity. What would you expect the results for each property test to have been?

CHAPTER

16 From fats and oils to soaps and biodiesel

The industrial production of many chemical substances requires the use of large amounts of raw materials. These raw materials, called feedstocks, are often obtained from naturally occurring sources.

Fats and oils are two such feedstocks. The production of soap and biodiesel from fats and oils makes use of organic reactions, some of which you will have encountered already. When the processes are used on an industrial scale, scientists have to consider issues such as sustainability and the environment, alongside economics and profitability. The principles of green chemistry can be used to inform choices around the conditions and reagents used in the processes.

At the end of this chapter you will be able to describe how soaps are made, how soaps and detergents clean and how to determine the structure of the soap molecule(s) produced from a given fat or oil.

You will also learn about the manufacture of biodiesel and the transesterification reaction in base-catalysed and enzyme-catalysed processes. The advantages and disadvantages of each process will be highlighted.

Science as a human endeavour

Scientific knowledge can be used to design alternative chemical synthesis pathways, taking into account sustainability, local resources, economics and environmental impacts (green chemistry), including the production of ethanol and biodiesel.

Science understanding

- chemical synthesis to form products with specific properties may require the construction of reaction sequences with more than one chemical reaction, and involves the selection of particular reagents and reaction conditions in order to optimise the rate and yield of the product
- the base hydrolysis (saponification) of fats (triglycerides) produces glycerol and the salt of a long chain fatty acid (soap)
- the structure of soaps contains a non-polar hydrocarbon chain and a carboxylate group; the structure of the anionic detergents derived from dodecylbenzene contains a non-polar hydrocarbon chain and a sulfonate group

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16.1 Fats and oils

SOURCES OF FATS AND OILS

'Fat' is a name used to describe a number of organic compounds belonging to a 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 are typically obtained from either plant or animal sources. Animal fats tend to exist as solids at room temperature. They are mainly **saturated** fats—all the carbon–carbon bonds are single bonds.

Olive oil, canola oil and palm oil are common plant oils. They usually exist as liquids at room temperature. Plant oils are mainly **unsaturated** fats—they contain one or more double or triple carbon–carbon bonds.

STRUCTURE OF FATS AND OILS

Fats and oils contain large **non-polar** molecules known as **triglycerides**. Non-polar molecules have no overall dipole present in the molecule. Fats and oils have 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 and oils are insoluble in water.

General structure of a fatty acid and glycerol

Triglycerides are synthesised by condensation reactions between a glycerol molecule and three **fatty acids**. Fatty acids are carboxylic acids with chain lengths of eight or more carbons atoms. Glycerol (propane-1,2,3-triol) is a relatively small molecule with three hydroxyl functional groups (Figure 16.1.1). 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 fatty acids have an even number of carbon atoms, usually between eight and 20 (Figure 16.1.1).

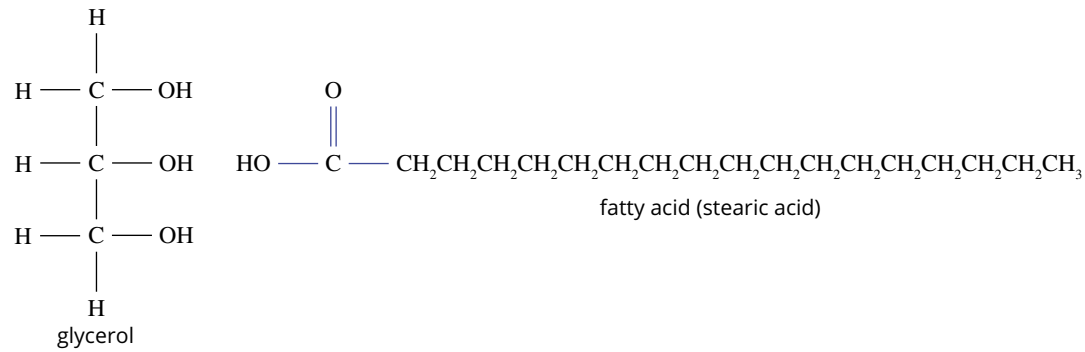


FIGURE 16.1.1 A glycerol molecule and a fatty acid molecule

Condensation reactions to form triglycerides

A condensation reaction can occur between an organic acid that contains a carboxyl group (–COOH) and an alcohol that contains a hydroxyl group (–OH). An **ester functional group** (–COO–) is formed, linking the two molecules. A molecule of water is also produced. You encountered condensation reactions in Chapter 14; reviewing the formation of esters in section 14.3 will help you to understand the chemical processes in this chapter.

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.

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** (this is highlighted in green in Figure 16.1.2). 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 16.1.2.

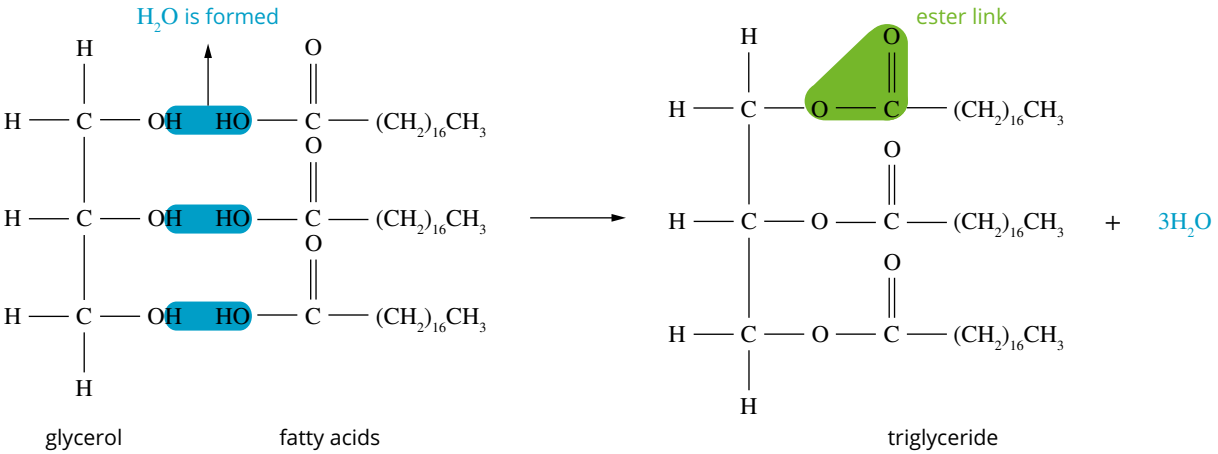


FIGURE 16.1.2 The reaction between glycerol and fatty acids produces a triglyceride and water.

In the example in Figure 16.1.2, the three chains on the triglyceride are identical, but triglycerides can often have two or three different fatty acid hydrocarbon chains that can differ in length. Some hydrocarbon chains may also contain one or more carbon–carbon double bonds.

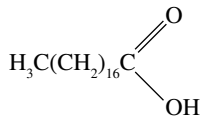
SATURATED AND UNSATURATED FATTY ACIDS

Fats are classified according to 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 structural formula of $CH_3(CH_2)_{16}COOH$.
- **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 structural formula is $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$.
- **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. Linoleic acid, which occurs in sunflower oil, has the structural formula $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$.

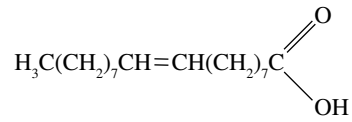
The structure and general formula of stearic acid, oleic acid and linoleic acid are shown in Figure 16.1.3.

saturated fatty acid



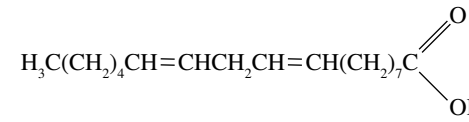
stearic acid
$C_{17}H_{35}COOH$

monounsaturated fatty acid



oleic acid
$C_{17}H_{33}COOH$

polyunsaturated fatty acid



linoleic acid
$C_{17}H_{31}COOH$

FIGURE 16.1.3 Examples of a saturated fatty acid, monounsaturated fatty acid and polyunsaturated fatty acid

USES OF FATS AND OILS

Fats and oils have a wide variety of uses, but the majority of applications are in food and related industries. Globally, this accounts for about 75% of production. The fats and oils may be used directly in food, as an ingredient, for frying food or as a fuel for cooking.

The other 25% of global production is used as a raw material to make new substances. Table 16.1.1 shows some other uses for fats and oils. Note that the predominant non-food uses by volume are in the production of **soap** and for manufacturing **biodiesel** (approximately 20%). Biodiesel is a fuel that can be used in vehicle engines. These two important uses of fats and oils will be explored further in the remainder of this chapter.

TABLE 16.1.1 Non-food uses of fats and oils

End use	Oil or fat used
Paints	Soybean oil
Inks	Soybean oil
Candles	Hydrogenated vegetable oils
Pharmaceuticals, e.g. pill formulations	Various vegetable oils
Thermoplastics	Linseed
Cosmetics, e.g. lipstick	Olive oil, cocoa butter
Soap	Tallow, olive oil, palm oil and others
Biodiesel	Palm, canola, sunflower, tallow and others

16.1 Review

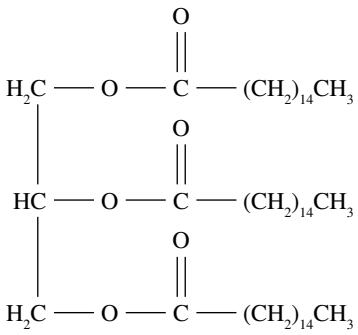
SUMMARY

- Fats and oils come from animal and plant sources.
- Animal fats are typically saturated fats.
- Plant oils are typically unsaturated fats.
- Fats and oils are triglycerides, which are molecules with three ester groups.
- Triglycerides can be synthesised from fatty acids and glycerol.
- Fats and oils are used in the food industry and in the manufacture of soap and biodiesel.

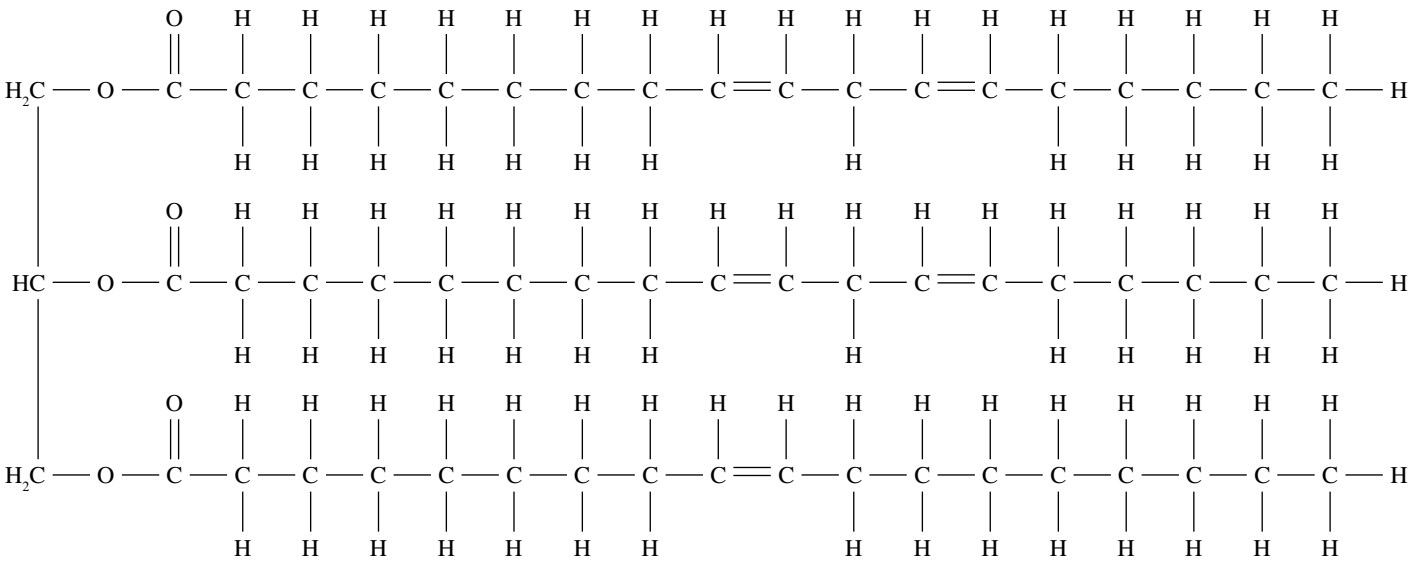
KEY QUESTIONS

1 Identify the most likely source, either animal or plant, for the following triglycerides and give an explanation for your choices.

a



b



2 For each of the structures in Question **1**, identify the ester groups in each molecule.

3 Draw the two molecules that form the fat given in Question **1a**.

16.2 Production of soaps

In the previous section, you were introduced to triglycerides (triesters) and their constituents, namely fatty acids (long-chain carboxylic acids) and glycerol (an alcohol with three –OH groups). In Chapter 14, you learnt how esters can be hydrolysed, and that hydrolysis with strong bases will produce a salt of the carboxylic acid and the alcohol that forms the ester. This knowledge is important in understanding the process of manufacturing soaps from oils.

SAPONIFICATION

Soap molecules contain a long hydrocarbon chain attached to a charged end. The structure of sodium stearate, a common soap, is shown in Figure 16.2.1.

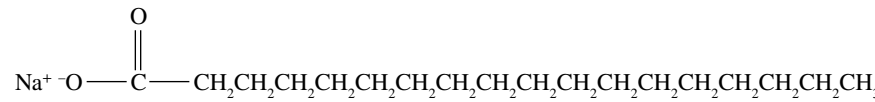


FIGURE 16.2.1 The formula of sodium stearate, a typical soap

To synthesise soap from a triglyceride, the ester bonds must be broken. In theory, water can be used for this reaction. Reactions in which 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 under alkaline conditions is known as **base hydrolysis**. When base hydrolysis is applied specifically to esters, it is called **saponification** (Figure 16.2.2).

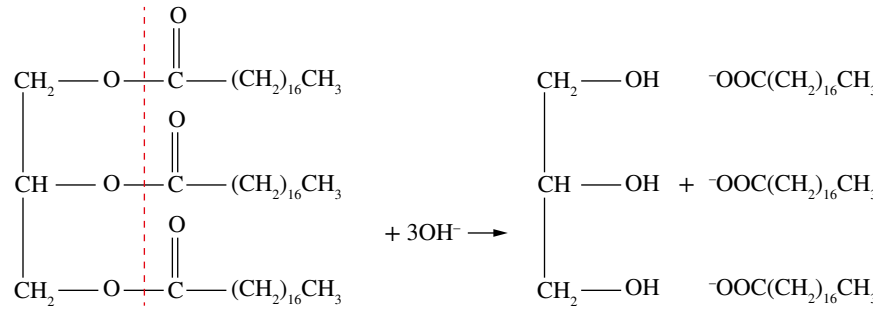


FIGURE 16.2.2 Base hydrolysis breaks the three ester bonds on the triglyceride along the dotted red line.

It is the fatty acid ion, combined with the metal ion from the base used for hydrolysis, that makes up the soap. For example, the soap potassium stearate (Figure 16.2.3) is formed when the triglyceride in Figure 16.2.2 reacts with potassium hydroxide.

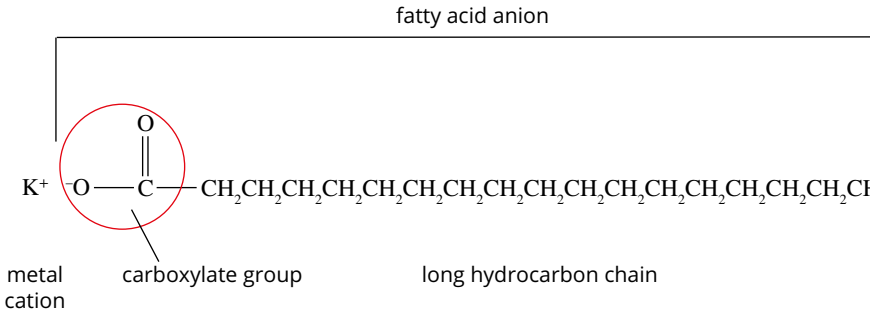


FIGURE 16.2.3 A soap, potassium stearate. Potassium stearate is described as the potassium salt of stearic acid.

All soaps are made up of a:

- long hydrocarbon chain. This part of the soap is non-polar. In potassium stearate (Figure 16.2.3), the hydrocarbon chain is an alkyl group because the hydrocarbon is saturated.
- **carboxylate** ion (COO^-) attached to the hydrocarbon tail. This is often referred to as the 'head' of the soap and is **polar**, meaning there is an uneven distribution of charge in this part of the soap. Carboxylate ions are the conjugate bases of carboxylic acids. In Figure 16.2.3, the stearate ion is the conjugate base of stearic acid ($CH_3(CH_2)_{16}COOH$).
- metal ion, normally Na^+ or K^+.

An alternative representation of the anion of a soap is shown in Figure 16.2.4.

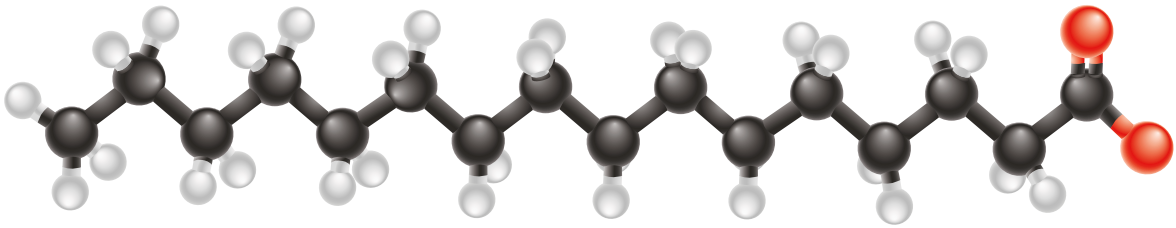


FIGURE 16.2.4 This alternative representation of the structure of a fatty acid anion in a soap uses coloured spheres for atoms (white for hydrogen, black for carbon and red for oxygen).

Even if a pure source of oil is used, the fatty acids in the triglyceride can vary. For this reason, in the general equation for saponification, chemists often represent the fatty acid hydrocarbon groups as R, R′ and R″, as shown in Figure 16.2.5.

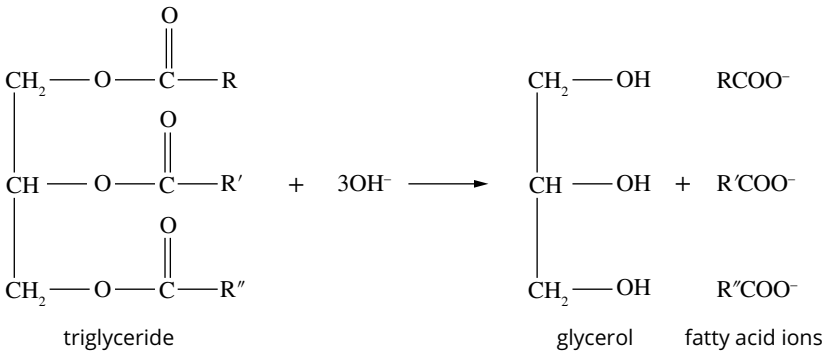


FIGURE 16.2.5 General equation for hydrolysis of a triglyceride. R, R′ and R″ represent different hydrocarbon groups.

SOAP PRODUCTION

Soap manufacturers usually select a triglyceride that is readily available in their region. Palm oil is popular in Asian countries, while olive oil is widely used in southern Europe.

Soap can be made in a school laboratory by heating a mixture of a suitable fat or oil with concentrated sodium hydroxide solution. The product is rinsed with water, which removes most of the glycerol and any residual sodium hydroxide. The soap may then be dried and moulded to shape. The laboratory process is very similar to that used by small soap manufacturers who use a traditional batch process. A batch process is one where reactants are placed in a vessel, the reaction takes place over a period of time and then the products are removed.

The industrial production of soap, as shown in Figure 16.2.6, is performed in enormous vats at high temperature and uses continuous processes. Continuous processes are ones where products are removed as reactants are being added to continue the reaction process.

High temperatures ensure the hydrolysis of all the oil present. This means all of the oil added is converted to soap. Soap is precipitated through the addition of sodium chloride and then removed by filtration. The remaining solution from the reaction is also removed and the glycerol is separated from the basic solution. While soap and glycerol are being removed, more oil and hydroxide are being added to the vat so that the saponification reaction continues.

Manufacturers vary the amounts and types of perfumes, stabilisers and other additives to give their product desirable properties, such as antibacterial and moisturising actions.

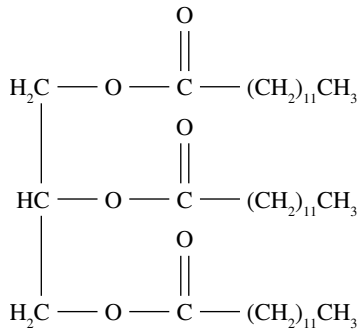
FIGURE 16.2.6 A soap production assembly line.

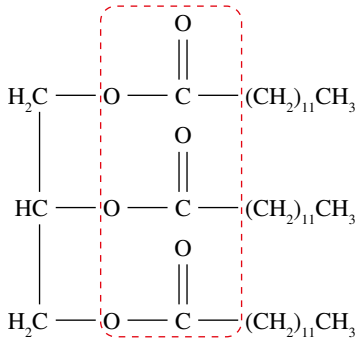
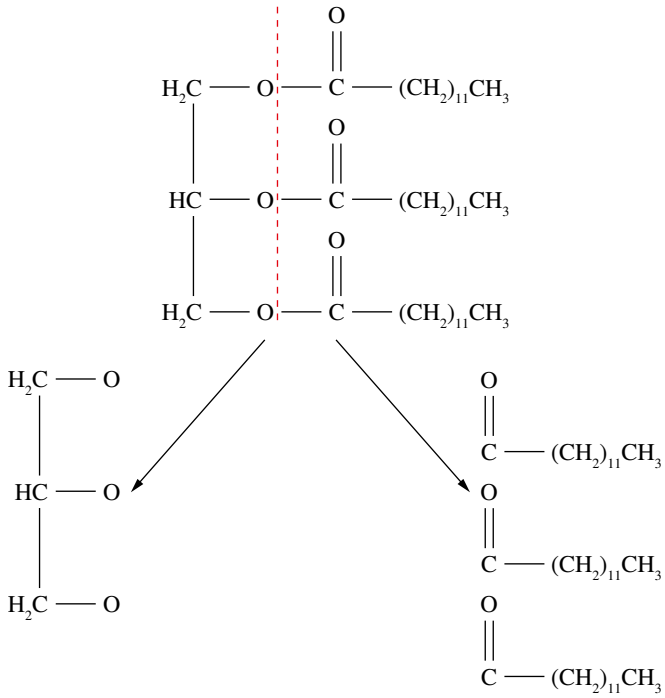
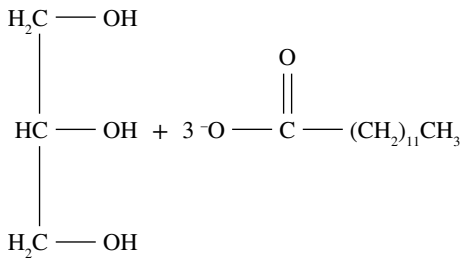
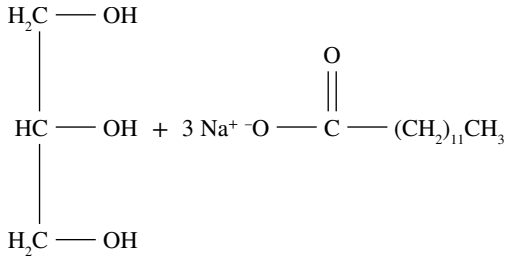
A by-product of soap manufacture is glycerol. Some soap manufacturers like to retain it in the soap to improve the moisturising properties, while others separate it out to use for other purposes. Glycerol is a common ingredient in the manufacture of gums and resins, paints, explosives and laxatives.

Worked example 16.2.1

DETERMINING THE PRODUCTS OF SAPONIFICATION FROM A TRIGLYCERIDE

The following triglyceride was reacted with sodium hydroxide to form a soap, sodium laurate. Give the products of this reaction.

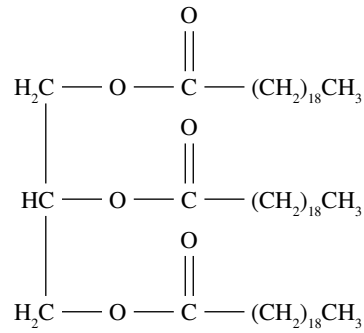


Thinking	Working
Identify the ester groups in the triglyceride.	
Split the molecule between each oxygen atom and the carbon in the fatty acid.	
Oxygen and hydrogen from sodium hydroxide must be introduced to produce glycerol and the carboxylate ion. A hydrogen atom is added to form glycerol. O is added to form the carboxylate ion.	
Add the metal ion from the hydroxide used to produce the molecule of soap made. Sodium hydroxide was used in this example. Note: In order to show the ionic nature of the bond between sodium and the ion of the fatty acid, charges are given in the structure.	Since sodium hydroxide was used, the metal ion is Na^+. 

Worked example: Try yourself 16.2.1

DETERMINING THE PRODUCTS OF SAPONIFICATION FROM A TRIGLYCERIDE

The following triglyceride was reacted with potassium hydroxide to form a soap. Give the products of this reaction.



LIMITATIONS OF SOAPS

In some parts of Australia, particularly Western Australia, soap has limited effectiveness. This is because the water supply in these regions contains high levels of metal ions such as Ca^{2+} and Mg^{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 mix 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 scum in wash tubs
- unsightly stains around basins and taps (Figure 16.2.8).

FIGURE 16.2.8 Lime scale around taps is caused by metal ions present in hard water.

CHEMFILE

Soap making—a way of life

The photo in Figure 16.2.7 shows how soap manufacturing is a way of life in Tripoli, in the north of Libya. A whole market is dedicated to the manufacture of soap and much of the produce is used in the nearby public baths.

This soap is made from oil extracted from the local olive trees. The olive oil is boiled in the cauldrons for 6 hours to ensure a smooth consistency and secret ingredients are added to ensure a unique product.

FIGURE 16.2.7 The manufacture of soap in Tripoli is part of the city's heritage. Families meet at a market and spend hours together cooking soap in large cauldrons.

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. One indication of hard water is the failure of the soap to produce a lather.

Metal ions can be removed by adding other negative ions, such as carbonate ions, to the soap. The carbonate ions soften the water by precipitating the magnesium ions as magnesium carbonate. An equation for the precipitation of unwanted magnesium ions through the addition of sodium carbonate is:

$$Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MgCO_3(s)$$

DETERGENTS

During World War I and II, several countries such as Germany experienced severe shortages of fats or oils for soap making. Chemists looked for alternative ways to form substances with long non-polar chains and charged ends, and the result was the development of **detergents**. Detergents are cleaning agents that do not suffer from some of the drawbacks of soaps. As you can see in Figure 16.2.9, a long hydrocarbon chain is present in detergents, but this time it is sourced from petroleum products. The cleaning mechanism of a detergent is similar to that of soap because their structures contain the same features.

In contrast to soaps, detergents do not form insoluble salts with calcium ions or magnesium ions. For this reason, they proved a popular replacement for soaps in hard water areas and they are now widely used in many different cleaning products, including many hand washes and shampoos.

Anionic detergents

Most detergents, like most soaps, are anionic, such as the alkylbenzenesulfonate detergent (Figure 16.2.9). **Anionic detergents** are those whose active constituent is a negatively charged species. This can be composed of a sulfonate group attached to a long carbon chain, often via a benzene ring within the structure.

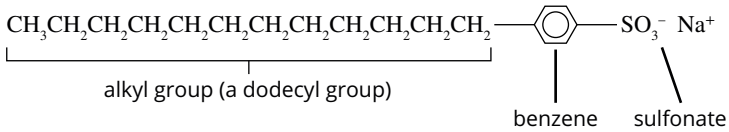


FIGURE 16.2.9 Structure of an alkylbenzenesulfonate detergent, sodium *p*-dodecylbenzenesulfonate.

Although the name of the detergent looks complex, it provides clues to the structure of the detergent.

- 'Alkyl' refers to the non-polar hydrocarbon chain.
- 'Dodecyl' means the hydrocarbon chain contains 12 carbon atoms.
- 'Benzene' is the hexagonally shaped aromatic hydrocarbon (sometimes called a phenyl group).
- 'Sulfonate' refers to the $-SO_3^-$ group, which makes a negatively charged end.

16.2 Review

SUMMARY

- Fats and oils are used to make soaps.
- Soap molecules contain a long, non-polar hydrocarbon section and a carboxylate group.
- Soaps are formed by a saponification reaction.
- Saponification is the base hydrolysis of a triglyceride to form glycerol and the salt of the fatty acid or acids present.
- Hard water is water containing significant concentrations of metal ions such as calcium and magnesium.
- Soaps form an insoluble salt with calcium and magnesium ions called 'soap scum' and make the cleaning action of soaps less effective.
- Detergents are made from petrochemicals and do not form insoluble salts with calcium and magnesium ions, making them more effective in hard water areas than soap.

KEY QUESTIONS

1 A hydrolysis reaction is one in which:
- **A** water is a product of the reaction
- **B** a soap is made as a product of the reaction
- **C** a molecule is split apart by reaction with water
- **D** water is removed from a substance.

2 Fill in the blanks for the following sentences.
The hydrolysis of a triglyceride can be achieved by using either _____ or _____ solutions. The reaction to make soap is called _____ and uses a base to catalyse the reaction. The soaps made are _____ of the fatty acids that form the triglyceride. The other product from saponification is _____ .

3 What is meant by the term 'hard water'?

4 What problems can hard water cause when using soap?

5 List as many similarities and differences as you can between soaps and detergents.

16.3 The cleaning action of soaps and detergents

The cleaning action of soap and detergent molecules can be explained by looking at their structure. Soap and detergent molecules are similar in structure and cleaning action, so the following explanation of the cleaning action of soap also applies to detergents.

SOAP IN WATER

In water, anions in soap tend to come together and form clumps. The **hydrophilic** ends are on the outer perimeter of these clumps where they will be in contact with the water. Hydrophilic means 'water loving' and typically refers to molecules or ions that can form strong forces of attraction with water. In the case of soaps, these forces of attraction are **ion–dipole forces**. Ion–dipole forces are produced between the ionic end of the soap, which carries charge, and the highly polarised O–H bond in water. The **hydrophobic** (non-polar) sections of the soap are in the centre of the clump where they are in contact with each other. Hydrophobic means 'water hating'. This clump is a stable arrangement called a **micelle**. The sodium or potassium ions are spectator ions in the cleaning solution. A diagram of a micelle is shown in Figure 16.3.1.

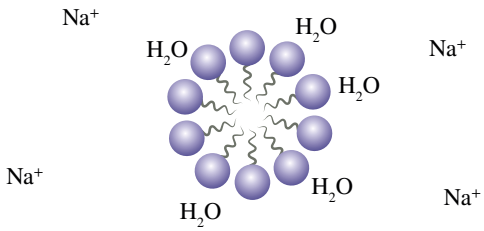


FIGURE 16.3.1 The arrangement of soap particles in a micelle. Micelles have a spherical shape.

CLEANING ACTION

During the washing of clothes, vigorous agitation is used to break up the 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 ends exposed to the water. As the agitation continues, the water molecules are attracted to the polar ends of the soap and the oil particle is lifted from the fabric, as shown in Figure 16.3.2.

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 from reattaching to the fabric (Figure 16.3.3). When the water is drained from the wash, the oil stains are drained away as well.

The non-polar chain and charged ends 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 and detergents is **surfactant**, which is a shortened version of 'surface active agent'. This process is the same whatever the surface happens to be: fabric, a ceramic plate, a glass bowl or skin.

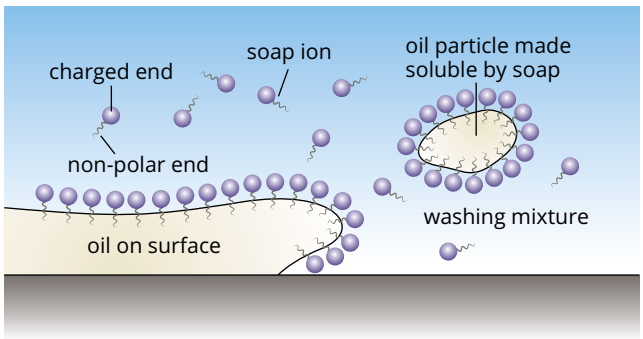


FIGURE 16.3.2 The cleaning action of soap. The non-polar chain of soap particles is embedded in an oil stain, while the charged part is in the water.

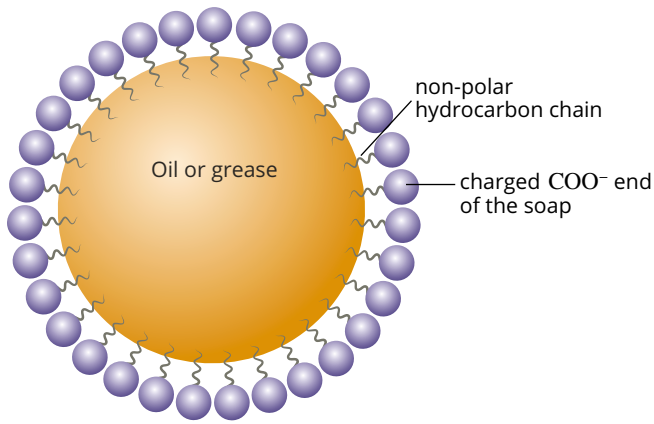


FIGURE 16.3.3 An oil or grease stain that has been lifted from the fabric

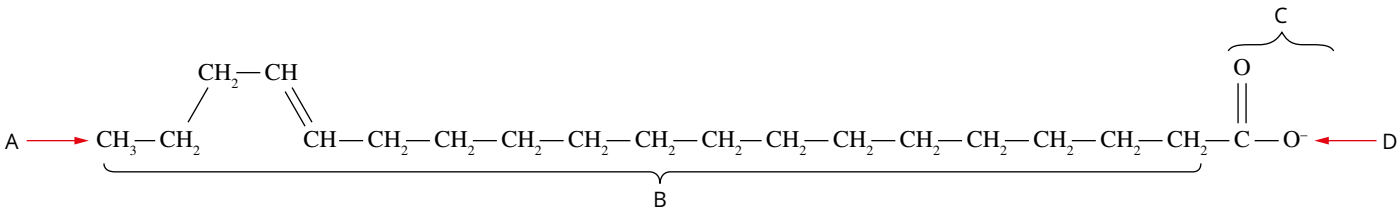
16.3 Review

SUMMARY

- The cleaning action of soaps and detergents is similar and can be explained by reference to their structure.
- There are two parts to the structure of soaps and detergents, which enable non-polar grease and oil to mix with water.
- Micelles form when a soap or detergent is dissolved in water.

KEY QUESTIONS

1 The structure shown below corresponds to the anion of a soap molecule dissolved is water. Identify parts A–D by choosing from the following: hydrophilic, non-polar tail, hydrophobic, polar head.



2 Fill in the blanks for the following sentences.
When enough soap is added to water, the anions of the soap molecule will form _____. Agitation breaks up these structures and allows the _____ part of the molecule to dissolve in the oil or grease. As more soap dissolves in the oil, the stain lifts from the fabric helped by the attractive forces between the water and the _____ end of the soap molecule.

3 Name the main intermolecular forces broken and formed when:

a a soap molecule dissolves in water

b a group of soap molecules form a micelle

c grease is removed from clothing.

16.4 Production of biodiesel

Biodiesel is a type of biofuel—a fuel that has been produced from plant or animal material (biomass). In this section, you will see how organic chemical reactions can be used to synthesise biodiesel.

THE NEED FOR BIODIESEL

The burning of **fossil fuels** is responsible for increases in the concentration of carbon dioxide in the atmosphere, and most scientists working in this field agree that that these changes are contributing to climate change. Fossil fuels are hydrocarbons geologically formed from the remains of living organisms. The increased use of biofuels is one approach to reducing carbon dioxide emissions.

Biodiesel is one of the most promising alternative fuels and its commercial use has increased over the last 20 years. In Australia, commercial biodiesel has been manufactured since 2006. Countries in Asia, including Indonesia, produce about 1.3 ML of biodiesel annually. Many Asian countries grow crops specifically to produce oils such as palm oil, which are then converted to biodiesel. Diesel containing 5% biodiesel has been available since 1995. All diesel-powered vehicles can run on 100% biodiesel. Biodiesel has some benefits compared to **petrodiesel**, which is a hydrocarbon fuel derived from crude oil. These benefits include improved engine wear and therefore engine lifespan.

Biodiesel is a mixture of organic compounds called esters. These esters are produced by a chemical reaction between vegetable oils or animal fats and an alcohol (most commonly, methanol (CH_3OH)).

At present, far more petrodiesel than biodiesel is consumed, both locally and internationally (Figure 16.4.1). Petrodiesel is a **non-renewable** resource, meaning once used it is not replenished and amounts worldwide are depleted. Australia's total diesel consumption is over 23 000 ML/year. Biodiesel comprises only 400 ML of this total. This gap is likely to close in the future as the biodiesel industry becomes the subject of extensive scientific research.

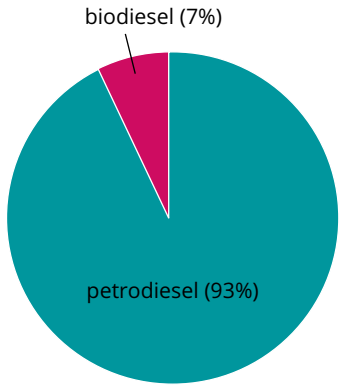


FIGURE 16.4.1 This pie chart shows world diesel consumption. Petrodiesel dominates world diesel consumption (2015 data).

TRANSESTERIFICATION

The structure of a typical biodiesel molecule is shown in Figure 16.4.2.

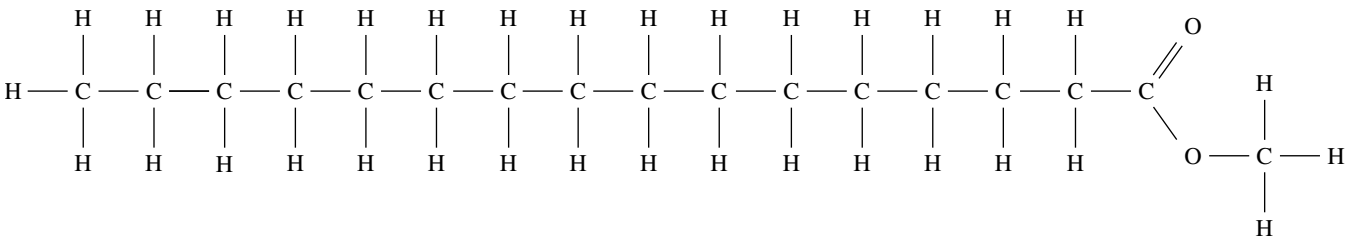


FIGURE 16.4.2 Structural formula of a typical biodiesel molecule

The usual raw material for the production of biodiesel is vegetable oil from sources such as soyabean, canola or palm oil. Recycled vegetable oil or animal fats can also be used.

The triglyceride is converted into biodiesel by warming it with an alcohol, usually methanol, in a process known as **transesterification**. The reaction requires a **catalyst**. A catalyst is a substance that provides an alternative reaction pathway that speeds up the rate of reaction and is not consumed in the reaction. The reaction can be carried out using a base, typically potassium hydroxide solution, or lipase, which is an enzyme, both of which catalyse the reaction. An **enzyme** is a protein produced by a living organism that functions as a catalyst.

In the transesterification reaction, the triglyceride is converted into glycerol and three ester molecules with long carbon chains. The ester molecules are the biodiesel product. The reaction is shown in Figure 16.4.3.

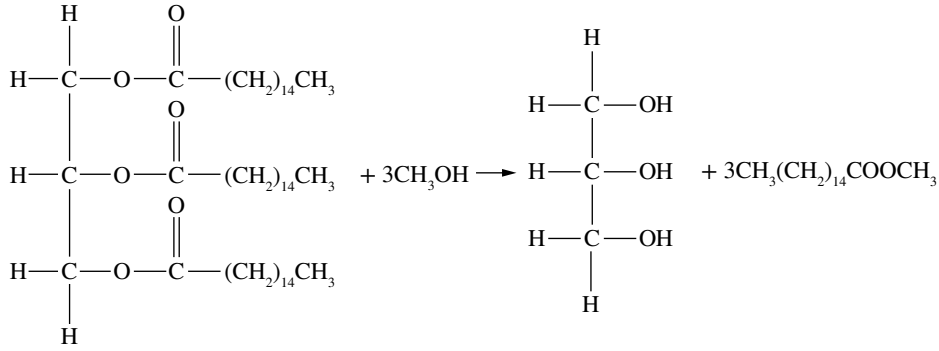


FIGURE 16.4.3 The reaction of a triglyceride with alcohol to form fatty acid esters (biodiesel) and glycerol

Molecules such as the typical biodiesel molecule shown in Figure 16.4.2 are sometimes referred to as **fatty acid esters**, because carboxylic acids with relatively long hydrocarbon chains are referred to as fatty acids. A fatty acid ester is one made from a fatty acid and simple alcohol.

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, which 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 16.4.4.

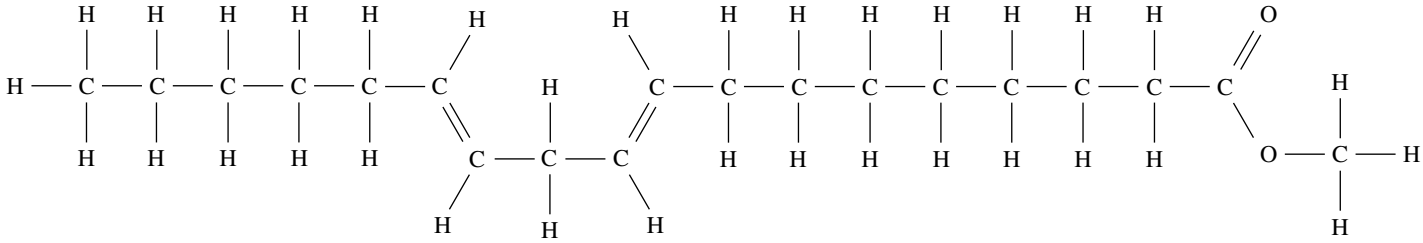


FIGURE 16.4.4 Biodiesel molecules derived from plants often contain carbon–carbon double bonds.

> The term 'saturated' refers to hydrocarbons that contain only single bonds between the carbon atoms. They are said to be saturated because each carbon atom is bonded to as many hydrogen atoms as possible. 'Unsaturated' means that there is at least one carbon–carbon double or triple bond within the hydrocarbon chain.

MANUFACTURING BIODIESEL

In the production of biodiesel, the triglycerides (usually an oil), methanol and a catalyst are added to a reactor in a batch process. The initial mixture is heated gently and left for at least 30 minutes; the time depends on the catalyst used and conditions selected. The reaction mixture is then pumped to a separator, as shown in Figure 16.4.5.

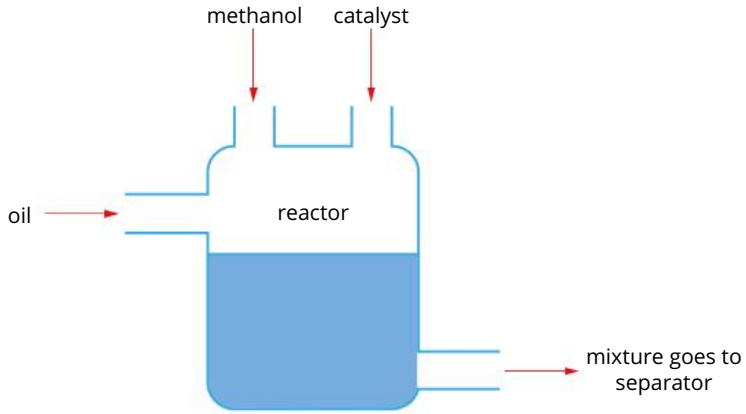


FIGURE 16.4.5 The first step in the production of biodiesel

One of the products, glycerol, is a relatively small molecule with three hydroxyl functional groups and is quite polar. Conversely, the long hydrocarbon chain on the methyl ester makes the molecule non-polar. This means that in the separator the two products do not dissolve in each other and separate into two distinct layers, like the oil and water shown in Figure 16.4.6.

FIGURE 16.4.6 A mixture of paraffin oil (coloured blue) and water (clear) separate into two distinct layers. In a similar way, biodiesel and glycerol are separated in the separator during the production of biodiesel.

The biodiesel and glycerol extracted from the separator are then distilled to remove any unreacted methanol, which is recycled back into the reactor. The biodiesel and glycerol can then be collected separately, as shown in Figure 16.4.7.

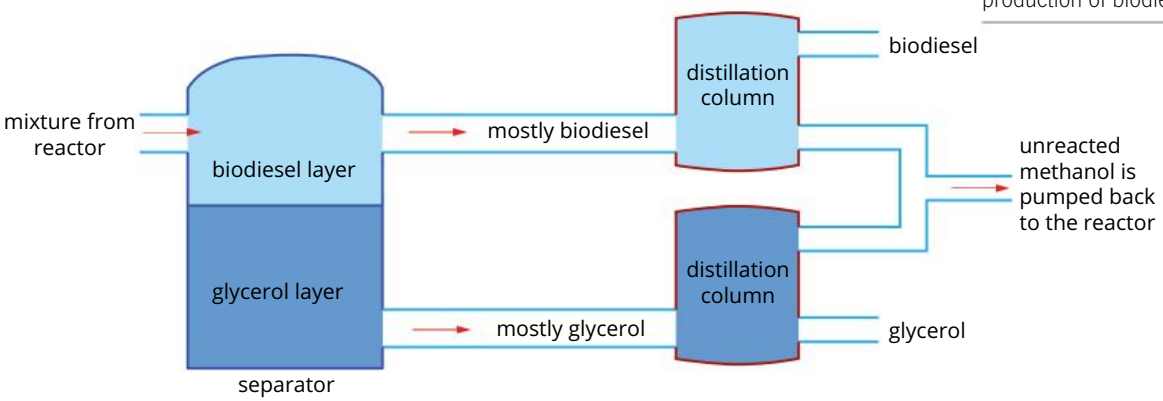


FIGURE 16.4.7 The separation of products of the transesterification process during the manufacture of biodiesel

The glycerol produced from this process is about 80% pure. Increased biodiesel production has resulted in an oversupply of glycerol to the market, leading to a fall in the price of glycerol. Finding uses for the excess glycerol would increase the economic viability of the biodiesel industry.

Choosing a catalyst

Two types of catalyst can be used in the production of biodiesel: the lipase enzyme, a naturally occurring enzyme (Figure 16.4.8); and a base, generally sodium hydroxide or potassium hydroxide.

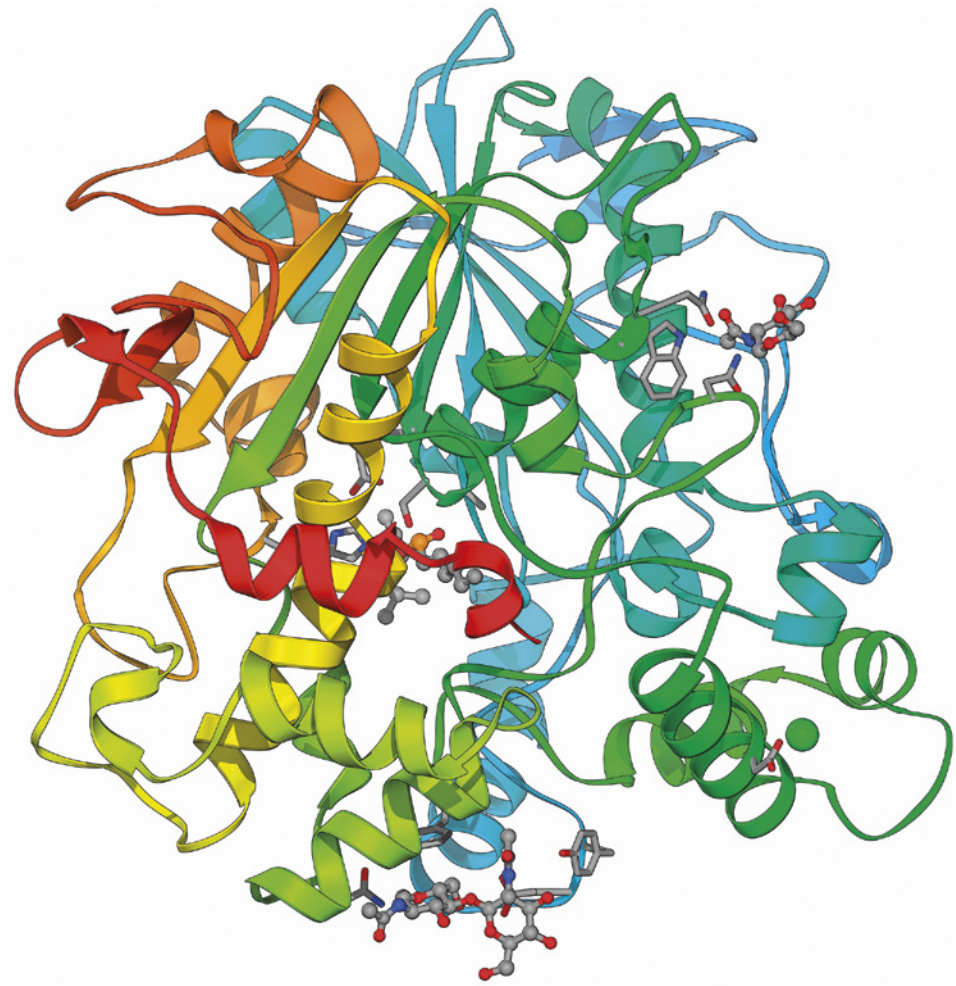


FIGURE 16.4.8 The structure of a lipase enzyme molecule. The lipase molecule is a large protein made up of many spiralled (alpha helix) structures.

At present, the base-catalysed process is used in almost all biodiesel plants. Unlike the lipase-catalysed production of biodiesel, the base-catalysed process can use methanol and operate at high temperatures, making the conversion process quicker and more economical. Using lipase instead of a base would be preferable because lipase can be used many times, while the base can only be used in one batch. Lipase also requires less energy to produce biodiesel and the transesterification process can be carried out at lower temperatures and pressures, which can reduce costs.

Unfortunately, the slow rate of reaction using naturally occurring lipase limits its use. Industry is researching possible ways of increasing the rate of the reaction using lipase, such as:

- chemical modification of the enzyme
- protein (genetic) engineering
- using organic solvents.

Table 16.4.1 summarises the differences in the two alternative methods for catalysing the production of biodiesel.

TABLE 16.4.1 Comparison of the operating conditions for base-catalysed and lipase-catalysed production of biodiesel

Method	Temperature (°C)	Pressure (kPa)	Time (min) in reactor	Catalyst use	Yield (%)
Base-catalysed	60–70	140–400	30–60	Only able to be used for one cycle of the production process	96–98
Lipase-catalysed	20–37	101.3	at least 150	Can be used many times	Typically 80 (can be as high as 92)

In the base-catalysed production of biodiesel, the amount of base added must be carefully monitored. When a mole ratio close to 3:1 of base to triglyceride is reached, soaps can form. Not only does soap formation reduce the conversion of triglycerides to biodiesel, it can also affect the separation process.

GREEN CHEMISTRY

Green chemistry is a set of 12 principles to guide chemists in producing environmentally sound products and processes. These principles demonstrate the breadth of the concept of green chemistry.

The 12 principles of green chemistry are:

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 excess reactants
10 design chemicals and products that are biodegradable
11 analyse in real time to prevent pollution
12 minimise the potential for accidents.

These principles were explained in more detail in Chapter 12.

The continued research and development of the lipase-catalysed reaction for the production of biodiesel focuses heavily on employing some of these principles. Optimising the process with these principles would make the reaction more environmentally acceptable and also economically attractive.

Wider environmental considerations

The burning of biodiesel and petrodiesel produces carbon dioxide, a greenhouse gas. In the case of biodiesel, carbon dioxide is absorbed from the atmosphere into the growth of the plant or animal from which the biodiesel is derived, reducing the net impact on greenhouse gas levels.

In Australia, waste oil is commonly used as a feedstock for the production of biodiesel (principle 7). Elsewhere, such as parts of Asia, crops are grown for the sole purpose of producing biodiesel. This requires massive land clearance, which destroys natural habitats. The intensive farming methods used require water and fertiliser. Additionally, farm machinery emits carbon dioxide and offsets a benefit of using biodiesel. These factors clearly increase the environmental impact of biodiesel, albeit indirectly.

The use of either form of diesel produces pollutants such as nitrogen oxides, carbon monoxide and unburnt fuel. 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, soyabean oil does not contain sulfur, but canola oil does. Biodiesel exhaust contains up to 20% less particulate matter than diesel.

CHEMISTRY IN ACTION

Biodiesel in Western Australia

Bioworks is a company based in Henderson, Western Australia. Currently, Bioworks produces 4 ML (4 000 000 L) of biodiesel per year and is expanding this production to 6 ML. Businesses around the state are paid for their waste oils from cooking and food preparation, which Bioworks processes into biodiesel.

The oils collected and used contain very little sulfur (<0.001%) compared to petrodiesel and so reduce atmospheric sulfur dioxide pollution. As the oils and fats are collected from local sources, the emissions associated with collection are minimised, making the process more attractive from a green chemistry perspective.

Jonathon Thwaites is a sustainability expert who has run his vehicle on biodiesel since 2006. He makes the biodiesel himself in his shed (Figure 16.4.9). His equipment includes a 200 L drum, which acts as the reactor vessel. Jonathon performs a titration to determine the amounts of base and methanol he must add. His cost of production is around 30 cents per litre, excluding his time. To make his biodiesel, Jonathon had to obtain licenses from his local council and must pay fuel tax to the Australian Taxation Office, which significantly increases the final cost of the biodiesel.

The initial investment in equipment, coupled with the time it takes to learn the process, the cost of tax and licensing and the varying price of petrodiesel, may make the potential financial saving of producing biodiesel unattractive to most people.

FIGURE 16.4.9 Jonathan Thwaites runs his vehicle on biodiesel made from waste oil in his backyard shed.

16.4 Review

SUMMARY

- There is a need to seek sustainable alternatives to fossil fuels for a number of reasons, including climate change and the increasing consumption of non-renewable energy sources.
- Biodiesel is a mixture of methyl fatty acid esters produced from a transesterification reaction.
- Transesterification involves the reactions of a triglyceride containing three ester groups with methanol to produce three methyl ester molecules and glycerol.
- The industrial manufacture of biodiesel is normally carried out using a base-catalysed reaction.
- Research continues to improve the use of lipase to catalyse a synthesis that employs green chemistry principles.

KEY QUESTIONS

1 What is the name of the reaction in which a triglyceride is broken down to form biodiesel molecules?

2 Determine if the following statements about biodiesel are true or false.

a Biodiesel can contain several different compounds.

b Biodiesel molecules contain ester groups.

c Biodiesel is an alkane.

d Three molecules of biodiesel can be obtained from each molecule of a triglyceride.

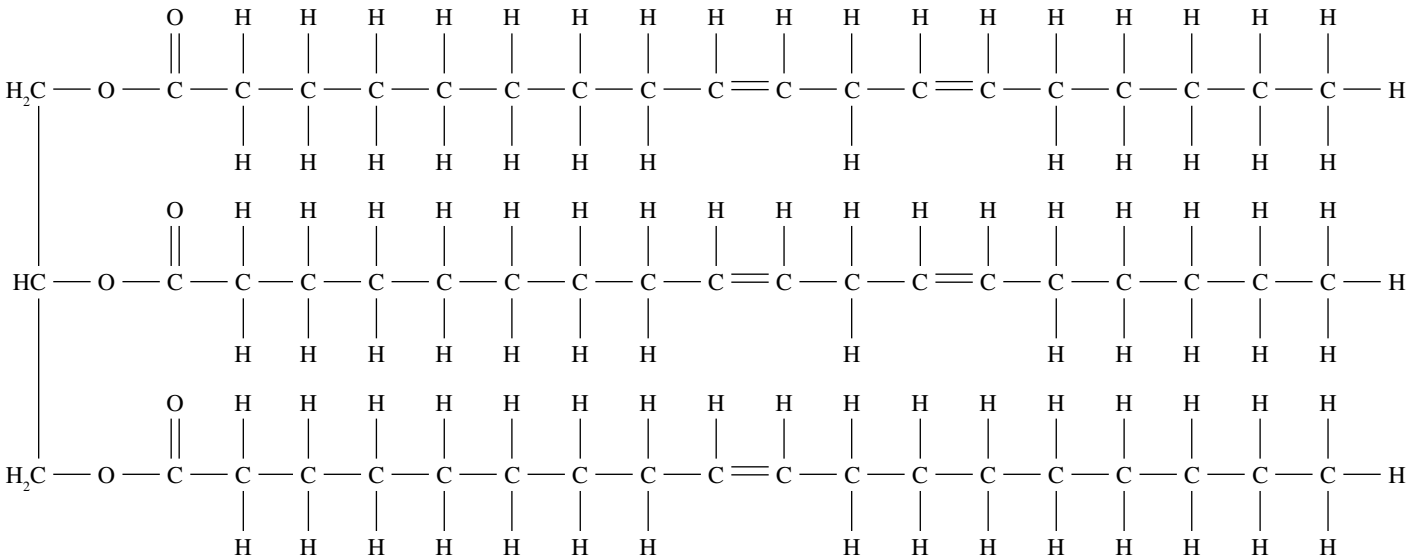
e All hydrocarbon chains in biodiesel molecules are saturated.

f Biodiesel is formed in a transesterification reaction.

3 Why are the CO_2 emissions from the use of biodiesel not considered as problematic as those produced from petrodiesel?

4 What are the advantages and disadvantages of the lipase-catalysed reaction compared to the base-catalysed manufacture of biodiesel?

5 Write an equation showing the reaction of the following triglyceride to produce biodiesel.



Chapter review

16

KEY TERMS

anionic detergent
base hydrolysis
biodiesel
carboxylate
catalyst
detergent
enzyme
ester functional group
ester link
fatty acid
fatty acid ester
fossil fuel
green chemistry
hard water
hydrolysis
hydrophilic
hydrophobic
ion–dipole force
lipid
micelle
monounsaturated fatty acid
non-polar
non-renewable
petrodiesel
polar
polyunsaturated fatty acid
saponification
saturated
saturated fatty acid
soap
surfactant
transesterification
triglyceride
unsaturated

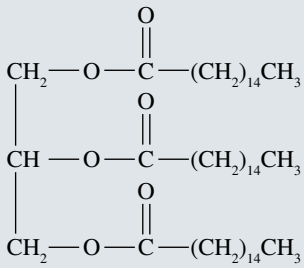
Fats and oils

1 Which two functional groups are directly involved in the formation of a triglyceride?

2 **a** Write an equation for the formation of the triglyceride glyceryl trioleate from the reaction of glycerol and oleic acid ($CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$).

b Draw the structure of glyceryl trioleate, showing the ester bonds.

3 A fat present in vegetable oil has the structure shown.



a Circle an ester functional group.

b Is this triglyceride saturated or unsaturated? Explain your answer.

Production of soaps

4 Which one of the following is the formula of a soap?

A $CH_3(CH_2)_{16}COOH$
B $CH_3(CH_2)_7CHCH(CH_2)_7COOLi$
C CH_3COONa
D $CH_3(CH_2)_{16}COOCH_3$

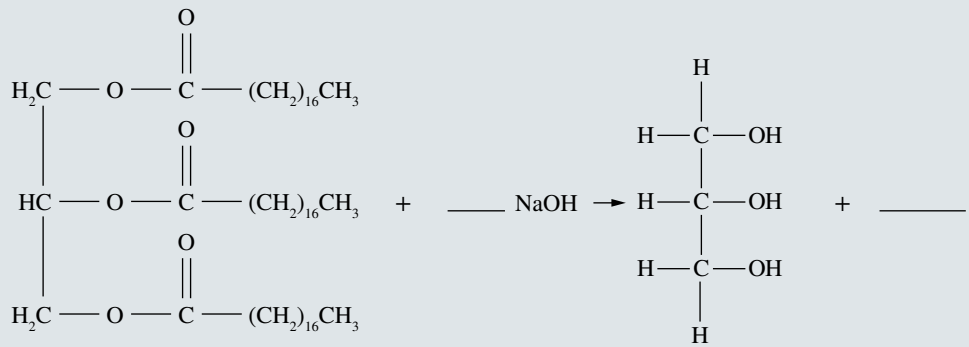
5 If 0.2 mol of a triglyceride undergoes saponification completely in excess base, determine the number of moles of:

a sodium hydroxide required for the reaction
b glycerol formed.

6 Complete the summary about saponification by using some of the following terms: carboxylate, acid, positive, hydrocarbon, triglyceride, ester, fatty, hydroxyl.

When a _____ undergoes saponification, a _____ _____ salt is formed. Particles of this substance have a long _____ chain, a _____ group and a _____ metal ion.

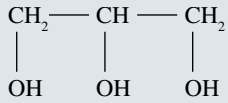
7 Copy and complete the equation showing the formation of soap in the reaction of the following fat with sodium hydroxide solution.



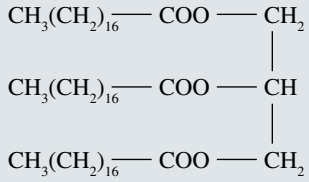
The cleaning action of soaps and detergents

8 Identify each of the following as a detergent, a soap, a fatty acid, a fat or glycerol.

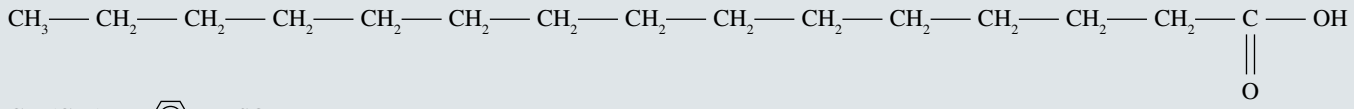
a



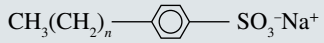
b



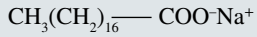
c



d



e

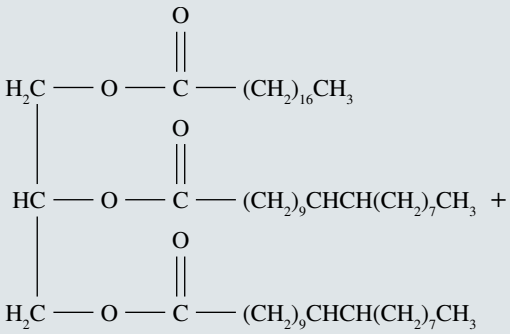


9 Both saturated and unsaturated fats can be used to make soap. What differences would you expect between a soap made with a saturated fat and a soap made with unsaturated fat?

Production of biodiesel

10 Briefly explain the need for biodiesel.

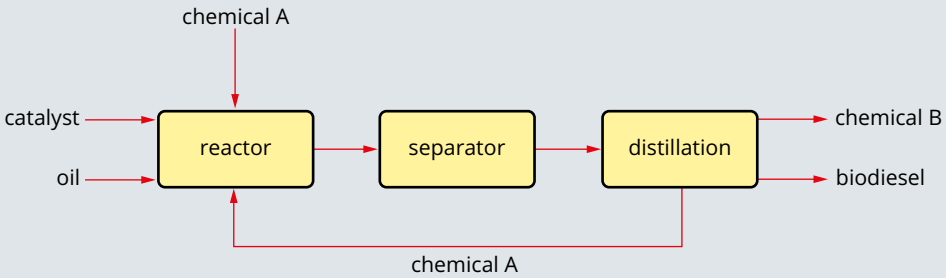
11 Complete a balanced transesterification reaction for the following triglyceride.



12 What does the term 'renewable feedstock' mean?

13 The transesterification reaction to make biodiesel requires the use of a catalyst. What is a catalyst?

14 Use the diagram below to identify the chemicals used in the following transesterification process.



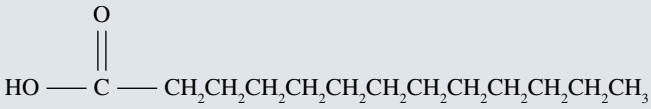
a Name chemical A.

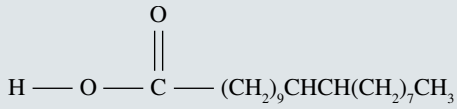
b Name chemical B.

15 Transesterification is a reversible reaction. Usually, about twice the stoichiometric amount of methanol is added in the base-catalysed reaction to make biodiesel. Using your knowledge of equilibrium, explain why this is done.

Connecting the main ideas

16 By using one or more of the following molecules, draw structures that match the following descriptions.

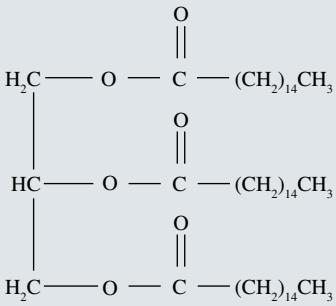




a a triglyceride likely to be from an animal source
b an unsaturated triglyceride
c a soap molecule made from the triglyceride in part **a**
d the biodiesel formed when part **b** undergoes transesterification

17 Suggest why, when adding a base to the triglyceride in the making of biodiesel, you should take care to ensure that the base-to-triglyceride stoichiometric ratio should not approach 3:1.

18 Compare and contrast saponification and transesterification reactions using palm oil to illustrate your answer.



palm oil

CHAPTER

17 From amino acids to proteins

Biochemistry is the study of all the chemical processes that take place within living organisms and is concerned primarily with what is happening on a molecular level with cells. Therefore, the interactions and reactions of the major macromolecules, proteins, DNA, carbohydrates and lipids are central to the study of biochemistry.

Proteins are important because they provide the molecular machinery of the cell; proteins act as enzymes, hormones and structural components and regulate the movement of other substances in and out of cells. In this chapter, you will learn about the structure of amino acids and how they react together to form proteins. You will also examine the interactions that control the folding of proteins into their three-dimensional structure and enable them to perform their functional role within the body.

Science understanding

- α-amino acids can be represented using a generalised structure
- the characteristic properties of α-amino acids include the formation of zwitterions and the ability to form amide (peptide) bonds through condensation reactions
- α-amino acids undergo condensation reactions to form polypeptides (proteins) in which the α-amino acid monomers are joined by peptide bonds
- the sequence of α-amino acids in a protein is called its primary structure
- secondary structures of proteins (α-helix and β-pleated sheets) result from hydrogen bonding between amide and carbonyl functional groups; hydrogen bonding between amide and carbonyl functional groups within a peptide chain leads to α-helix structures while hydrogen bonding between adjacent polypeptide chains leads to β-pleated sheets
- the tertiary structure of a protein (the overall three-dimensional shape) is a result of folding due to interactions between the side chains of the α-amino acid in the polypeptide, including disulfide bridges, hydrogen bonding, dipole–dipole interactions, dispersion forces and ionic interactions

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17.1 Amino acids

FIGURE 17.1.1 Spiders can produce silk using a strong protein called fibroin to form webs and protect their eggs.

> **i** 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).

In this section, 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 17.1.1)
- transportation of substances across cell membranes or around the body; for example, many proteins form channels in the cell membrane through which specific substances may travel (Figure 17.1.2)
- antibody molecules of the immune system.

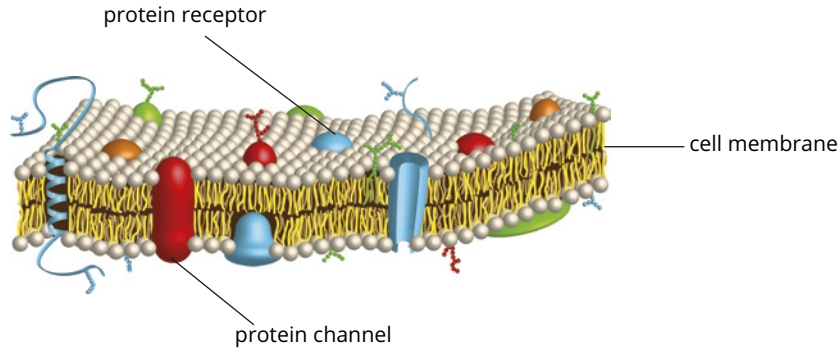


FIGURE 17.1.2 Many proteins are associated with the phospholipid membrane surrounding each cell. They act as channels, allowing other molecules to pass through. They also act as receptors in signalling pathways, carrying signals or messages into the cell from the external cell environment.

Plants can manufacture all of the amino acids required to make proteins. Plants synthesise amino acids from simple inorganic ingredients—such as carbon dioxide, water and nitrates—obtained from the atmosphere and soil. However, animals cannot do this. Although animals can synthesise some of the amino acids they require, they must obtain the other amino acids they need 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 of 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 17.1.3.

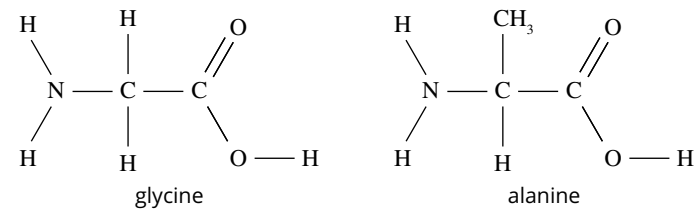


FIGURE 17.1.3 The structures of amino acids glycine and alanine

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 17.1.4.

Amino acids, such as those shown in Figure 17.1.4, are known as **α-amino acids**. This is because the amino group and the carbon atom of the carboxyl group are attached to the same carbon atom. This atom is known as the α-carbon. α-Amino acids are also sometimes called 2-amino acids.

The 20 α-amino acids used to make human proteins are listed in Table 17.1.1 on page 460, along with their three-letter abbreviations.

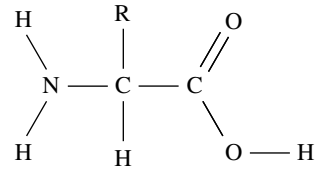


FIGURE 17.1.4 General structural formula of an α-amino acid. Different amino acids have different groups of atoms as the R group.

Properties of side chains in amino acids

The major difference between one amino acid and another is the group of atoms that make up the **side chain** (sometimes called **R groups**). 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).

> Amino acids are commonly given three-letter abbreviations. For example, alanine is represented by Ala and glycine is represented by Gly.

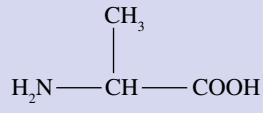
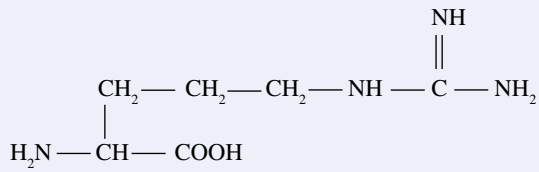
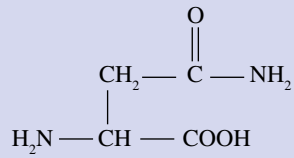
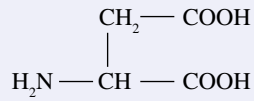
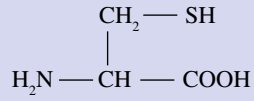
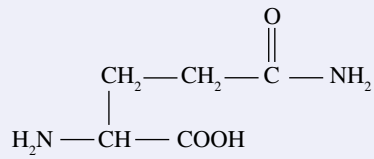
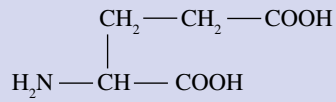
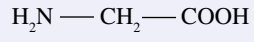
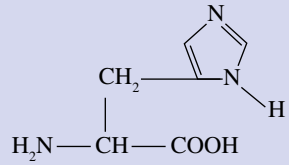
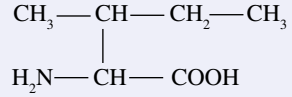
ESSENTIAL AND NON-ESSENTIAL AMINO ACIDS

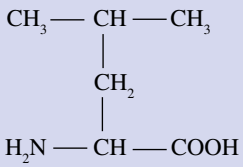
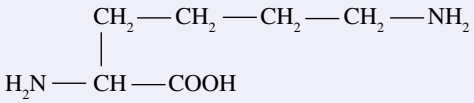
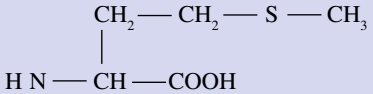
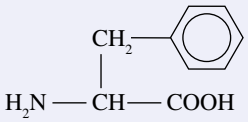
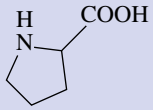
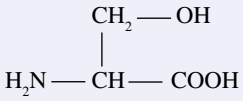
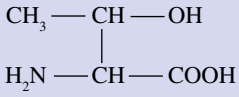
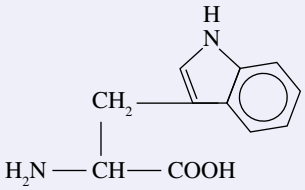
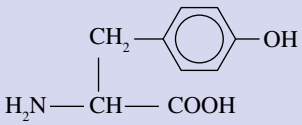
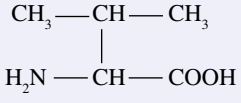
Within the cells in our bodies, humans can synthesise 11 of the 20 amino acids required to make proteins. These proteins sustain bodily functions. The other nine amino acids (isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, valine and histidine (in infants)) must be provided directly through the proteins you 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 17.1.5. Although this disease is characterised by low overall protein intake, it is thought that the lack of the sulfur-containing amino acids cysteine and methionine are particularly important in the disease development. '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 protein-rich breast milk to a diet that is high in carbohydrates and lacking in protein.

FIGURE 17.1.5 This child is suffering from kwashiorkor, which is a form of malnutrition caused by a protein-deficient diet.

TABLE 17.1.1 Amino acids found in the human body, with their three-letter symbols and structure

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	

CHEMFILE

Essential amino acids—the work of William C. Rose

William Cumming Rose (1887–1985) was an American biochemist who devoted his professional life to the study of amino acids and their role in metabolism. He conducted many experiments on rats and discovered that rats were unable to survive on the 19 known amino acids as their sole nitrogen source. This led Rose to isolate and identify the final amino acid—threonine. This was a laborious task given the techniques available at the time.

Rose then turned his attention to human metabolism and tried to determine which amino acids are essential in our diets. Graduate students were paid $1 a day to eat mixtures of corn starch, sucrose, butter fat, corn oil, vitamins and mixtures of purified amino acids as their only food source. The students' total nitrogen excretion was measured by analysing their faeces and urine, which they had to deliver to the laboratory each day. Rose observed that when particular amino acids were missing in their diets, subjects experienced dizziness, exhaustion and nervousness. In this way, he concluded that there were eight essential amino acids for humans. Histidine was later added to the list as it was found to be essential for infants.

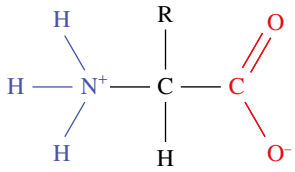


FIGURE 17.1.6 Structure of a zwitterion of an amino acid molecule

A balanced diet

Proteins from animal sources contain all the essential amino acids. As Table 17.1.2 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 17.1.2 Foods deficient in one or more of the nine essential amino acids

Food	Amino acid deficiency
Legumes	Methionine
Soyabeans	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.

ACID–BASE PROPERTIES OF AMINO ACIDS

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 17.1.6 and is called a **zwitterion** or dipolar ion. A zwitterion is a molecule that contains positive and negative charges but has no charge overall.

The relatively high melting point of pure crystalline amino acids is due to the zwitterion being present in the solid state, meaning that the amino acids are held together by ionic bonds in the solid state. These ionic bonds require a large amount of energy to break, resulting in a high melting point.

Acid–base properties of amino acids

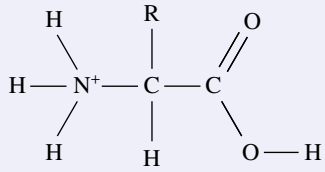
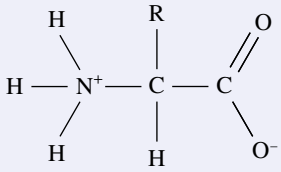
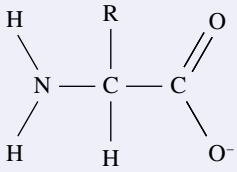
The dual acidic and basic nature of amino acids means that in a solution, different chemical forms of an amino acid can be in equilibrium. The predominant form depends on the pH of the solution and the particular amino acid concerned.

- 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 17.1.3, the charge on the predominant form of the amino acid depends on the pH of the solution.

TABLE 17.1.3 Formation of cations, anions and zwitterions when amino acids are in solutions of various pH

Low pH	Intermediate pH	High pH
 cation	 zwitterion (no overall charge)	 anion

Effect of the side chain on the acid–base properties of amino acids

If the side chain contains a functional group with acid–base properties, it is possible for other charged forms 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 17.1.7). On the other hand, at a pH of 2, lysine exists predominantly as an ion with a charge of 2+ (Figure 17.1.8).

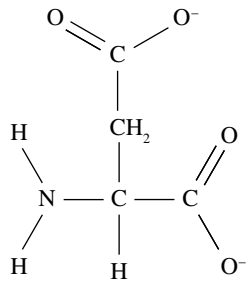


FIGURE 17.1.7 At pH 12, aspartic acid has a charge of 2–.

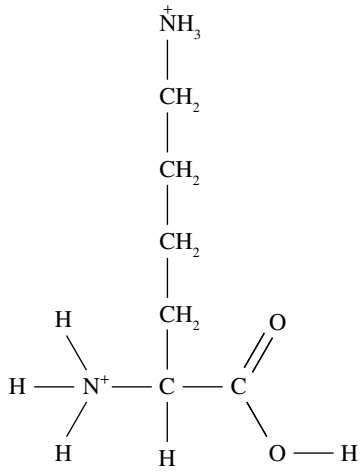


FIGURE 17.1.8 At pH 2, lysine has a charge of 2+.

17.1 Review

SUMMARY

- α-Amino acids have the structure shown in Figure 17.1.9.

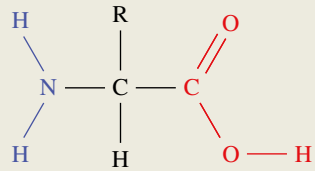


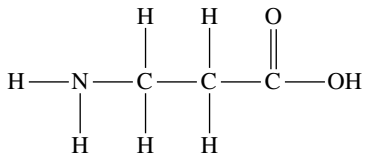
FIGURE 17.1.9 General structure of an α-amino acid.

- Amino acids contain a carboxyl group (highlighted in red in Figure 17.1.9), an amino group (highlighted in blue in Figure 17.1.9), a hydrogen atom and a side chain, all bonded to the same carbon atom.
- There are 20 different amino acids found in human proteins.
- 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 amino acids.
- The side chain may be a non-polar group of atoms or a group of atoms that includes a polar functional group. The side chain 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.

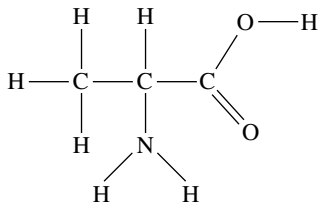
KEY QUESTIONS

1 Which one of these molecules is not an α-amino acid?

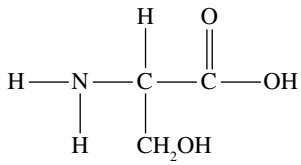
A



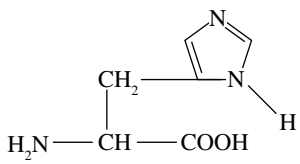
B



C



D



2 Why should essential amino acids be included in a healthy diet?

3 Draw the structures of the following amino acids at the specified pH.

a serine at low pH

b alanine at high pH

c glutamic acid at high pH

4 Use your understanding of bond polarity and the acid–base properties of functional groups to complete the following table, which 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?
$-CH(CH_3)_2$		
$-CH_2COOH$		
$-CH_2C_6H_5$		
$-(CH_2)_4NH_2$		

17.2 The formation of proteins

In this section, 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 that make up a polymer by a condensation polymerisation reaction 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. This type of polymerisation reaction was explored in detail in section 15.3.

Many biologically important molecules are produced by this type of reaction. These molecules include proteins, DNA, cellulose and starch. Insulin (see Figure 17.2.1) is a small protein that is 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 17.2.1 This young girl is injecting herself with insulin to control diabetes. Diabetes is a group of diseases associated with abnormally high levels of sugar in the blood.

DIPEPTIDES

As you learnt in Chapter 15, 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, which links the two molecules. A molecule of water is also produced, as shown in Figure 17.2.2.

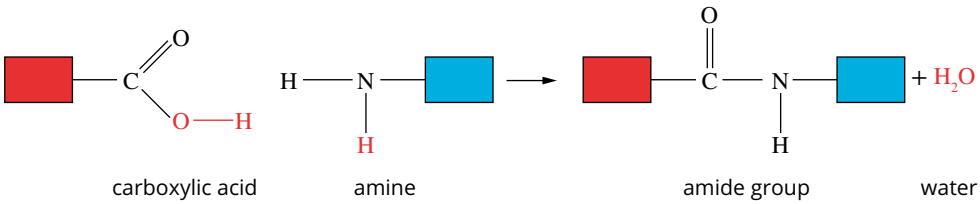


FIGURE 17.2.2 An amide group forms when a carboxyl group reacts with an amino group. A water molecule is also produced. The red and blue boxes represent the remaining atoms in the amino acids involved in this reaction.

Because α-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 is formed that links the molecules together. This amide link is sometimes also called a **peptide link**. The bond between the carbon and the nitrogen atoms in the amide group is called a **peptide bond**.

Molecules made from amino acids are often called peptides. When two amino acid molecules react together, as shown in Figure 17.2.3, the product is referred to as a **dipeptide**.

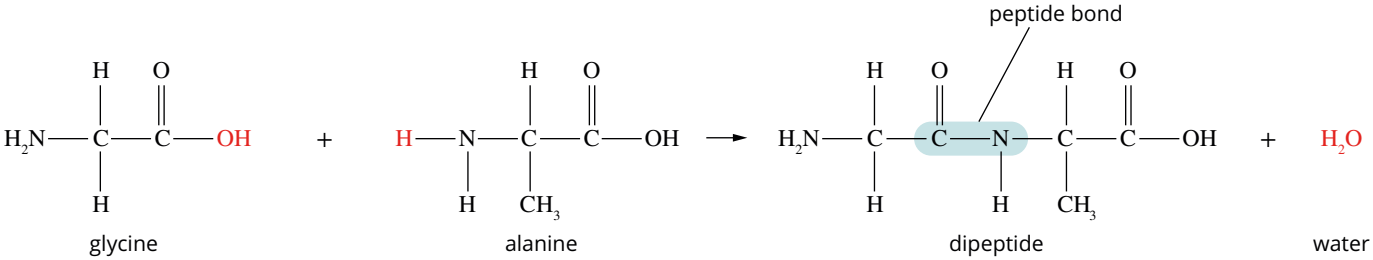


FIGURE 17.2.3 A condensation reaction between two amino acids, glycine and alanine to form the dipeptide Gly–Ala. Note how the carboxyl and amino groups react to form the dipeptide and water.

Each time a pair of different amino acids reacts in this way, there are two possible product molecules, depending on which ends of the two molecules react together (Figure 17.2.4).

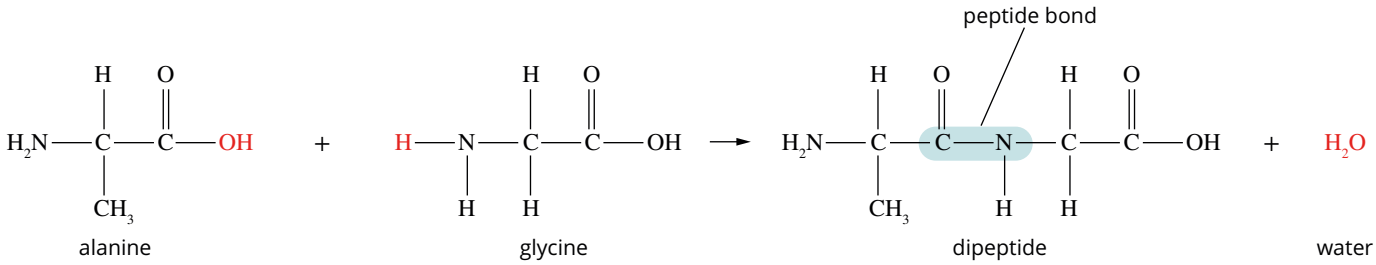


FIGURE 17.2.4 Another dipeptide molecule (Ala–Gly) formed from the reaction between glycine and alanine

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 listed in Table 17.11 of α-amino acid structures (page 460). By convention, the structure is drawn so that the free amino group is on the left and the free carboxyl group is on the right. When naming a polypeptide or protein, the order of the amino acids is also given in this direction, from the free amino group to the carboxyl group. A polypeptide consisting of six amino acids is shown in Figure 17.2.5. The polypeptide would be named as Ala–Glu–Gly–Cys–Val–Lys. Note that the alanine amino acid has a free amino group, and is called the **N-terminal** amino acid. The lysine has a free carboxyl group and is called the **C-terminal** amino acid.

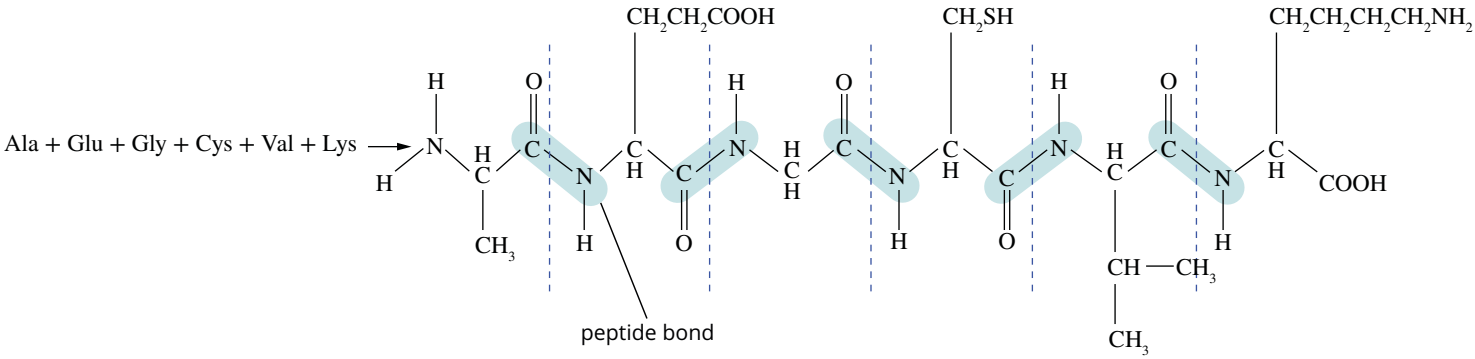


FIGURE 17.2.5 The polypeptide Ala–Glu–Gly–Cys–Val–Lys. Note that the amino acids are named in order from the N-terminal to the C-terminal. The peptide bonds between each amino acid are shaded.

A polypeptide constructed from more than 50 amino acids is usually called a protein. As longer molecules, proteins generally have a more complex three-dimensional structure than polypeptides. This will be discussed in sections 17.3 and 17.4.

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, containing a total of 51 amino acids. The sequence of amino acids in the two chains is shown in Figure 17.2.6. You can also see that the chains are linked by covalent bonds between sulfur atoms from the side chains of the cysteine units.

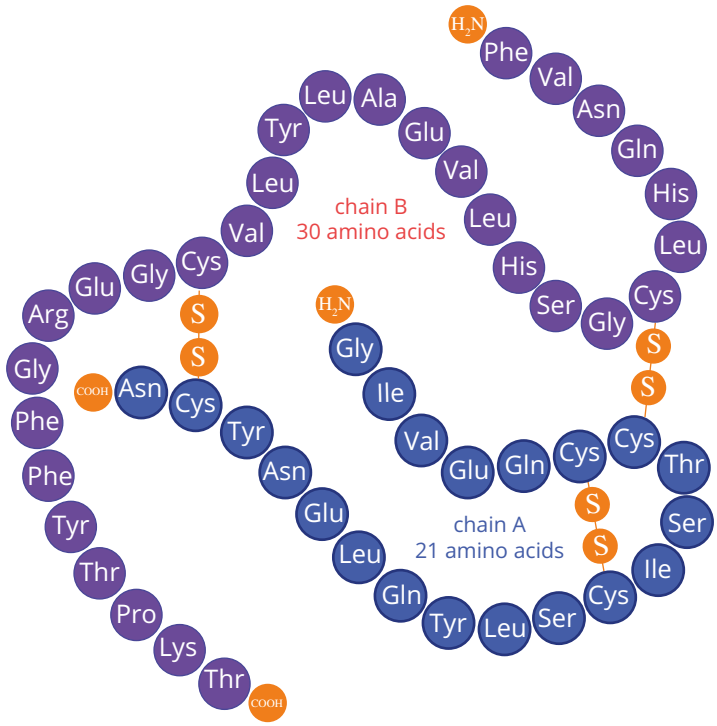


FIGURE 17.2.6 The amino acid sequence in the human insulin molecule. The polymer contains 51 amino acid units.

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.

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.

CHEMFILE

Fred Sanger—a pioneer of protein sequencing

Fred Sanger (Figure 17.2.7) was awarded two Nobel Prizes in Chemistry. The first was for his work on protein sequencing. Sanger determined the order of different amino acids in the two chains of the insulin protein. Sanger's second Nobel Prize was for his work on DNA sequencing.

FIGURE 17.2.7 Fred Sanger (1918–2013) did pioneering work on protein and DNA sequencing.

Born in England in 1918, Sanger grew up very interested in nature and science. Sanger decided not to follow in his father's footsteps and study medicine because he felt that a career in science would give him a better chance to become a problem solver.

Sanger completed his science degree at the University of Cambridge in England in 1939. He then studied amino acid metabolism for his PhD before starting work on identifying the amino acid sequence of (bovine) insulin extracted from cattle (Figure 17.2.8). Sanger was the first person to determine a protein sequence and was awarded his first Nobel Prize in 1958, in recognition of his important discovery.

By this stage, Sanger had moved on to study DNA-related problems, collaborating with other eminent scientists, including Francis Crick and John Kendrew. Solving the problem of DNA sequencing became a natural extension of his work in protein sequencing. In 1980, Sanger shared the Nobel Prize with Paul Berg and Walter Gilbert for his contribution to the determination of the nucleotide sequence in DNA.

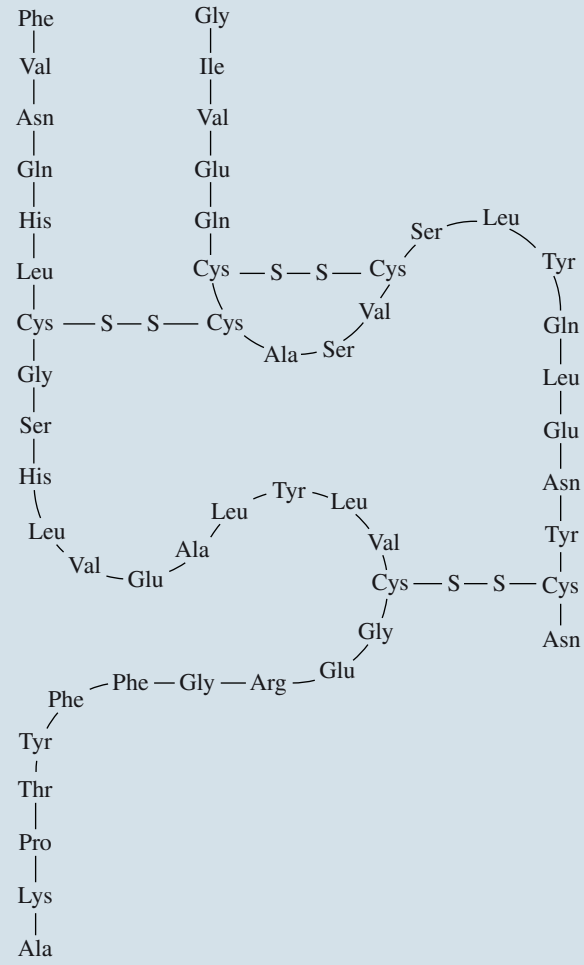


FIGURE 17.2.8 The amino acid sequence of bovine insulin. Its sequence of amino acids differs from human insulin by just three amino acids.

17.2 Review

SUMMARY

- The carboxyl group and amino group of two α-amino acids can take part in a condensation reaction that links them through a peptide bond.
- Water is also produced as a by-product, making this reaction an example of a condensation polymerisation reaction (see Figure 17.2.9).
- In a similar manner, several amino acids combine to produce a polypeptide.
- Proteins are large polypeptide chains containing approximately 50 or more amino acids.

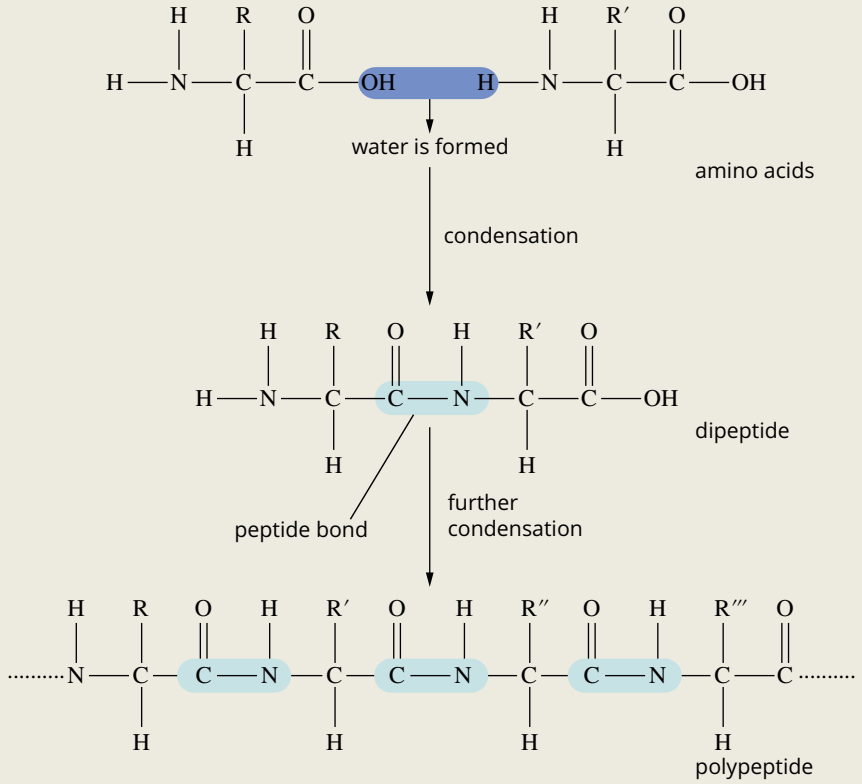


FIGURE 17.2.9 Condensation polymerisation of amino acids.

KEY QUESTIONS

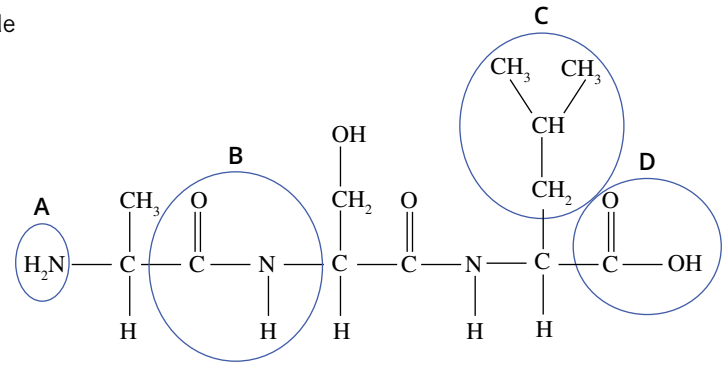
1 Match the terms on the left with their descriptions on the right.

Tripeptide	By-product of the reaction that produces polypeptides
Side chain	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 tripeptide is shown below.

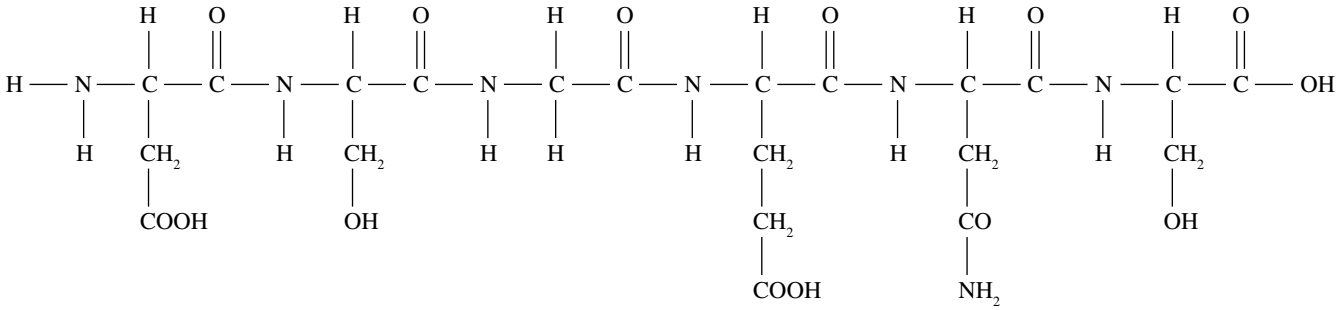
a Identify the parts labelled A–D.

b Give the names of the three amino acids in the tripeptide molecule.



17.2 Review *continued*

3 Which one of the following statements about the polypeptide shown below is correct?



A This polypeptide contains only two carboxyl groups.
B Five water molecules were produced in the reaction to form this polypeptide.
C Six different amino acids were used to make this polypeptide.
D This polypeptide was produced by an addition polymerisation reaction.

4 **a** Draw structural formulas of serine and cysteine.
b Write an equation to show the formation of a dipeptide from these amino acids.
c Write the formula of another dipeptide that could be formed from these two amino acids.
d Name the type of reaction in part **b**.

17.3 Primary and secondary 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 (see Figure 17.3.1) was one of the first proteins to have its amino acid structure determined. It is made up of 153 amino acids.

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 section, you will investigate the primary and secondary structures of proteins.

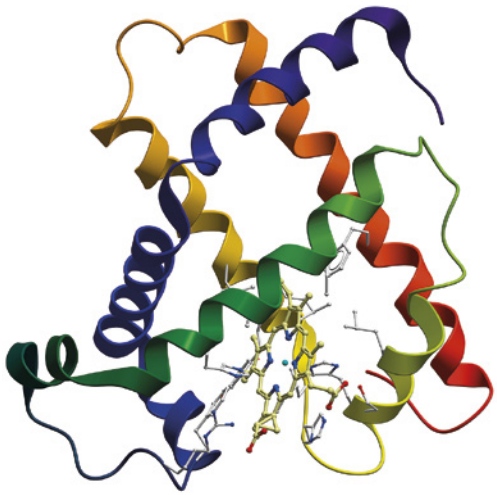


FIGURE 17.3.1 A representation of myoglobin. Myoglobin is a protein consisting of 153 amino acids in one polypeptide chain. This protein is found in muscle tissue where it binds to oxygen.

PRIMARY STRUCTURE OF PROTEINS

The number, type and sequence of the amino acid units in a protein is known as the protein's **primary structure**. As you can see in Figure 17.3.2, 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.

i The function of a protein is a consequence of its shape, which in turn is determined by the order in which amino acids are joined together, the primary structure.

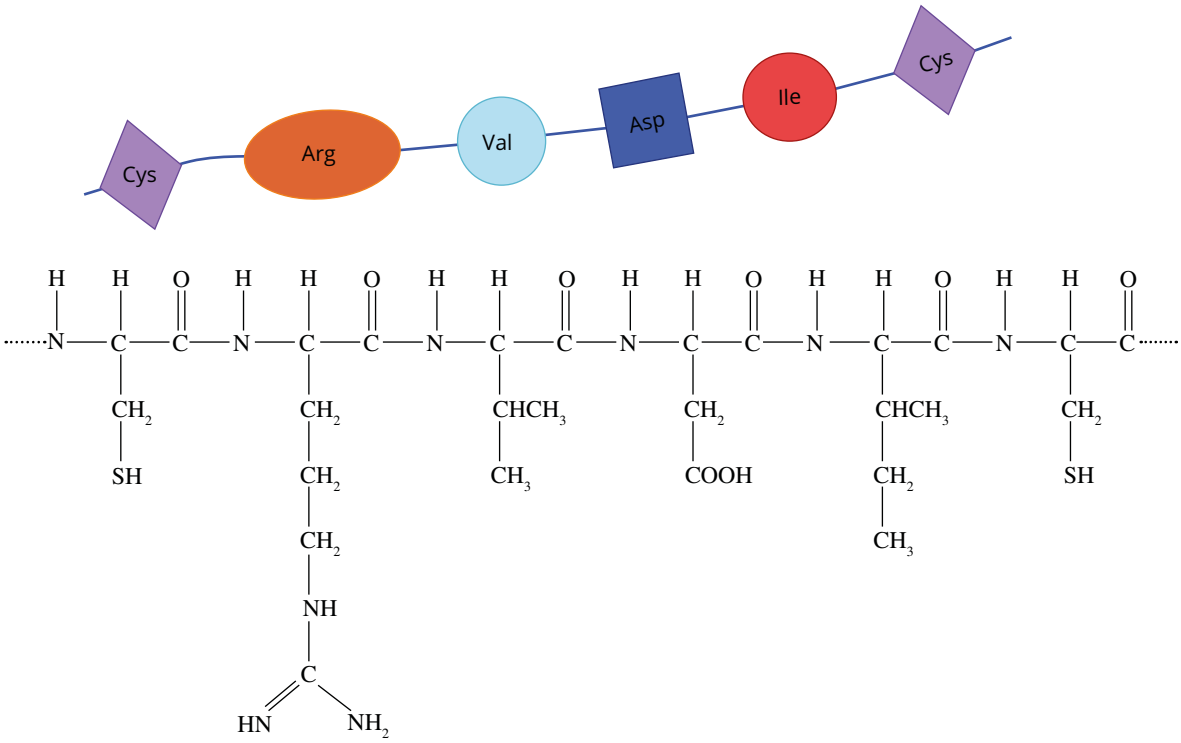


FIGURE 17.3.2 A small section of a protein molecule showing the primary structure represented by three-letter abbreviations and its structural formula

The three-dimensional shape of a protein is determined by the precise order in which its amino acids are joined together. This is due to the many interactions between nearby amino acids, leading to the folding of the protein chain. 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 importance of the primary structure to the function of a protein can be seen in genetic conditions such as cystic fibrosis. The protein affected by cystic fibrosis functions in healthy individuals allows chloride ions to move across cell membranes. It is a large protein, consisting of 1480 amino acids. The disease is caused by genetic mutations that involve either deleting or swapping just one amino acid in the sequence. This tiny change in the primary structure affects the overall three-dimensional shape of the protein and prevents it from working normally, causing mucus to build up in the lungs and pancreas.

CHEMISTRY IN ACTION

Protein sequencing

The primary structure of a protein is found experimentally by the process of protein sequencing (Figure 17.3.3).

The amino acids in a polypeptide can be identified by heating the polypepetide in concentrated (6 M) 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 indicate 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 bonds 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.

FIGURE 17.3.3 This scientist is preparing to use an automated microsequencer machine to analyse the amino acid sequence of samples of protein.

SECONDARY STRUCTURE OF PROTEINS

Coiling and pleating 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 17.3.4).

This 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.

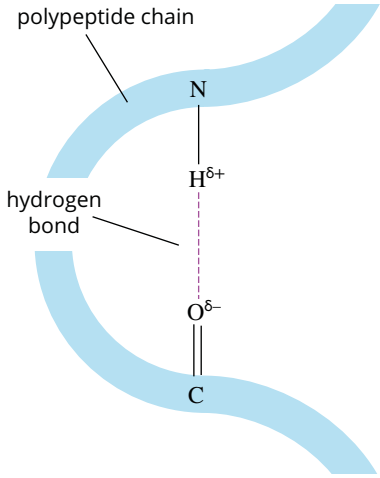


FIGURE 17.3.4 Hydrogen bonds can form between the polar –NH group in one peptide link and the polar –C=O group in another peptide link further along the polypeptide chain.

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 in the polypeptide chain. The hydrogen bonds result from the attraction between the partial positive charge on the H of a –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 (see Figure 17.3.5).

Some amino acids are more likely to be found in an α-helix than others. Both proline and glycine, for example, are unlikely to exist in an α-helix structure. Due to its ring structure, proline's structure is too rigid to allow it to form part of a helix. Conversely, the fact that glycine only has a hydrogen atom for its R group means that it introduces too much flexibility and reduces the stability of the α-helix structure.

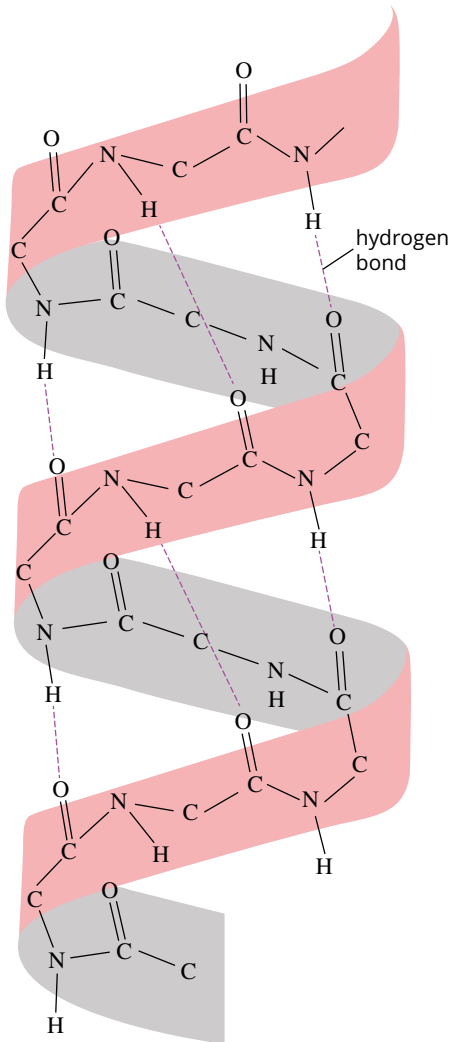


FIGURE 17.3.5 A polypeptide chain coils in an α-helix due to hydrogen bonds. The side chains (R groups) and hydrogen atoms on the α carbons have been omitted for clarity.

β-Pleated sheets

Hydrogen bonds can also form between peptide links 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 (Figure 17.3.6).

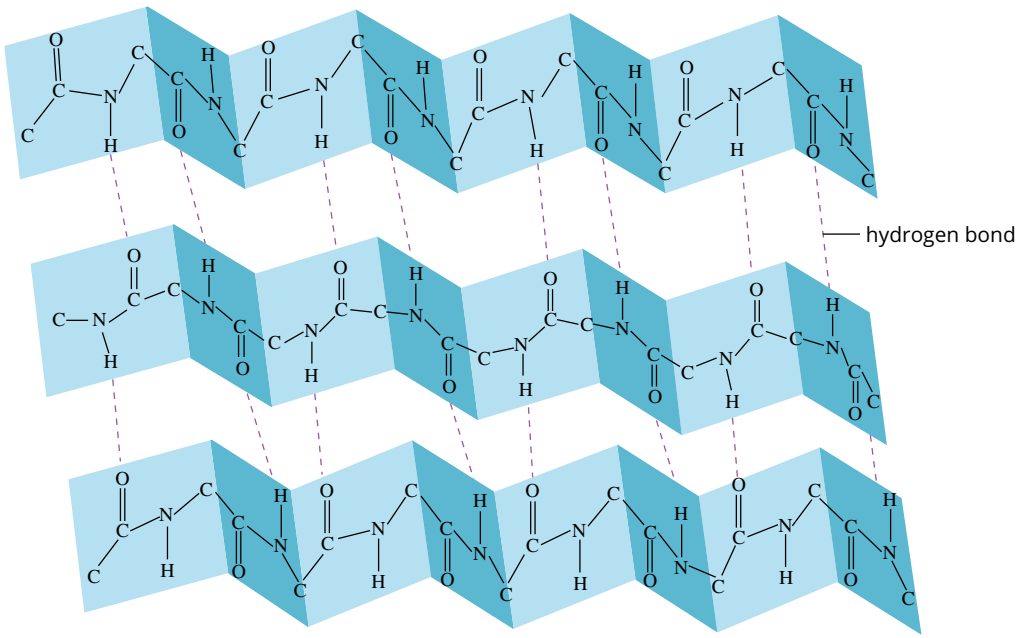


FIGURE 17.3.6 β-Pleated sheet. Hydrogen bonds between the sheet are shown as dashed lines. The side chains (R groups) and hydrogen atoms on the α carbons have been omitted for clarity.

Silk is a protein with a β-pleated sheet structure. The polypeptide chains involved mainly contain the amino acids glycine, alanine and serine, as shown in Figure 17.3.7. Notice that every second R group is H. With only these small side groups, sections of the protein molecule in silk can line up closely, enabling strong hydrogen bonds to form between these adjacent sections and producing β-pleated sheets.

The secondary structure of a protein results from hydrogen bonding between the C=O and N–H groups in the peptide links along the protein backbone. This leads to the formation of α-helices or β-pleated sheets.

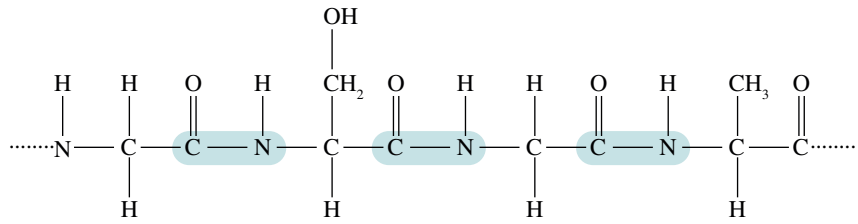


FIGURE 17.3.7 The amino acid sequence that is found in large parts of the β-pleated sheets in the silk protein. Peptide bonds are shaded blue.

CHEMFILE

Modelling protein structure

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.

A computer-generated model of a protein is shown in Figure 17.3.8.

There are wide variations in the relative amounts of α-helix and β-sheet structures in individual proteins, with many proteins containing several regions of both.

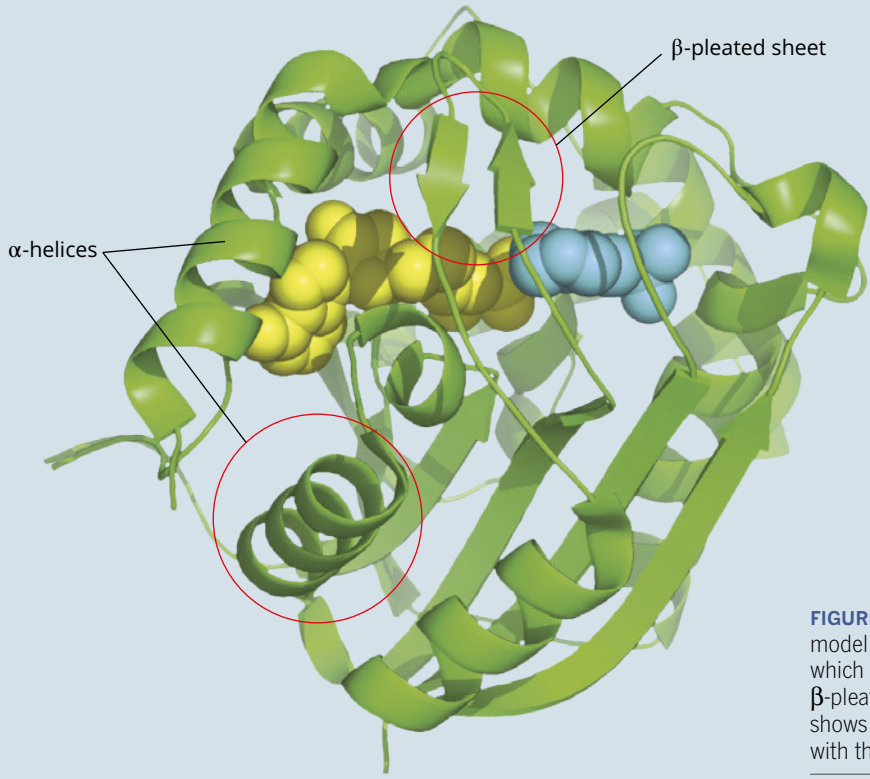


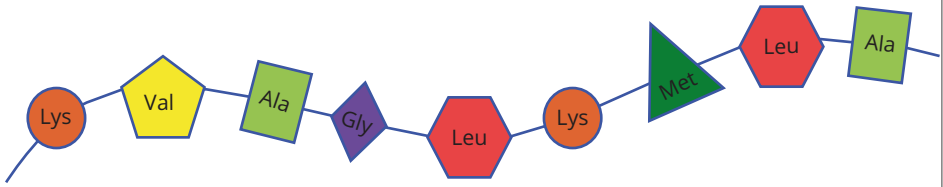
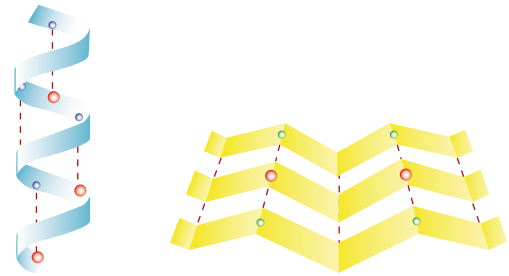
FIGURE 17.3.8 Computer-generated model of a protein (green and yellow) in which several regions of α-helices and β-pleated sheets are seen. The blue part shows drug-like molecules interacting with the protein.

17.3 Review

SUMMARY

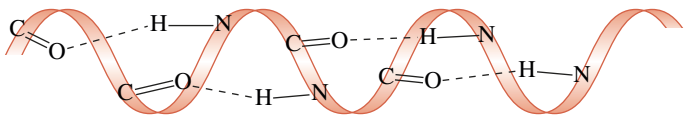
- There are 20 different α-amino acids from which tens of thousands of different protein molecules are synthesised by cells. Each protein has a unique structure and function in the organism.
- The complex structure of these large molecules is often considered in distinct levels. The primary and secondary levels are summarised in Table 17.3.1.

TABLE 17.3.1 Primary and secondary structures 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 –C-N bonds, known as peptide bonds 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  α-helix β-pleated sheet	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.

KEY QUESTIONS

1 The following diagram shows a section of a protein.



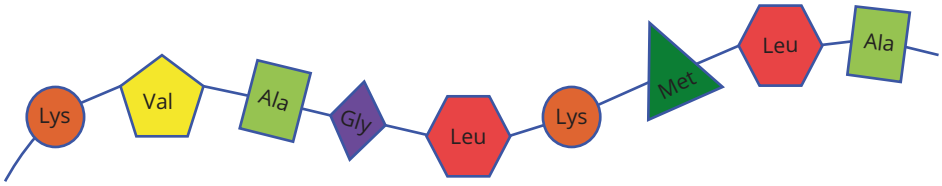
a What secondary structure is represented by the diagram?

b How does this type of secondary structure form? Refer to particular atoms and functional groups associated with the bonding that forms this structure.

17.3 Review *continued*

2 Why is it important to be able to determine the specific sequence of amino acids in a protein?

3 The following diagram represents a section of a polypeptide molecule. Complete the paragraph by filling in the blanks. You may need to refer to the Table 17.1.1 on page 460 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 _____ bonds. 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 _____, _____, _____.

4 How do α-helices and β-pleated sheets differ?

17.4 Tertiary structure of proteins

In the previous section, you learnt that the sequence and order of amino acid units in a protein chain is called the primary structure of the protein. 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.

In this section, you will examine the overall three-dimensional shapes of proteins and the types of bonds that cause proteins to adopt their different shapes. These bonds are due to forces between the different functional groups in the side chain of amino acid units.

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). The protein can twist back over itself to create a unique shape, which is responsible for the protein's function (see Figure 17.4.1).

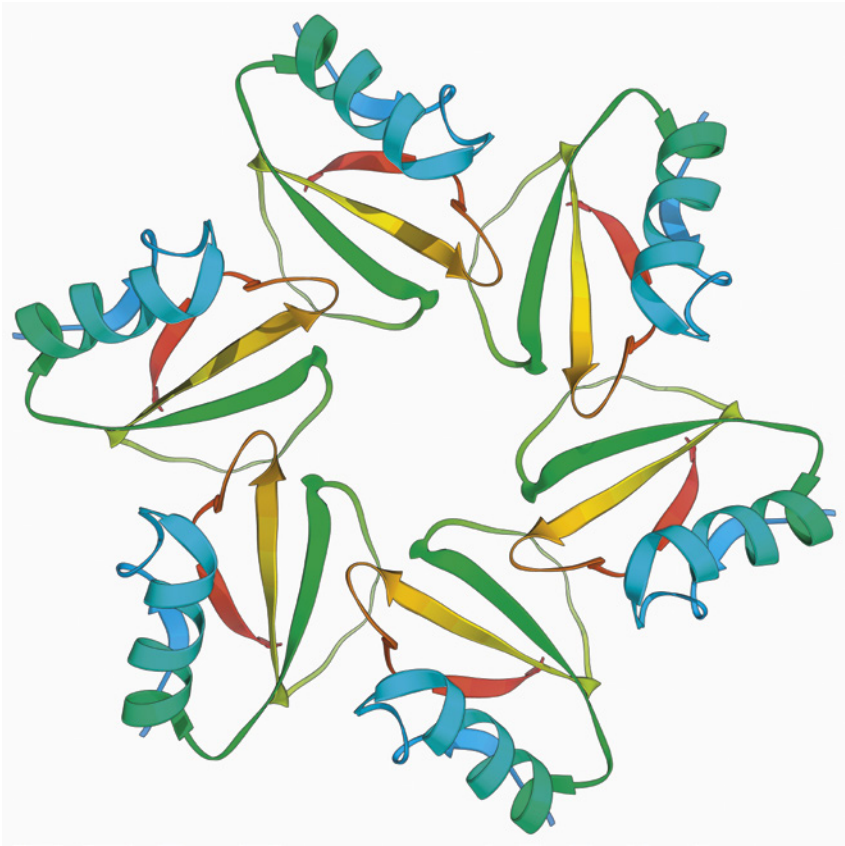


FIGURE 17.4.1 A model representing the tertiary structure of the protein CI2 (Chymotrypsin inhibitor 2), showing how the α-helices and β-pleated sheets are folded to produce a three-dimensional structure

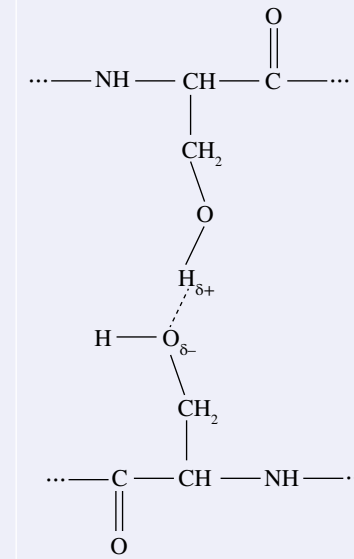
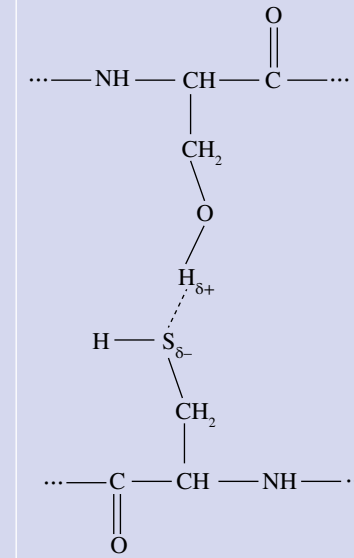
The side chains of the amino acid units making up the polypeptide chain influence the overall three-dimensional shape of the molecule. These side chains can interact with each other in a number of ways, causing the protein to fold into its three-dimensional shape. Side chains can be relatively large (such as in phenylalanine), contain polar functional groups, or 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.

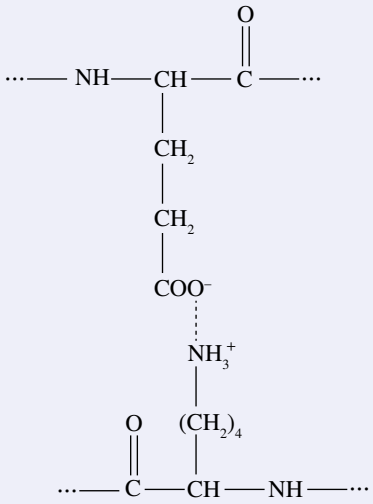
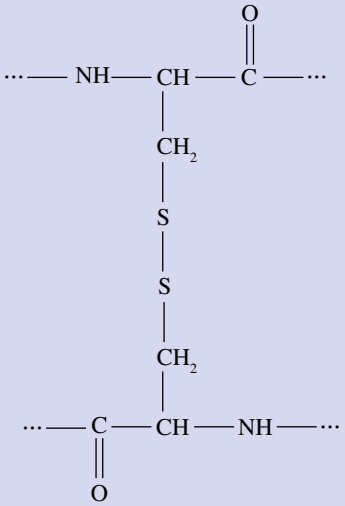
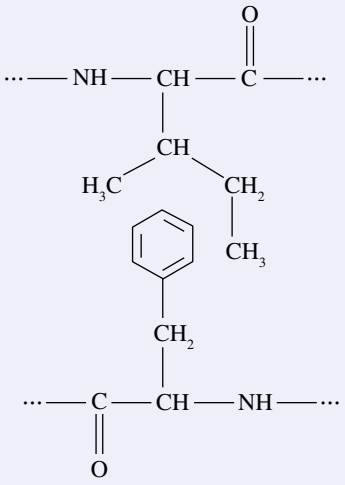
Side chains of amino acids influence the properties of the amino acid. There are four main groups of amino acids, which can be classified as polar, non-polar, acidic or basic. These were discussed in section 17.1 (page 459).

Bonding in the tertiary structure of proteins

Five types of attractions that are important in protein folding are summarised in Table 17.4.1, which also identifies the features of the side chains that are involved.

TABLE 17.4.1 Types of bonds formed from interactions of specific side chains in different regions of the protein

Bond type	Required components in side chain	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

Bond type	Required components in side chain	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

CHEMISTRY IN ACTION

X-ray crystallography

Scientists use a technique called X-ray crystallography to determine the three-dimensional structures of large molecules such as proteins. The first step in this process is producing large enough quantities of the protein to enable it to be purified. This is usually achieved using cells that have been genetically modified to produce large quantities of the target protein.

A single protein molecule is not large enough to be analysed by this technique, so scientists produce protein crystals, in which the molecules are arranged in a regular pattern, in order to magnify the signal. This can be a difficult technique and requires a long experimental process to determine the conditions (temperature, pH, salt concentration, time) under which the protein will form suitable crystals.

The crystal is then placed in front of an X-ray source and the pattern of X-rays that passes through is recorded (Figure 17.4.2). The pattern formed and the relative brightness of the dots is determined by the arrangement of the electrons in the crystal. Computer programs then use this map of electron density to determine the position of each atom in three-dimensional space; that is, the tertiary structure of the protein.

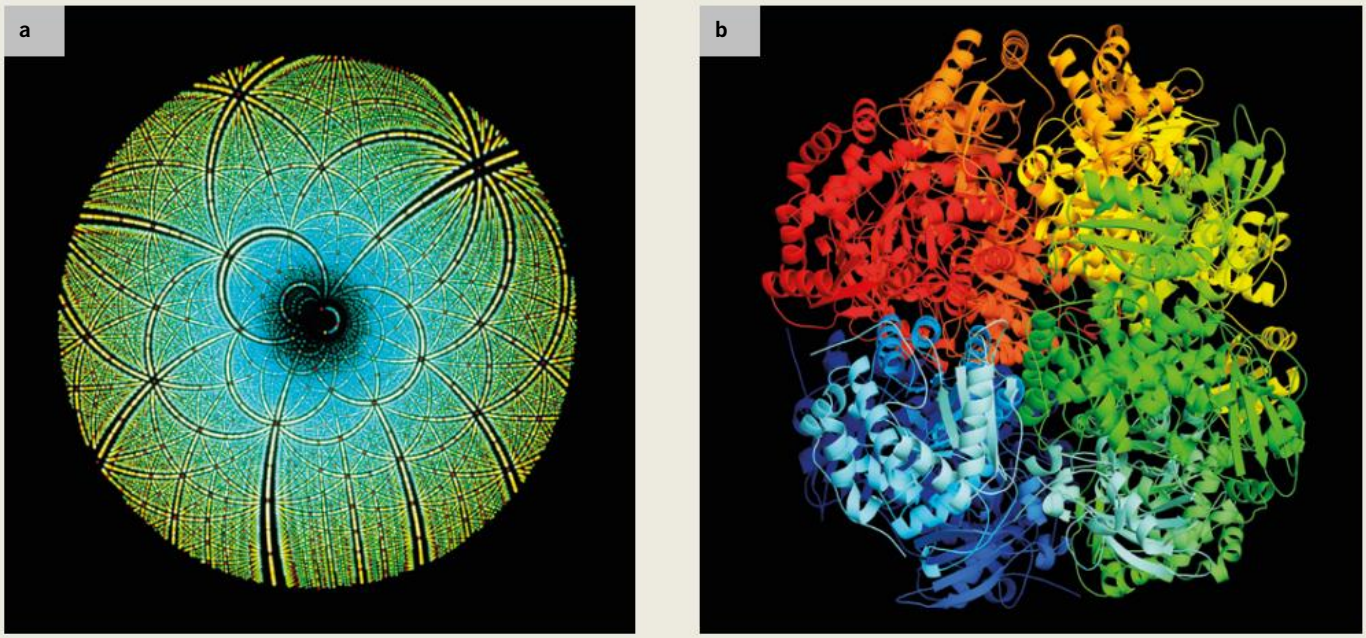


FIGURE 17.4.2 Rubisco is the most common protein in nature. Found in all plants, rubisco fixes carbon dioxide during photosynthesis. (a) The X-ray diffraction pattern produced when rubisco crystals are bombarded by X-rays. (b) The three-dimensional structure of rubisco, determined from the X-ray diffraction pattern.

An enormous variety of protein shapes exist as a result of the different types of bonds that can fold a polypeptide into a three-dimensional shape. Some proteins resemble flat sheets, others are long and helical, and others are compact and globular.

CHEMFILE

Alzheimer's disease

The three-dimensional shape of a protein is critical to its function. Several diseases are linked to proteins that have not folded properly into their three-dimensional shape; these are called protein misfolding diseases and include Alzheimer's disease. Although the causes of Alzheimer's disease are not well understood, the disease is characterised by the accumulation of dense plaques in the brains of sufferers (Figure 17.4.3). These plaques eventually lead to the degeneration of affected neurons.

These plaques consist of aggregations of the short protein amyloid beta. In healthy people, this protein is soluble. However, in Alzheimer's patients, the protein changes shape and forms a crossed structure rich in β-sheets. Many similarly misfolded amyloid beta protein chains then combine to form long fibrils. In this form, the amyloid beta protein is insoluble and forms the plaques on neurons.

Many other proteins can form amyloid fibrils when they misfold. These proteins are generally also rich in β-sheets and have been linked to diseases such as type 2 diabetes, Huntington's disease, Parkinson's disease, atherosclerosis and bovine spongiform encephalopathy (mad cow disease). When this process occurs in the heart (cardiac amyloidosis), the heart tissue becomes stiff and thickened. This is often a fatal condition, commonly known as 'stiff heart syndrome'. It is not known what causes these proteins to misfold.

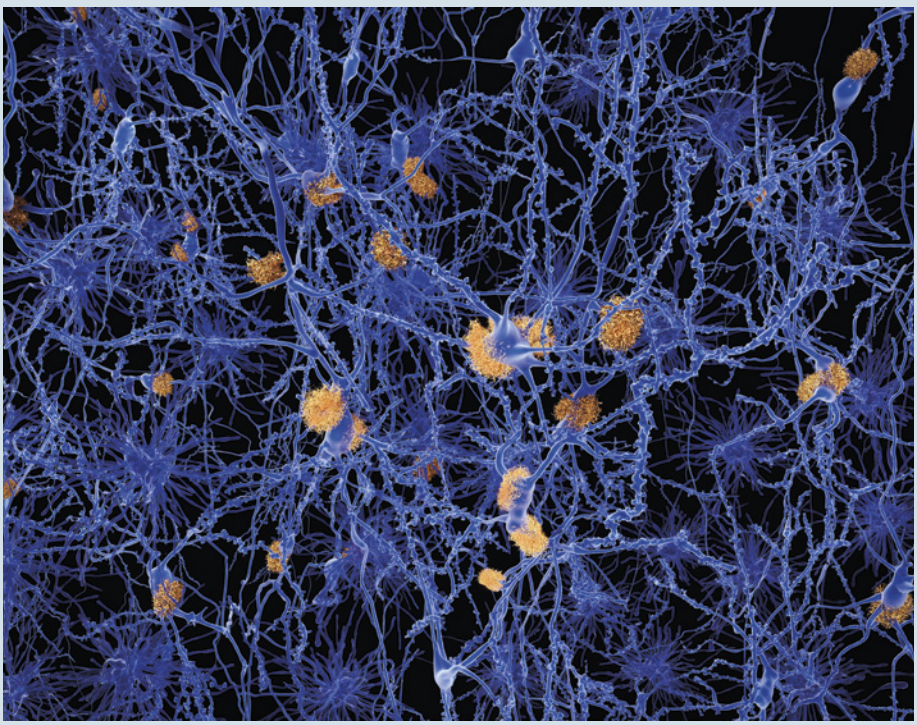


FIGURE 17.4.3 An illustration showing the formation of amyloid plaques (orange) among neurons (blue) in the brain of an Alzheimer's patient. The plaques lead to degeneration of affected neurons.

EXTENSION

Quarternary 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.

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 3 months in the human body. Each red blood cell contains approximately 250 million molecules of haemoglobin.

Figure 17.4.4 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 side chains are least exposed to water molecules. The polar side chains are hydrophilic and are therefore located near the outer surface.

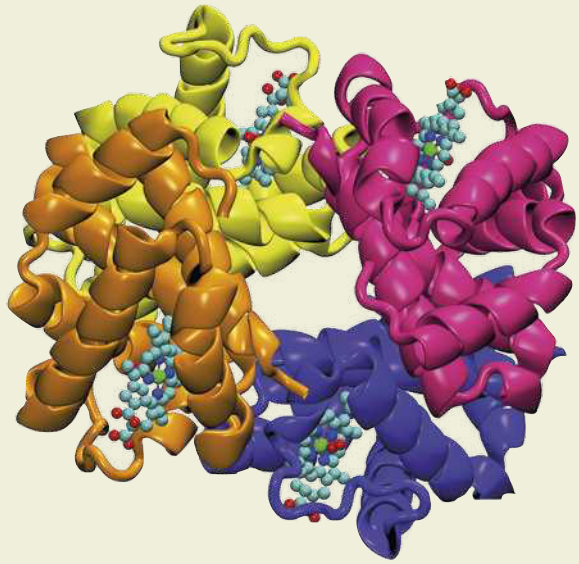


FIGURE 17.4.4 A representation of the structure of haemoglobin. Within each subunit is a haem group (light blue). Each group contains one atom of iron (green). In this model, the haem groups are oxygenated and the oxygen molecules are shown as paired red spheres.

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.

17.4 Review

SUMMARY

- The complex structure of large molecules such as proteins is often considered in distinct levels. The overall three-dimensional shape adopted by a protein molecule is called its tertiary structure (Figure 17.4.5).
- Many bond types produce the three-dimensional shape of proteins:
  - dispersion forces, such as between two non-polar side chains, e.g. $-CH(CH_3)_2$
  - dipole–dipole attractions
  - hydrogen bonds between polar functional groups in side chains, such as –OH and –C=O
  - covalent bonds in disulfide bridges, such as between cysteine's R groups
  - ionic interactions between charged R groups.
- The three-dimensional shape of a protein is critical to its function.

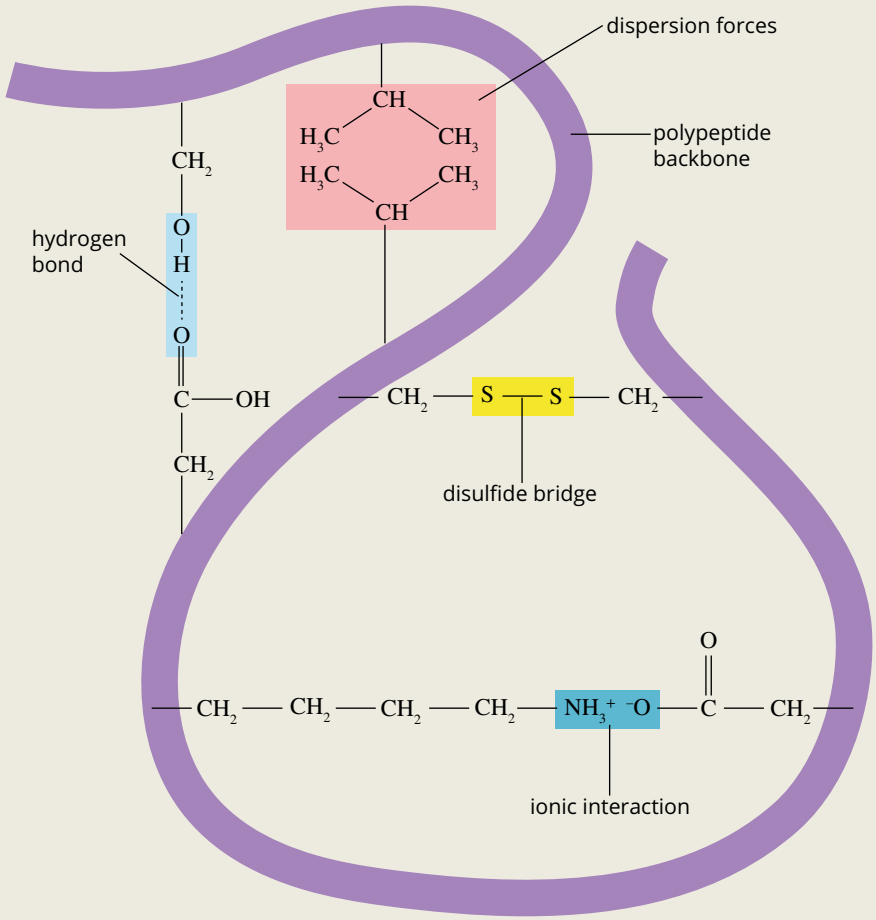


FIGURE 17.4.5 Protein tertiary structure

KEY QUESTIONS

1 Identify the levels of protein structure in which hydrogen bonds may contribute to the structure. More than one option may be correct.

A primary structure
B secondary structure
C tertiary structure

2 List the five main bond interactions that occur when side chains in different regions of a polypeptide chain interact with each other. Give examples of the required components in side chains involved in such interactions, and an example of an amino acid that has a side chain of this type.

3 Identify the major type of bonding that would exist between the side chains of the following pairs of amino acids. You can assume that the conditions are such that any amino side group is positively charged and any carboxyl side group is negatively charged.

a proline and leucine
b glutamic acid and lysine
c glutamine and serine
d cysteine and cysteine

Chapter review

17

KEY TERMS

α-amino acid
α-helix
amide
amino functional group
amino acid
β-pleated sheet
C-terminal
carboxyl functional group
condensation polymerisation
condensation reaction
dipeptide
essential amino acid
hydrolysis
hydrophobic
monomer
N-terminal
peptide bond
peptide link
polypeptide
primary structure
protein
quaternary structure
secondary structure
side chain (R group)
tertiary structure
tripeptide
zwitterion

Amino acids

1 Select the correct statement about amino acids.

A Amino acids contain only the elements C, H, O and N.

B All 20 amino acids needed by humans are known as essential amino acids.

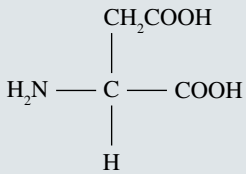
C Amino acids may contain more than one nitrogen atom.

D The functional group on an amino acid side chain is always non-polar.

2 What two functional groups are present in all amino acids?

3 Draw the general structure of an amino acid. Colour the amino group in blue and the carboxyl group in red.

4 Aspartic acid, shown below, is one of the non-essential amino acids. 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 pH:

i much greater than 2.8

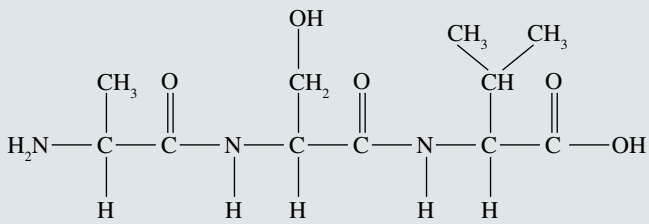
ii much less than 2.8

iii 2.8.

The formation of proteins

5 Which two functional groups react when a protein such as insulin is formed from its constituent amino acids?

6 The following diagram shows a tripeptide molecule. Select the correct statement about this tripeptide.



A Three water molecules were released when this molecule was produced.

B This molecule can undergo hydrolysis to produce three different amino acids.

C There are four amino acids in this molecule.

D There are three carboxyl groups in this molecule.

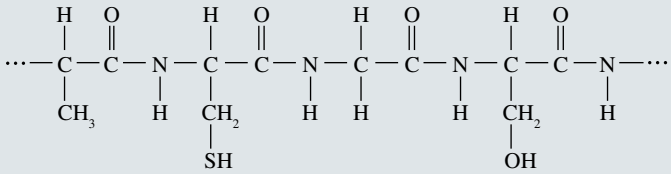
7 When alanine and glycine react, two different dipeptides can be formed.

a Write the condensed structural formula of each dipeptide at pH 7.

b How many tripeptides 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**, what can you say about the number of different proteins possible?

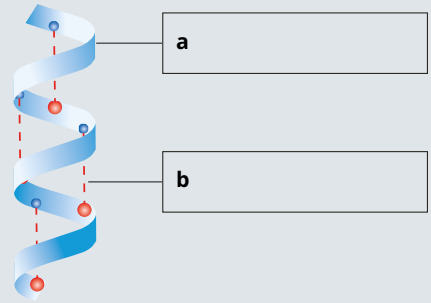
d Circle the peptide bonds in the section of the protein chain shown below.



e Name the amino acids that make up this section of the chain.

Primary and secondary structures of proteins

8 Identify the type of bonding represented by labels **a** and **b** of the following diagram. Identify the type of secondary structure in **c**.

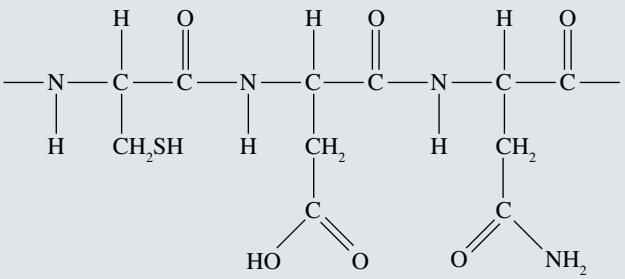


c The structure is _____.

9 How does a β-pleated sheet structure form in a protein?

Tertiary structure of proteins

10 Circle the parts of the polypeptide segment that might be involved in forming bonds responsible for the tertiary structures of the protein molecule.



11 Mutations can cause the wrong amino acid to be inserted into a protein chain when it is being assembled. In some instances, such a mistake has no effect on the function of the protein but in others it disables the protein. Explain how a single change in a protein's primary structure could cause such dramatically different results.

12 Explain what is meant by the primary, secondary and tertiary structures of a protein.

13 Name the type of interaction most likely to occur in the following pairs of amino acids, which are part of the same polypeptide chain. Assume that the amino groups are in the NH_3^+ form and the carboxyl groups are in the COO^- form.

a aspartic acid and lysine

b cysteine and tyrosine

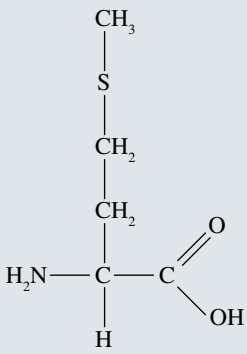
c leucine and isoleucine

14 Keratin is the protein that makes up our hair and nails and the horns and claws of mammals. Keratin is approximately 14% cysteine. This is why hair produces a pungent smell when burnt—the sulfur in the cysteine amino acids produces sulfur-containing gases. The cysteine amino acids in keratin are also responsible for much of the protein's strength and toughness. Explain this, using your knowledge of the interactions that are responsible for a protein's tertiary structure.

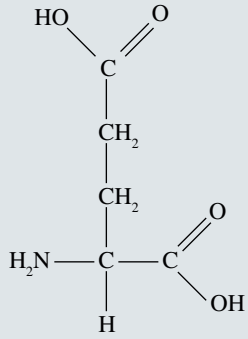
15 There are two possible mutations in a protein that result in the wrong amino acid being inserted in the protein chain in the place of leucine. These mutations result in either an isoleucine or a serine being inserted instead of leucine. Which mutation would have the greatest effect on the tertiary structure? Explain your answer.

Connecting the main ideas

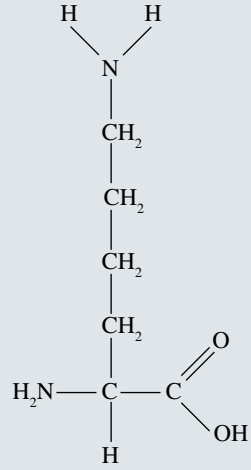
16 Use the structures of the three amino acids and a peptide group labelled A–D below to complete the statements that follow.



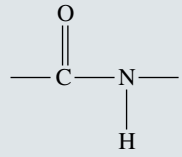
A



B



C



D

The side chain of molecule _____ might become positively charged if the pH is sufficiently _____. If this molecule were present in a protein, the side chain could take part in ionic interactions that contribute to the protein's tertiary structure.

The polar bonds that are present in _____ are responsible for the hydrogen bonds in an α-helix, contributing to the secondary structure of the protein.

If there are two molecules of _____ in close proximity within a protein, they can form covalent bonds with each other. These covalent interactions contribute to the tertiary structure of the protein.

17 In a water-soluble protein, are the following amino acids most likely to be present on the surface of the protein, or hidden within the protein structure?

a Leucine
b Lysine
c Phenylalanine
d Aspartic acid

18 The amide links that form between amino acids are integral to both the primary and secondary structure of a protein. Explain this statement.

CHAPTER

18 Uses of proteins

Proteins provide the molecular machinery within biological systems. They have also been used to perform functional roles outside the body. For example, the enzyme systems within yeast have been used for thousands of years to assist in the production of bread and alcoholic beverages. Similarly, in more recent years, enzymes have been increasingly used to catalyse reactions involved in industrial processes. In Chapter 17, you learnt about the interactions that govern the folding of proteins into their functional three-dimensional shapes. In this chapter, you will learn about how the shape of proteins is related to their function, focusing particularly on the role of enzymes, both within biological systems and in industrial applications.

Science as a human endeavour

The Protein Data Bank (PDB) houses an international repository of 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.

Science understanding

- secondary structures of proteins (α-helix and β-pleated sheets) result from hydrogen bonding between amide and carbonyl functional groups; hydrogen bonding between amide and carbonyl functional groups within a peptide chain leads to α-helix structures while hydrogen bonding between adjacent polypeptide chains leads to β-pleated sheets
- the tertiary structure of a protein (the overall three-dimensional shape) is a result of folding due to interactions between the side chains of the α-amino acid in the polypeptide, including disulfide bridges, hydrogen bonding, dipole–dipole interactions, dispersion forces and ionic interactions
- enzymes are protein molecules which are biological catalysts and can be used on an industrial scale to produce chemicals that would otherwise require high pressure or temperature conditions to achieve an economically viable rate, including fermentation to produce ethanol versus hydration of ethene

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18.1 Investigating proteins

Proteins are required for the structure, function and regulation of all the processes that take place within cells. Therefore, investigating the structure and function of proteins is critically important to scientists. A greater knowledge of proteins provides insight into biological processes and offers potential targets for drug discovery. For this reason, scientists share information about protein structure and function in online databases.

ROLE OF PROTEINS IN BIOLOGICAL SYSTEMS

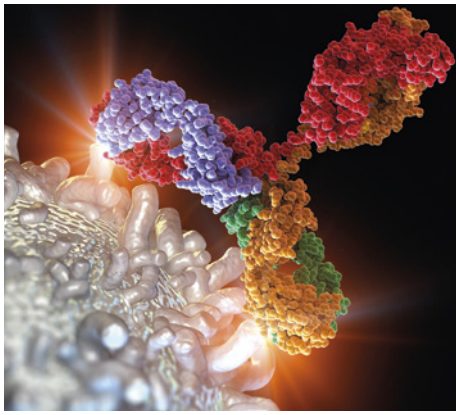


FIGURE 18.1.1 The Y-shape of this protein, an antibody (multi-coloured), enables it to interact with and attack a foreign substance (white) that has entered the body.

In order to survive, your body produces thousands of different proteins, each one with its own unique function. For example, proteins can act as enzymes to catalyse biochemical reactions, as hormones, as structural components in cells, and as part of the immune system, and some proteins assist with the transportation of substances across cell membranes. Proteins are critical to almost every chemical process within our bodies.

The function of a protein is closely linked to its structure. As you learnt in Chapter 17, the specific sequence of amino acids in a protein results in a unique three-dimensional shape that enables the protein to function correctly.

The function of a protein depends on its three-dimensional shape.

For example, antibodies are large Y-shaped proteins that your immune system uses to recognise foreign materials such as bacteria and viruses (Figure 18.1.1). The shape of the antibody molecules allows them to recognise and bind to these pathogens. All antibodies have a very similar structure and shape, with the exception of the region at the tip of the Y-shape. Your body contains millions of different antibodies, each with a slightly different structure that allows each one to recognise a slightly different pathogen.

CHEMISTRY IN ACTION

Investigating protein function—knockout mice

One way in which scientists can investigate protein function is through using genetically engineered knockout mice. Scientists are able to inactivate or 'knock out' genes in the mice, preventing their cells from synthesising specific proteins.

For example, leptin is a protein hormone that regulates appetite in mammals by signalling to the brain when the animal is full or satiated. The function of this protein was discovered by examining a strain of mice with a mutation that prevents them from producing leptin. These mice gain weight rapidly throughout their lives and often reach a weight three times that of unaffected mice (Figure 18.1.2).

The leptin knockout mice have been used to investigate the causes of obesity and many of the processes involved in obesity-related diseases such as type 2 diabetes.

FIGURE 18.1.2 A leptin knockout mouse next to a normal mouse. The knockout mice grow up to three times larger than normal mice despite eating a low-fat diet. Examining the differences between the two mice enables scientists to determine the function of the leptin protein.

PROTEIN DATA BANK

The **Protein Data Bank** (PDB) is a database that contains the amino acid sequence and three-dimensional shapes of large biological macromolecules, such as proteins and nucleic acids. It provides research scientists with a means of rapidly sharing their findings with one another. More than 100 000 structures have been posted on the PDB since 1973 and are freely available to all. The PDB can be accessed online.

Most of the structural data is obtained from X-ray crystallography experiments, as discussed in section 17.4. More recently, nuclear magnetic resonance (NMR) spectroscopy has also been used to determine the three-dimensional structure of proteins. Once uploaded to the PDB, the protein structure can be visualised in a number of different ways (Figure 18.1.3).

The PDB also includes a large amount of additional information, such as the known functions of proteins, their location within the cell and any molecules that they are known to interact with. Understanding the structure of a large molecule helps in understanding its function. Such knowledge can be used to gain a better understanding of the role of a protein in human health and disease.

For example, cyclooxygenases are enzymes that catalyse one of the steps involved in the production of prostaglandins. Prostaglandins are involved in inflammation and pain signalling. The PDB entry for cyclooxygenase shows the three-dimensional shape of the enzyme and lists the molecules that are known to interact with it and affect its function. These include the common pain killer salicylic acid (aspirin) and many other anti-inflammatory drugs such as ibuprofen (Figure 18.1.4).

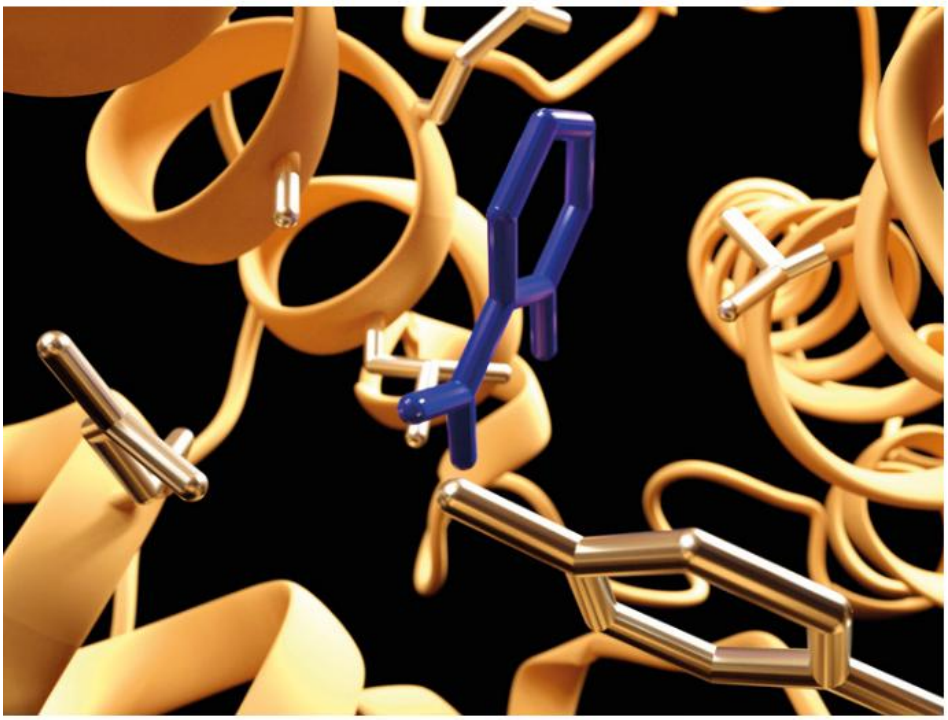


FIGURE 18.1.4 Aspirin is converted to salicylic acid and ethanoic (acetic) acid in the body. The binding of salicylic acid (blue) deactivates the cyclooxygenase enzyme (yellow) and prevents it from producing prostaglandins that are involved in pain signalling and inflammation.

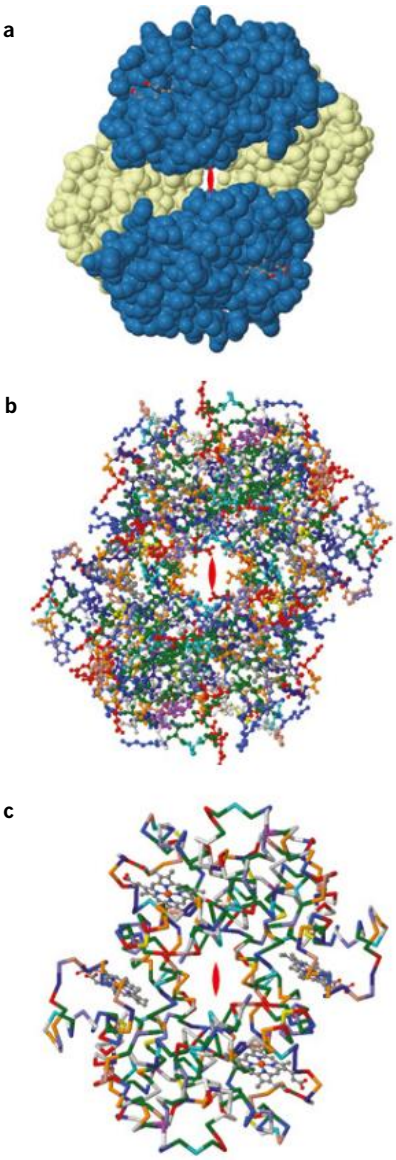


FIGURE 18.1.3 The Protein Data Bank enables scientists to view protein structures in a number of different ways. (a) A space-filling model showing four subunits of the protein haemoglobin. (b) A ball and stick model showing all amino acids in different colours. (c) The backbone of the protein haemoglobin, with amino acids in different colours. Hydrogen bonds are shown as dashed lines. The position of the haem group in the protein is visible, with the orange Fe^{2+} ion in the centre.

CHEMFILE

Drug discovery

Historically, drugs were discovered either by chance or by analysing the compounds present in traditional remedies. For example, in the 1970s, one of the compounds present in the herb sweet wormwood (*Artemisia annua*) was found to have anti-malarial properties. This herb had been used for over 2000 years in China as a traditional treatment against the malaria-causing parasite *Plasmodium*, carried by mosquitoes (Figure 18.1.5). The isolated compound, known by the name artemisinin, is now widely used as an anti-malarial drug throughout the world. The 2015 Nobel Prize in Physiology or Medicine was awarded for this discovery. However, the problem with this approach to drug discovery is that it can take a long time and there are often issues with isolating the active compound in sufficient quantities.

FIGURE 18.1.5 Coloured scanning electron micrograph of a female mosquito, carrier of the parasite *Plasmodium*, which causes malaria.

With greater access to protein structural data, it is now common for scientists to use a more targeted approach to discover potential drugs. Using this approach, scientists begin by identifying the proteins that are involved in particular disease conditions. They can then screen chemical libraries, containing large numbers of small molecules, to identify compounds that bind to the particular protein of interest. These compounds are then tested in cells and animal models to examine their biological action. Alternatively, the large number of molecules in chemical libraries can be tested directly in diseased cells in order to identify potential drugs. The development of databases such as the PDB assists in this drug discovery process because the databases hold information about protein structure and the molecules that are known to interact with them, as well as possessing sophisticated search functions.

Many drugs have been developed in this way in recent years. One such example is a new drug (DDD107498), which also shows promise as an anti-malarial treatment. The development of this drug is extremely timely because there are signs of malaria parasites developing resistance to artemisinin. DDD107498 was discovered by testing a chemical library containing 4371 compounds against the malaria parasite. One compound was found to destroy the parasite at each stage in its life cycle. It was then modified slightly to improve its suitability as a single-use drug, and is currently undergoing further testing.

18.1 Review

SUMMARY

- Proteins perform many functional roles within living organisms. The function of every protein is closely linked to its three-dimensional shape.
- The Protein Data Bank (PDB) is a database of three-dimensional structures of large biological molecules such as proteins.

KEY QUESTIONS

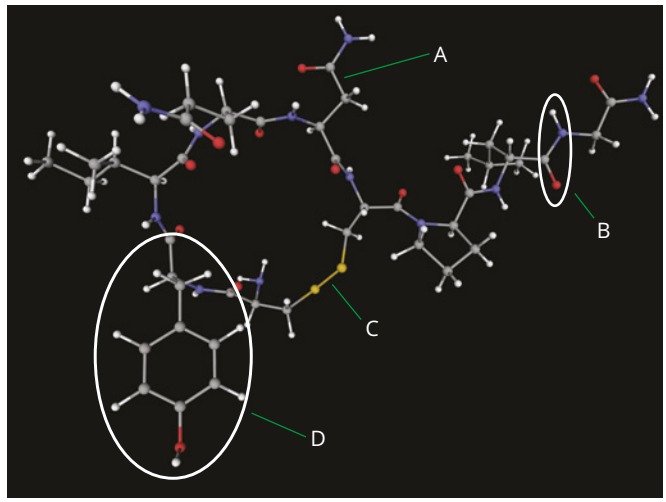
1 When a scientist determines the primary structure of a new protein, the PDB can enable the function of the protein to be predicted. Explain this process.

2 Why is it important that the PDB is freely available?

3 Oxytocin is a hormone that causes contractions during child birth. It is a polypeptide containing nine amino acids in the sequence:

Cys–Tyr–Ile–Gln–Asn–Cys–Pro–Leu–Gly

The image of oxytocin shown here is a 'ball and stick' computer model. The colour code of the atoms is as follows: carbon (grey), oxygen (red), nitrogen (blue), hydrogen (white) and sulfur (yellow). Use this model and the labels to describe the chemical structure of this polypeptide. In your answer, name the type of chemical bond labelled A and explain the significance of the groups labelled B–D.



18.2 Enzymes

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 section, 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 the equivalent of taking 1 second to complete a task that normally takes 300 years.

ROLE OF ENZYMES

As you learnt in Chapter 1, for a reaction to occur, the reactants need to collide with each other with sufficient energy and the correct orientation. Catalysts are able to increase the rate of reaction by providing an alternative reaction pathway with a lower activation energy, thereby increasing the proportion of reactant particles with sufficient energy to react (Figure 18.2.1). Inorganic catalysts and biological catalysts (enzymes) act in a similar way and share the following characteristics. Both inorganic catalysts and 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.

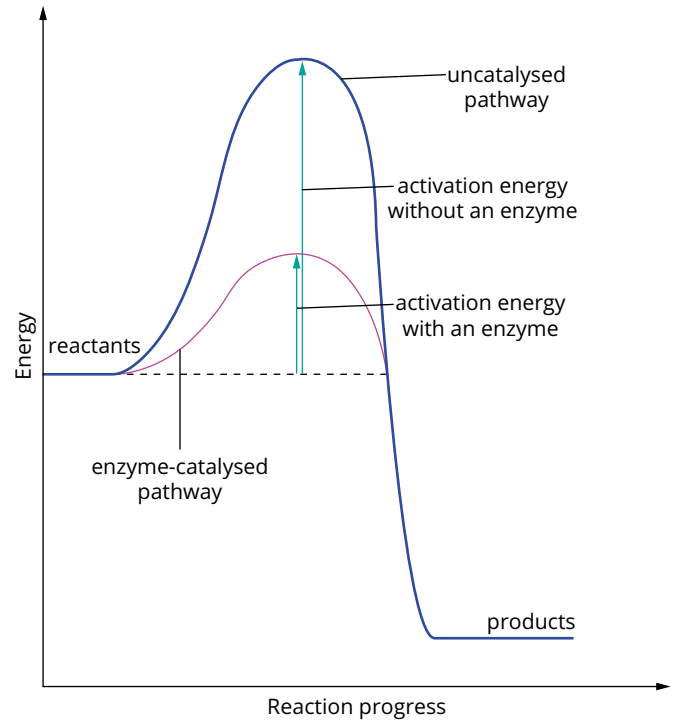


FIGURE 18.2.1 Both inorganic catalysts and enzymes lower the activation energy of a reaction by providing an alternative pathway by which the reaction can occur.

However, there is a significant difference between the behaviour of enzymes and the behaviour of inorganic catalysts. An inorganic catalyst, such as metallic platinum, can catalyse many different reactions, often involving a variety of reactants. Enzymes can 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, despite being very similar, the two sugars lactose and sucrose are broken down by two different enzymes in our bodies. The models of enzyme action developed by scientists must account for this specificity. Enzymes are also more sensitive than inorganic catalysts to changes in reaction conditions.

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.

The catalytic action of enzymes is specific for a single reaction or type of reaction.

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 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**.

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 18.2.2 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.

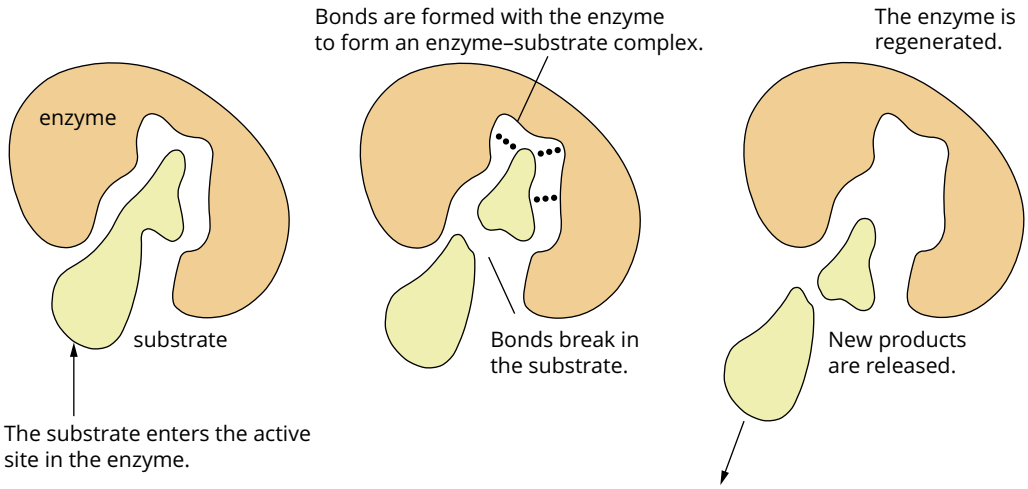


FIGURE 18.2.2 Steps in the action of an enzyme, according to the lock-and-key model

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.

Example—hydrolysis of proteins

The digestion of proteins into smaller polypeptide molecules by enzymes, called proteases, can be understood by using the lock and key model. As you learnt in Chapter 17, amino acids are joined together by peptide bonds to form a protein in a condensation reaction. This reaction can be reversed and the peptide bonds broken by the addition of water in a hydrolysis reaction. However, due to the strength of the peptide bonds, this hydrolysis reaction does not occur very rapidly without the presence of an enzyme.

Trypsin is an enzyme that breaks a protein chain next to a lysine or arginine amino acid (on the C-terminal side). It binds to the protein chain at that point and weakens that particular peptide bond, reducing the amount of energy required for it to react with a water molecule (Figure 18.2.3).

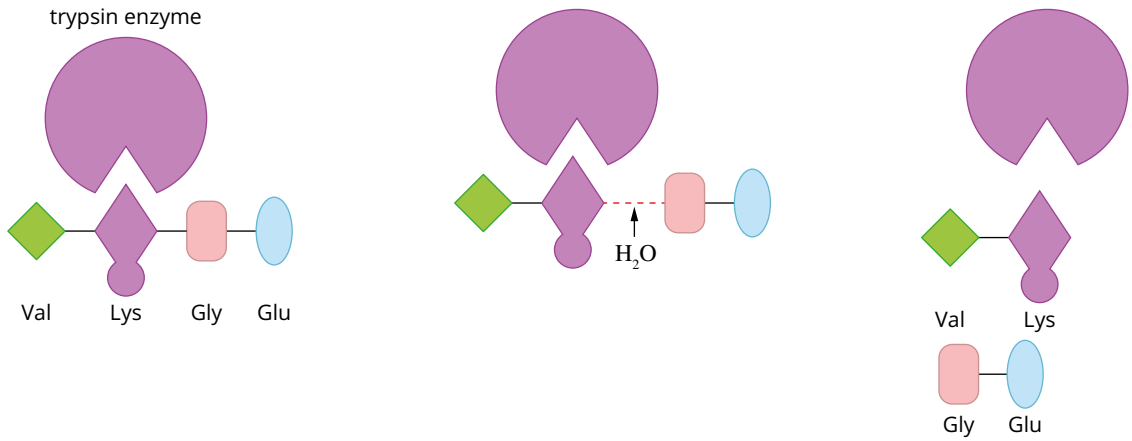


FIGURE 18.2.3 Trypsin is an enzyme that catalyses the hydrolysis of a protein chain next to an arginine or lysine amino acid. Its specific shape enables it to bind to the protein chain at that point and weaken a peptide bond, meaning that less energy is required for it to be broken by reaction with a water molecule.

The types of intermolecular bonds formed between an enzyme and a substrate are the same as those that determine 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. In the example above, both lysine and arginine contain amine groups (NH_2) on their respective side chains. These amine groups form hydrogen bonds with the active site of the trypsin enzyme, forming the enzyme–substrate complex.

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 larger number of chemical reactions.

As Figure 18.2.4 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.

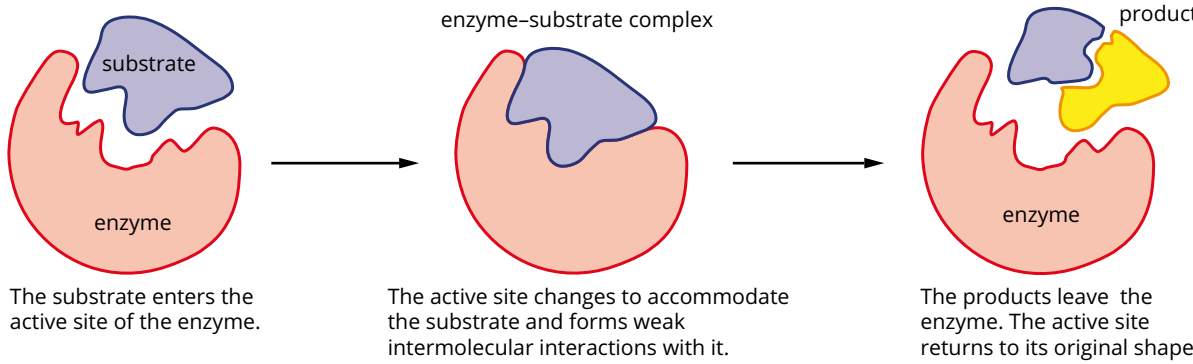


FIGURE 18.2.4 Steps in the action of an enzyme, according to the induced fit model

CHEMISTRY IN ACTION

From lock-and-key to induced fit

The development of the lock-and-key and induced fit models of enzymes is a good example of how scientific ideas change over time as new evidence becomes available.

Emil Herman Fischer (Figure 18.2.5) was a remarkable chemist. He was awarded the Nobel Prize in Chemistry in 1902 for his work on identifying the 16 isomers of the aldo-hexoses, the family of sugars that glucose belongs to. His work on biomolecules and the precise stereochemistry of their different forms led him to propose the lock-and-key model of enzyme–substrate interactions.

This model formed the main explanation for the interactions in enzyme active sites and receptor sites until the American chemist Daniel Koshland (Figure 18.2.6) proposed the induced fit model of enzyme interactions.

Koshland described his model as more like a hand in a glove, where the enzyme is flexible, not rigid, and can change shape slightly on binding of the substrate. Figure 18.2.7 shows a simplified version of Fischer's lock-and-key model and Koshland's induced fit model. Koshland was able to build on the hypothesis put forward by Fischer to develop what is now considered to be a more accurate representation of enzyme interactions.

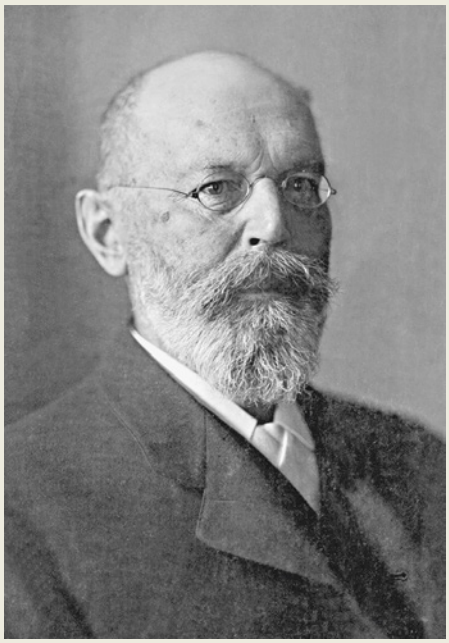


FIGURE 18.2.5 Emil Hermann Fischer (1852–1919) proposed the lock-and-key model of enzyme–substrate interactions.

FIGURE 18.2.6 Daniel Koshland (1920–2007) further developed Fischer's lock-and-key model by proposing the revised induced fit model for enzyme interactions.

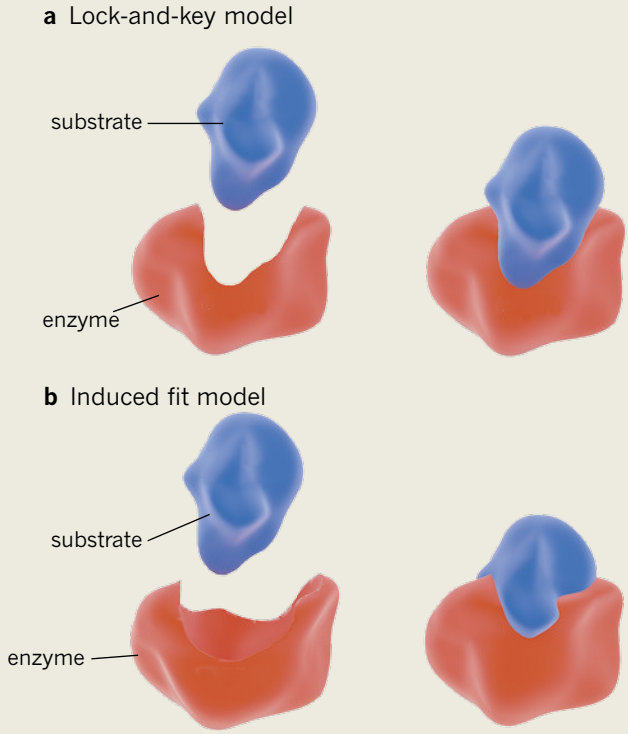


FIGURE 18.2.7 The two models of enzyme interaction proposed by (a) Fischer and (b) Koshland. The development of these models is an example of how scientific ideas change over time, being refined and adapted as new insights and discoveries are made.

EXTENSION

Coenzymes

Many enzymes cannot function without the presence of a coenzyme. A coenzyme is a non-protein organic compound that interacts with an enzyme and changes its functionality. Coenzymes are small compared to protein molecules. Similarly, some enzymes require inorganic atoms or molecules such as metal ions to function correctly. These are called cofactors rather than coenzymes.

Many coenzymes are derived from vitamins. Vitamins are essential micronutrients that are required in small amounts as part of a balanced diet. Figure 18.2.8 shows the coenzyme folic acid bound into dihydrofolate reductase, an enzyme found in *Escherichia coli* bacteria in the human gut.

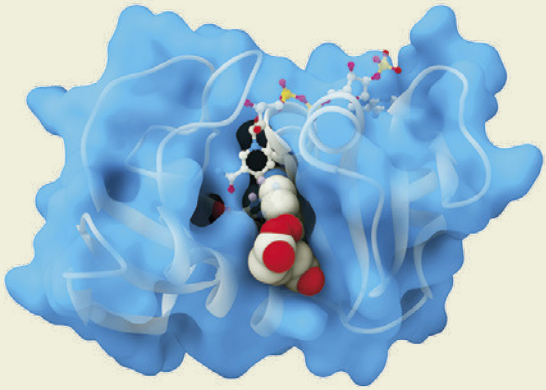


FIGURE 18.2.8 Folic acid acts as a coenzyme, binding to the dihydrofolate reductase enzyme.

Coenzymes interact with the enzyme during catalysis and their role is often to act as carriers of electrons or specific groups of atoms. They change the surface shape of the enzyme and hence the binding properties of the active site, allowing the enzyme to better interact with the substrate.

Before binding to the coenzyme, the enzyme is inactive. You can see this in Figure 18.2.9. Once the coenzyme is bound, the newly formed enzyme–coenzyme complex can interact fully with the substrate and the catalytic process can occur.

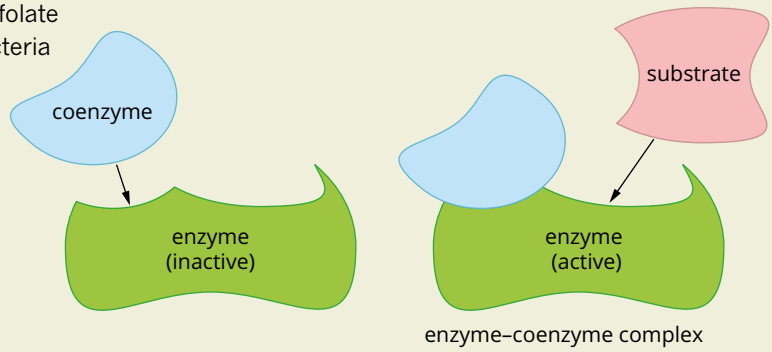


FIGURE 18.2.9 Coenzymes work by binding to particular enzymes. The newly formed complex can bind to the substrate, allowing the reaction to be catalysed.

Unlike an enzyme, a coenzyme may be changed as a result of the reaction as it accepts or donates an electron or group of atoms. If it accepts a particular group of atoms in one biochemical reaction it helps catalyse, there will be other reactions in which it is restored to its original form by the loss of the group.

18.2 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 may only catalyse one specific reaction or a reaction with a particular chemical bond or functional group.
- There are thousands 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.
- The earliest model to account for enzyme action was the lock-and-key model.
- A newer model for enzyme action is the induced fit model. This model accounts for the flexibility of many enzymes' active sites.

KEY QUESTIONS

1 The enzyme glucokinase catalyses the first step in the oxidation of sugar in human liver cells, in a process called glycolysis. Which one of these statements about this process is correct?

A Many other enzymes can also catalyse this reaction.
B Glucokinase increases the activation energy of this reaction.
C Glucokinase is able to catalyse many other reactions.
D Glucokinase is a protein.

2 **a** The steps in the action of an enzyme involve, in particular, an active site and a substrate. Use a diagram to describe in detail 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.

3 Identify whether each of the statements 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.

18.3 Enzymes: dependence on pH and temperature

As you learnt in the previous section, enzymes share many characteristics with inorganic catalysts. By lowering a reaction's activation energy barrier, both enzymes and inorganic catalysts increase reaction rate without altering the equilibrium position or being changed themselves by the process. One significant difference between the two types of catalysts is the sensitivity of enzymes to reaction conditions such as temperature and pH (Figure 18.3.1).

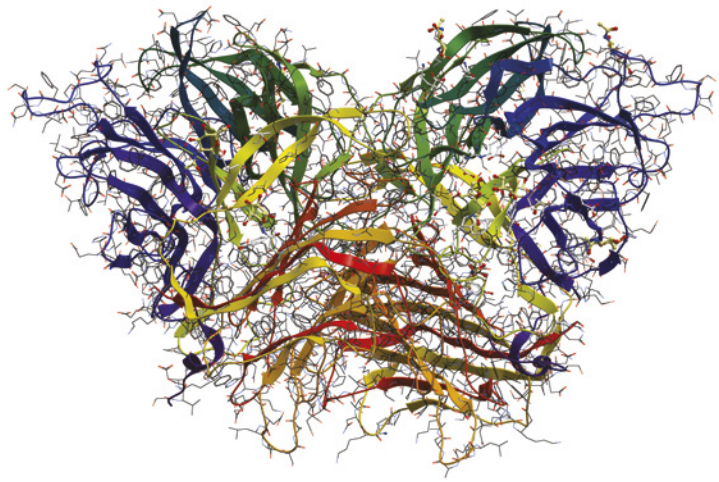


FIGURE 18.3.1 A ribbon model of the enzyme invertase (also called sucrase), which catalyses the hydrolysis of sucrose. It operates under mild conditions, but is very sensitive to changes in temperature and pH.

DEPENDENCE ON pH

Enzymes operate effectively only within a narrow pH range, as the graph in Figure 18.3.2 shows. Salivary amylase catalyses the breakdown of starch to a disaccharide, maltose, in the relatively neutral environment of the mouth. Pepsin catalyses the breakdown of proteins to amino acids in the acidic conditions of the stomach. Activity of these enzymes drops off drastically outside their normal conditions.

Pepsin is active only at pH values below 3 and amylase is active between pH 5 and 9. The pH at which the **enzyme activity** is greatest is known as the enzyme's **optimum pH**. The optimum pH of pepsin is 1.5, while the optimum pH of salivary amylase is 7.2.

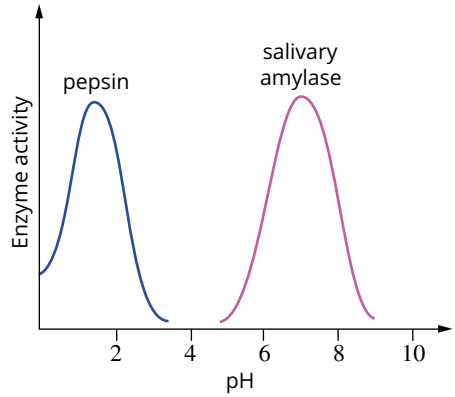


FIGURE 18.3.2 Enzymes are only effective in a narrow pH range. Pepsin is a protein-digesting enzyme secreted into the stomach. Salivary amylase is the enzyme in human saliva. These enzymes are most effective at very different pH values.

Acid–base properties of enzymes

You will recall that α-amino acids (those found in living systems) can form zwitterions, with the general structure shown in Figure 18.3.3. A zwitterion has both a positive and negative charge within the molecule.

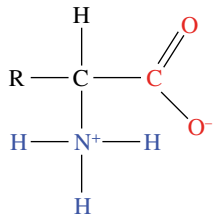


FIGURE 18.3.3 The general structure of a zwitterion of an amino acid. Different amino acids have different side chains, represented by the R group.

Amino acids have different charges depending on the pH of the surrounding environment.

- At high pH, the $-NH_3^+$ group can act as an acid, donating a proton to become an $-NH_2$ group.
- At low pH, the $-COO^-$ group can act as a base, accepting a proton to become a –COOH group.

As the following equation shows, the charge on the predominant form of the amino acid present in a solution depends on the pH of the solution.

$$\underset{\text{cation}}{\overset{\text{Low pH}}{{}^+H_3N\text{–}CH(R)\text{–}COOH}} \rightleftharpoons \underset{\text{uncharged zwitterion}}{\overset{\text{Intermediate pH}}{{}^+H_3N\text{–}CH(R)\text{–}COO^-}} \rightleftharpoons \underset{\text{anion}}{\overset{\text{High pH}}{H_2N\text{–}CH(R)\text{–}COO^-}}$$

Just as the ionisation of the amino and carboxyl groups in amino acids depends on pH, some of the side chains of the amino acids may also be affected by changing the pH.

Intermolecular attractions between the side chains of a polypeptide maintain a protein's overall three-dimensional structure. Some bonds that determine the tertiary structure of an enzyme may be disrupted as changes in pH alter the ionisation of some side chains.

For example, the ionic interactions shown in Figure 18.3.4 might occur at pH 7 between side chains of the amino acid units along the protein chain, but not at pH 3 or 10. The change from neutral pH to an acidic pH of 3 would mean the carboxylic acid on the side chain is not likely to ionise and will therefore not carry the negative charge required for the ionic interaction to occur. The opposite situation would be true with a change from neutral pH to the basic pH 10. At the higher pH, the amino group in the other side chain would not act as a base, remaining uncharged and unable to participate in the ionic interaction.

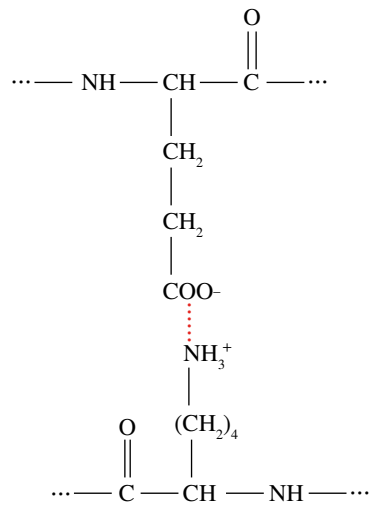


FIGURE 18.3.4 An ionic interaction linking two parts of a polypeptide chain. Ionic interactions between side chains of amino acids in proteins are dependent on pH. One R group contains $-NH_3^+$ and another R group contains $-COO^-$.

In this way, changes in pH can have a large impact on the stability of enzyme structure. As the tertiary structure of the enzyme is disrupted, the enzyme's active site changes shape and enzyme activity decreases. Extremely high or low pH values generally cause complete loss of activity for most enzymes. Drastic changes to pH can result in a permanent change to the shape of an enzyme through a process called **denaturation** (see page 500).

Changes in pH alter the charge of side chains containing amino and carboxyl functional groups.

DEPENDENCE ON TEMPERATURE

Enzyme activity is also affected by temperature. The graph in Figure 18.3.5 shows the effect of temperature on the rate of a reaction involved in carbohydrate metabolism. You can see from the steep sides of the curve that the rate of reaction drops off quickly either side of a narrow temperature range (30–40°C).

The temperature at which the enzyme activity is greatest is known as the enzyme's **optimum temperature**. Enzymes that operate inside human cells have an optimum temperature of about 37°C.

At temperatures above and below the optimum temperature, enzyme function is impaired. This is one of the reasons that conditions such as hypothermia and fever (when you have an abnormally low or high temperature) are life-threatening.

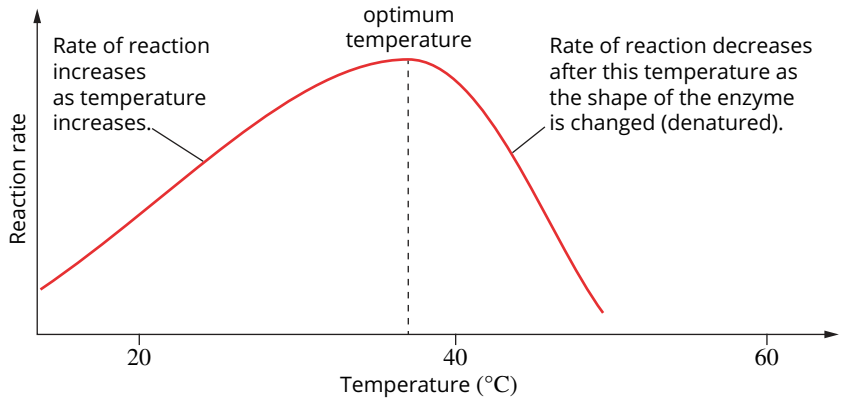


FIGURE 18.3.5 Effect of temperature on rate of reaction for an enzyme-catalysed reaction. Enzymes are only effective in a relatively narrow range of temperatures. Reaction rate is highest at the optimum temperature.

An increase above or decrease below the optimum temperature has a different effect on an enzyme.

- As the temperature increases above the optimum temperature, the increased kinetic energy of the molecules disrupts the structure of the enzyme. The increased movement throughout the enzyme breaks some of the intermolecular forces responsible for the tertiary structure. This change in three-dimensional shape of the enzyme means the active site can no longer effectively catalyse the reaction, so the reaction rate decreases rapidly.
- As the temperature decreases below the optimum temperature, the enzyme and substrate molecules have lower kinetic energies, resulting in less frequent and less energetic collisions between the molecules. Additionally, under the induced fit model discussed in section 18.2, enzymes need a certain amount of flexibility so that the shape of the active site can change upon substrate binding. When the temperature is too low, the enzyme is not flexible enough for this change of shape to take place, and therefore it cannot function properly.

Denaturation

Once the temperature becomes too high, the increased kinetic energy of the polypeptide chains of the enzyme breaks some of the bonds between side chains of the amino acid units, and new bonds are formed. A change in the enzyme's tertiary structure causes a change in the shape of the active site and the enzyme loses its catalytic activity. It is said to be denatured. This change to the protein structure is often irreversible (Figure 18.3.7).

CHEMFILE

Hyperthermophiles

A hyperthermophile is a type of bacterium that thrives in extremely hot environments, at temperatures of 60°C and higher. Many hyperthermophiles can also withstand other environmental extremes, such as high acidity or radiation. Hyperthermophiles were first discovered in 1965, in the hot springs of Yellowstone National Park, USA (Figure 18.3.6). Since then, more than 70 different species of bacteria capable of withstanding these high temperatures have been discovered.

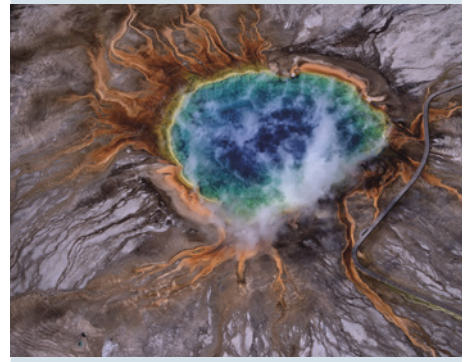


FIGURE 18.3.6 An aerial photograph of the large geothermal spring in Yellowstone National Park, Wyoming, USA. The water's temperature can reach more than 70°C. The bright colours in the pool are due to minerals that are deposited from the evaporation of water. The colour differences within the pool are due to different species of hyperthermophilic bacteria.

In order for hyperthermophiles to survive under these extreme conditions, their proteins must be able to maintain their three-dimensional shape at high temperatures rather than being denatured. Indeed, many of the proteins in these organisms have higher levels of hydrogen bonding and ionic interactions stabilising their three-dimensional shape than similar proteins in normal bacterial cells.

These hyperthermostable proteins are of interest commercially, because they may be able to catalyse industrial processes at higher temperatures, increasing the rate of reaction.

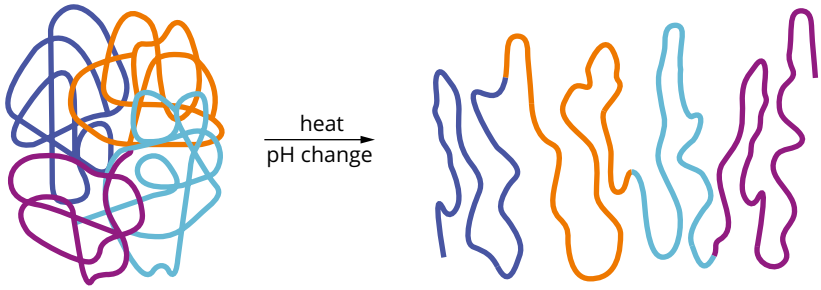


FIGURE 18.3.7 The specific three-dimensional shape of enzymes is lost when denaturation occurs.

Enzymes can also be denatured by a change in pH. As discussed earlier, when the pH is above or below the enzyme's optimum pH, the enzyme's overall three-dimensional shape can also be disrupted. Substantial changes in pH can change an enzyme's structure permanently.

Comparing denaturation with hydrolysis

Even though increased temperature and variations in pH can permanently change the tertiary structure of an enzyme, the primary structure of the protein, the covalently bonded sequence of amino acids, remains intact.

You will recall from Chapter 17 that the breakdown of proteins occurs through a process called hydrolysis. The hydrolysis of a protein molecule involves breaking the covalent peptide bonds. This is shown in Figure 18.3.8.

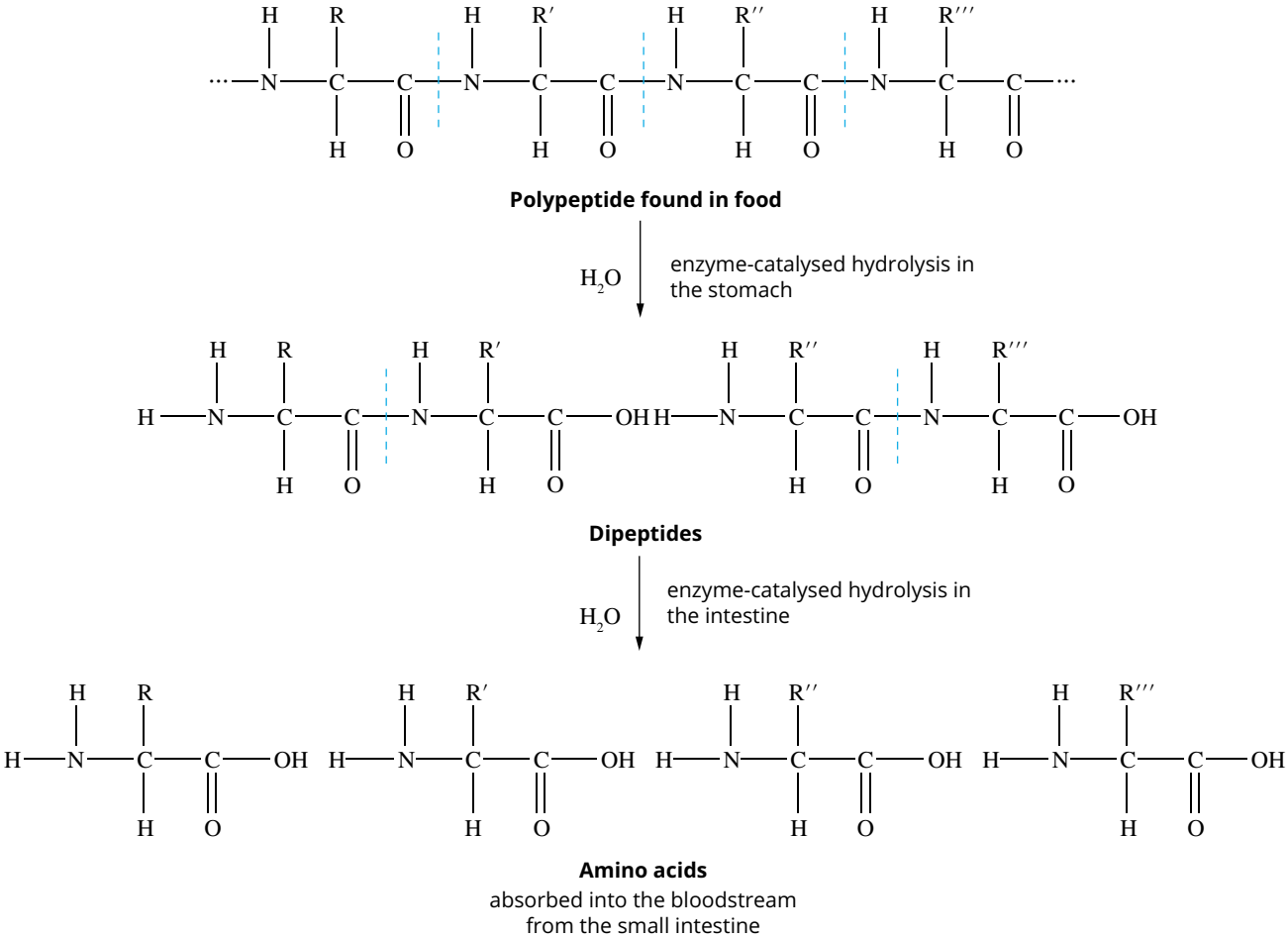


FIGURE 18.3.8 Digestion of protein in food. The blue dashed lines indicate where peptide links are broken during hydrolysis of the polypeptide.

The products of hydrolysis are shorter polypeptide chains or individual amino acids. Note that water is a reactant in this process. One water molecule is consumed for each peptide bond broken.

In the laboratory, extreme conditions are required to hydrolyse a protein. Typically, the protein sample is heated in 6 mol L^{-1} hydrochloric acid for 24–72 hours.

CHEMFILE

Denaturing egg white

When egg white is heated, the clear liquid turns into an opaque solid. This is an everyday example of the denaturing of a protein. Egg white contains a protein called albumin. The denatured protein has very different chemical and physical properties from the original protein.

The protein in egg white can be denatured in a variety of ways. Some are irreversible, such as the cooking of an egg; others are reversible.

If you add salts such as ammonium sulfate to egg white, the water that surrounds the proteins is drawn away and forms ion–dipole bonds with the ions of the salt. Without the protective layer of water stabilising its tertiary structure, the protein denatures and precipitates out of solution. If you add enough water to hydrate the ions and the protein strands, the protein refolds and dissolves back into solution. In this instance, the denaturation of the protein is reversible.

When denaturation occurs because the hydrogen bonds in the protein molecules are disrupted, the process is irreversible. This can happen when the protein is heated, such as when you boil or fry an egg (Figure 18.3.9), or when protein is mixed with strong acids such as nitric acid. When an egg white is heated, the hydrophobic amino acid side chains that were hidden within the folded albumin molecules are exposed and aggregate together by forming dispersion forces, changing the texture and colour of the egg white.

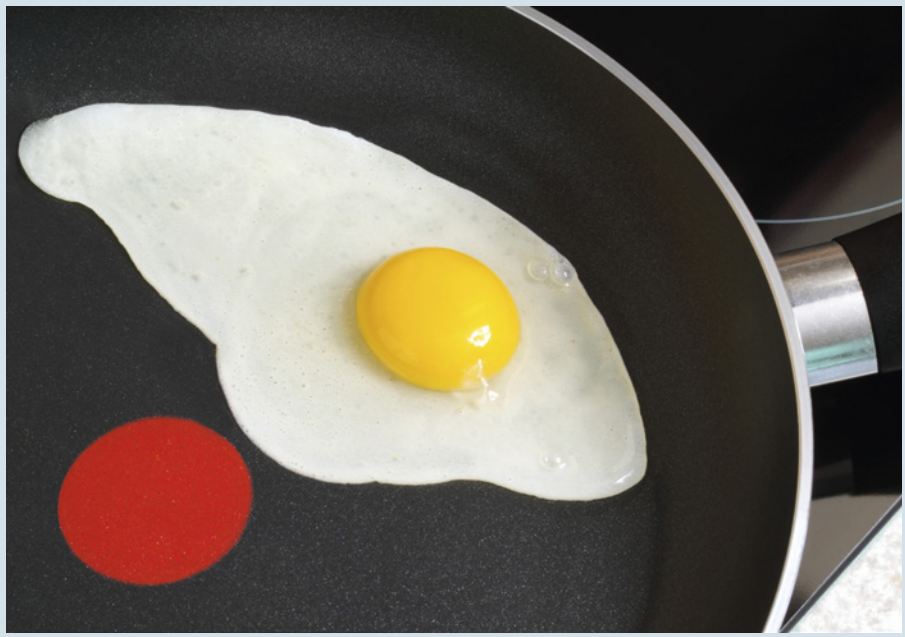


FIGURE 18.3.9 When an egg white is heated, the hydrogen bonds maintaining the tertiary structure are disrupted and the protein albumin irreversibly unfolds (denatures).

18.3 Review

SUMMARY

- Enzymes operate over an extremely mild and narrow set of conditions when compared with inorganic catalysts.
- Enzymes are very sensitive to changes in pH and temperature.
- An enzyme is said to be denatured if its tertiary structure is disrupted; for example, by high temperatures or pH changes.
- When an enzyme is denatured, the shape of its active site is changed and its catalytic activity is lost.
- During the hydrolysis of a protein, the primary structure is broken down as peptide links are broken. This occurs during digestion of food.
- The temperature at which the enzyme activity is greatest is the enzyme's optimum temperature.
- High temperature denatures an enzyme because the increased kinetic energy of the polypeptide chain disrupts the enzyme's tertiary and quaternary structure.
- At lower temperatures, fewer, less energetic collisions occur per unit time between the enzyme and substrate so the rate of reactions is slower.
- The pH at which the enzyme activity is greatest is the enzyme's optimum pH.
- The charges on some side chains in the polypeptide chain of an enzyme depend on the pH of the solution.
- Changes to the charges on the side chains that occur as pH changes can result in a new tertiary structure for an enzyme.
- The optimum pH and temperature of an enzyme usually match the conditions in which the enzyme operates.

KEY QUESTIONS

1 The structure of proteins can be disrupted by denaturation or hydrolysis. Describe each process and the bonds that are disrupted for each.

2 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 side chains of a polypeptide chain are important in maintaining the enzyme's tertiary structure. Complete the following table for each of the side chains listed.

Structure of side chain	Is the side chain acidic or basic or neither?	Is the side chain positively charged, negatively charged or neutral?	
		In a solution of pH 2	In a solution of pH 11
$-CH_2COOH$			
$-CH_2CH(CH_3)_2$			
$-CH_2OH$			
$-(CH_2)_4NH_2$			

3 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 denatured.

a What is meant by 'denatured'?

b Describe what usually occurs to the structure of an enzyme when the enzyme is denatured.

c Does the primary structure of the carbonic anhydrase enzyme change during the process?

d Why is the function of the enzyme closely related to its tertiary structure?

4 One of the key differences between enzymes and inorganic catalysts is how they are affected by their environment.

a How can a change in pH effect enzyme activity?

b What effect does decreasing the temperature have on enzyme activity?

18.4 Enzymes in industry

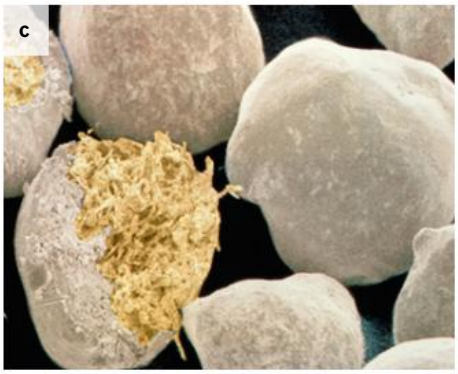


FIGURE 18.4.1 Enzymes are used in a number of different commercial applications. (a) Malted barley is mixed with water and heated during the brewing of beer. Enzymes in the malt break down the starch into simple sugars. (b) The enzymes in yeast consume sugars and produce carbon dioxide, causing bread to rise. (c) A scanning electron micrograph of a biological washing powder. The capsules contain enzymes that break down fats, oils or proteins that may have stained the clothing.

Enzymes have been used for thousands of years to produce food such as cheese, wine and bread. More recently, they have been increasingly used in industrial processes and in a range of commercial applications (Figure 18.4.1). For example, washing powders often contain enzymes such as proteases, lipases and amylases, which break down proteins, fats and starches respectively. These enzymes are able to break down many of the molecules found in common stains and have the advantage of being biodegradable.

Enzymes are also being used increasingly in industrial processes to catalyse reactions. For example, several companies are using the enzyme lipase to catalyse the production of biodiesel as an alternative to the traditional base-catalysed process. This process was discussed in greater detail in Chapter 16.

ADVANTAGES AND DISADVANTAGES

There are advantages and disadvantages to using enzymes as catalysts in industrial processes. These are summarised in Table 18.4.1.

TABLE 18.4.1 Advantages and disadvantages of using enzymes as industrial catalysts

Advantages	Disadvantages
· Enzymes are specific, so that they only catalyse one particular reaction or type of reaction. · In general, enzymes are effective at biological temperatures and pH levels. This saves energy and cost as high temperatures and pressures are not required. · Enzymes are not consumed in the reaction, so they can be used for a long period of time. · Enzymes are biodegradable and therefore cause less environmental pollution.	· Enzymes are very sensitive to changes in temperature and pH. Reaction conditions must therefore be tightly controlled. · Certain chemicals can also change the structure of enzymes and cause them to lose their function. · Enzymes can be expensive to produce. · Enzyme-catalysed reactions generally take place in aqueous solutions. It can be difficult to separate the products from the reaction mixture.

The key advantage of using enzymes as industrial catalysts is that, in general, they function optimally under biological conditions. This removes the need for high pressures and temperatures to be used to maintain a fast rate of reaction, thereby reducing the energy costs and safety considerations involved in the process. This addresses some of the ideas of green chemistry discussed in Chapter 12. Due to their unique shape, enzymes are also extremely specific, catalysing only one particular reaction or type of reaction. This can increase the efficiency of the industrial process in that side-reactions do not take place.

The major disadvantage of using enzymes as industrial catalysts is that they are very sensitive to changes to pH and temperature. As discussed in section 18.3, changes in temperature and pH affect the interactions between amino acids on the surface of the enzyme. This can lead to a change in the enzyme's three-dimensional shape and a loss of enzyme function. The presence of other molecules in the reaction mixture may also adversely affect the shape of the active site and hence the function of the enzyme.

PRODUCTION OF ETHANOL

The production of ethanol is a large global industry. In 2015, over 100 billion litres of ethanol were produced worldwide. Ethanol has many uses, including as industrial solvents, antiseptics, precursors for other chemical reactions, and in alcoholic beverages. However, its major use is as a fuel source, particularly in Brazil and the United States. It can be produced by two different processes: fermentation, which is an enzymatic process using corn, sugar cane or other grains as a starting material; or the hydrolysis of ethene, which uses crude oil as a starting material.

Fermentation

For thousands of years, humans have used enzymes to convert starches from grains and sugars to ethanol in the process known as **fermentation**. In this process, amylase enzymes are used to catalyse the breakdown of the polysaccharide starch to glucose. Then the fermentation process uses other enzymes from yeast organisms to convert small sugar molecules, such as glucose and fructose, into ethanol and carbon dioxide, according to the following equation:

$$C_6H_{12}O_6(aq) \rightarrow 2CH_3CH_2OH(aq) + 2CO_2(g)$$

In wine-making, yeasts are found naturally present on the surface of grapes and in wine cellars and do not need to be added to the fermentation mixture. However, in beer brewing, yeast is added to the barley mixture to catalyse the fermentation process. Margaret River, a region in the south of Western Australia, is known for its winemaking (Figure 18.4.3). Many boutique breweries have also recently opened in the region.

FIGURE 18.4.3 Palmer Wines is in the Margaret River Region, Western Australia.

The fermentation process is also used commercially to produce purified forms of ethanol for other purposes, such as as a fuel. While starches and sugars are often used as the raw materials for fermentation, another polysaccharide called cellulose, which is found in biomass such as woody plants, can also serve as a raw material for fermentation. Aside from producing a valuable chemical, the use of cellulose to produce ethanol reduces the need to dispose of waste materials in landfill or by burning.

The grains and other matter used for industrial fermentation are prepared by grinding and crushing, adding water and then heating to 85–105°C in the presence of cellulase and amylase enzymes. This process breaks down the polysaccharides present in the raw materials into simple sugars called monosaccharides that can undergo fermentation.

After being cooled, the processed raw materials undergo fermentation in fermentation tanks. The process stops when the ethanol content is 15–18%, at which point the yeast cells and their enzymes can no longer function. The fermented mixture then undergoes repeated distillations to purify the ethanol. When cooled, the resulting liquid contains about 96% ethanol and 4% water. This process is depicted in Figure 18.4.4.

CHEMFILE

Producing enzymes for industry

Industrial applications generally require large quantities of enzymes that are only produced naturally in tiny quantities. Scientists use microorganisms, such as yeast and bacterial cells, to produce the quantities of enzymes required (Figure 18.4.2). The microorganisms are genetically modified so that the enzyme of interest is expressed (synthesised) at much higher concentrations than usual. After sufficient enzyme has been produced, the cells are removed from the reaction mixture and the enzyme is purified.

FIGURE 18.4.2 A microbe fermentation unit for the production of drugs, hormones and enzymes for medical and industrial use. It is used to ferment microbes that have been genetically engineered to produce a drug or enzyme.

Enzymes that are to be used for industrial applications require very little processing and purification. However, if they are to be used for medical or therapeutic applications, a far more rigorous purification process is needed. Enzymes such as lipase, used to catalyse the production of biodiesel, is manufactured by industrial means. Similarly, the protein insulin, used to treat diabetes, is also produced for medicinal use by a microbial system.

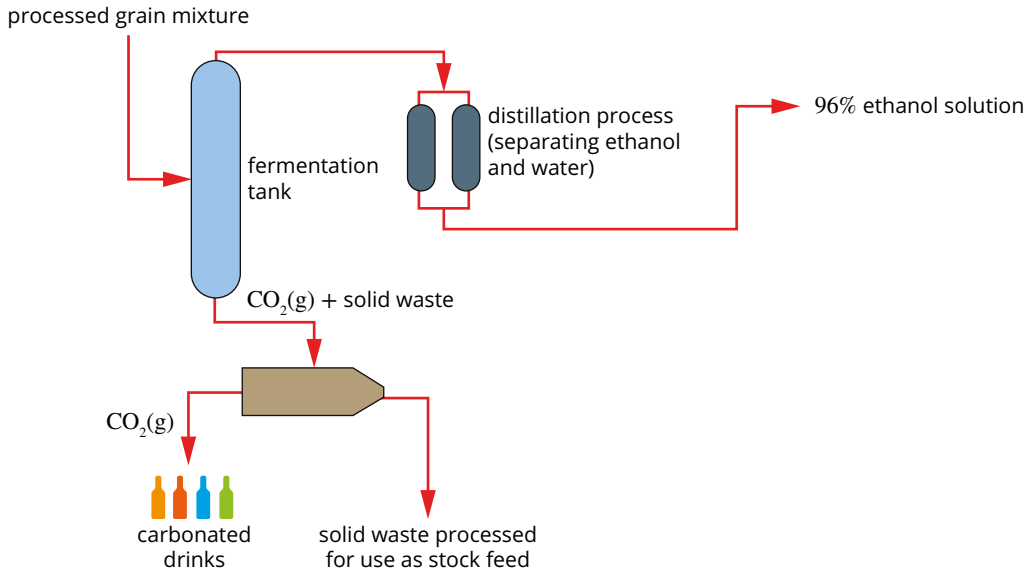


FIGURE 18.4.4 The industrial process for manufacturing ethanol. The products of the fermentation process are separated by distillation.

Once the fermentation and distillation processes are complete, the 96% ethanol mixture is then dehydrated, leaving ethanol that is 99.7% pure. If the ethanol is not being used for alcoholic beverages, the final ethanol is then poisoned by adding up to 5–10% of another chemical such as methanol, to make it unsuitable for consumption as drinking alcohol.

CHEMISTRY IN ACTION

Brewing beer

Beer is one of the world's oldest alcoholic drinks, dating back to over 5000 years ago. Indeed, during the building of the Great Pyramids in Giza, Egypt, there are reports that workers were given a daily ration of 4–5 litres of beer to help them perform their work.

There are four major ingredients in beer: barley, hops, water and yeast, although other additives are often used.

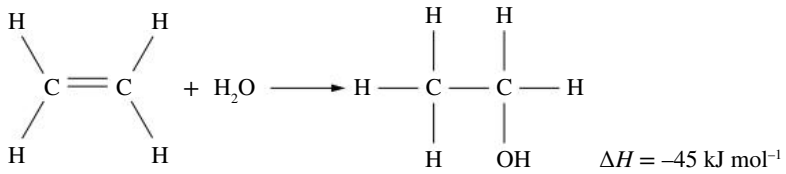
The first step in the process of brewing beer involves extracting the sugars from the barley. To do this, the barley is heated and dried a number of times (a process called malting), before being steeped in hot water for about an hour (a process called mashing). Hops, the small fruit of a vine plant, are then added to provide bitterness to the mixture, balancing the sugar content. Other spices are often added at this stage. After the mixture is filtered, yeast is then added and the fermentation process begins (Figure 18.4.5). Enzymes in the yeast convert the sugar to ethanol and carbon dioxide. This process may take place over a period of up to several weeks, depending on the type of beer being made. Some beer is artificially carbonated to produce its fizz, whereas other beer is left to age for a period of time, allowing the carbon dioxide from the fermentation process to build up.

FIGURE 18.4.5 Copper kettles at Becks Brewery in Bremen, Germany

Industrial production of ethanol by hydration of ethene

While the fermentation process is the most common way of producing ethanol industrially, it is not the only method. Around 7% of total ethanol is produced by the hydration reaction between ethene and water.

Ethene is obtained from the catalytic cracking of larger hydrocarbon molecules in crude oil. The ethene is then reacted with steam to produce ethanol, according to the following addition reaction:



The conditions for this reaction must be carefully selected to ensure that a compromise is reached between the reaction rate and yield. The forward reaction in this process is exothermic and there are more reactant gas particles than product gaseous particles. A moderate temperature of 270–300°C is used, together with a catalyst of phosphoric acid coated on a porous solid.

A relatively high pressure of 6000–7000 kPa is used, as the cost associated with maintaining the reactants at higher pressures is outweighed by the increases to reaction rate and yield.

Each pass of the reaction mixture through the reactor only yields a conversion of about 5% of the ethene to ethanol. The reaction mixture is cooled to liquefy the ethanol, but this also liquefies unreacted water, meaning that a solution of ethanol and water is collected. Unreacted ethene is heated and cycled back into the reactor, as depicted in Figure 18.4.6.

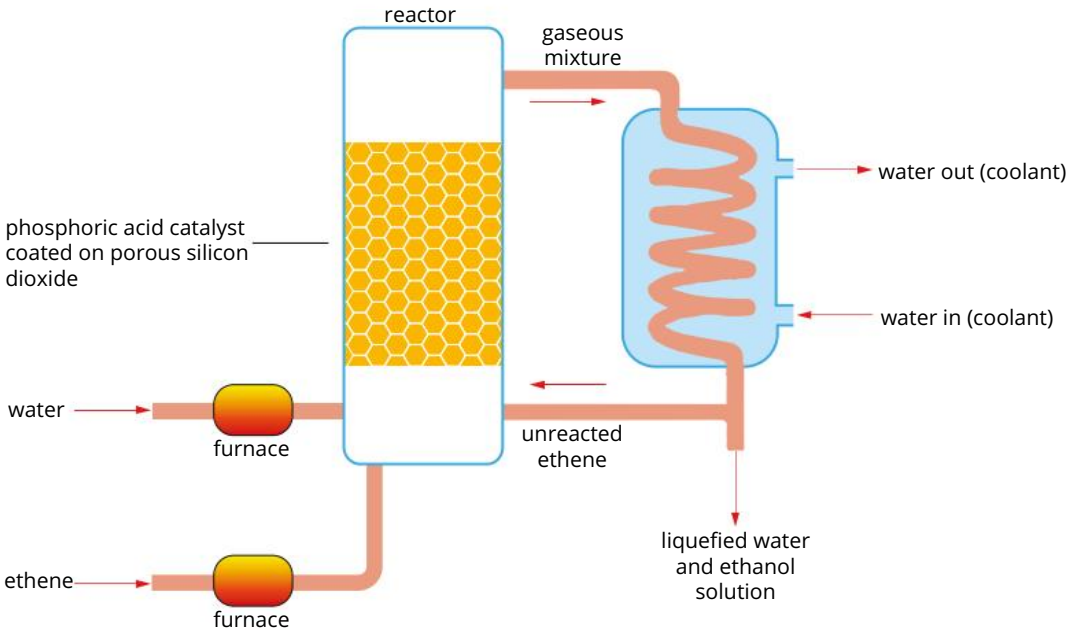


FIGURE 18.4.6 Steps in the industrial process for the hydration of ethene to ethanol

Comparison of industrial methods for ethanol production

The two methods for production of ethanol, by fermentation of glucose and hydration of ethene, have their own advantages and disadvantages. Table 18.4.2 summarises the major differences between the processes.

The use of enzymes as catalysts in fermentation, as opposed to inorganic phosphoric acid, means that fermentation is run at much lower temperatures and pressures. The reduced temperatures and pressures for fermentation result in a significant saving in costs, compared to the hydration of ethene.

TABLE 18.4.2 Comparison of fermentation process and hydrolysis of ethene

Factor	Fermentation process	Hydrolysis of ethene
Temperature	Low temperatures	Moderate temperatures
Pressure	Normal pressures	High pressures
Catalysts	Amylase and cellulase to produce simple sugars and yeast enzymes for fermentation	Phosphoric acid
Purification required	Many distillations required	Limited distillations required
Raw materials used	Monosaccharides from grains and other plant material	Ethene from crude oil
Renewable	Yes—plant matter is renewable	No—crude oil is not renewable
Cost	Low	High

The advantage of producing ethanol from the hydration of ethene is that the reaction has no by-products, so the products are only ethanol and water. In the fermentation process, many different organic molecules are produced or present in small quantities due to the many different enzymes in yeast and the different compounds present in the starting mixture. Also, in some locations there are limited crops to source raw materials for fermentation, whereas crude oil may be readily available.

Fermentation is usually the preferred method for production due to the renewable nature of the process and lower cost of the ethanol produced.

18.4 Review

SUMMARY

- The general advantages and disadvantages of using enzymes versus inorganic catalysts in the chemical industry are:
  - enzymes are effective at low temperatures, whereas inorganic catalysts usually do not function well at low temperatures. This reduces the cost of maintaining high temperatures
  - enzymes catalyse specific reactions, whereas inorganic catalysts often catalyse multiple reactions, generating unwanted by-products and reducing yields
  - enzymes have to be cultivated and collected, which can be a lengthy and expensive process.
- The main differences between the fermentation process and the hydration of ethene for producing ethanol are:
  - fermentation uses enzymes as the catalyst, whereas hydration of ethene uses phosphoric acid
  - fermentation uses lower temperatures and pressures, but requires more distillation cycles
  - the raw materials used for fermentation are renewable, usually a local grain, whereas the hydration of ethene uses crude oil, which is a non-renewable source of chemicals.

KEY QUESTIONS

1 What is the percentage yield if 100 g of ethene is converted into 150 g of ethanol using the hydrolysis of ethene reaction?

2 A moderate temperature of around 300°C is used in a reactor when producing ethanol using the hydration process. What is the reason for using a moderate temperature?

3 There is a significant cost involved in maintaining the high pressures used in the hydration process. Use your knowledge of chemical equilibrium to explain why high pressures are employed.

Chapter review

18

KEY TERMS

active site
denaturation
enzyme
enzyme activity
enzyme–substrate complex
fermentation
induced fit model
lock-and-key model
optimum pH
optimum temperature
Protein Data Bank
substrate

Investigating proteins

1 Indicate whether the following statements are true or false. If false, explain why.
- **a** Proteins with similar tertiary structures are likely to have a similar function.
- **b** The PDB enables protein structures to be visualised in different ways.
- **c** A mutation that causes one amino acid in a protein to be exchanged will always result in a loss of protein function.

2 Protein structures need to be determined experimentally. They cannot be predicted from the primary structure. X-ray crystallography analyses often reveal that amino acids that are far apart in the primary structure of a protein are very close to each other in the protein's three-dimensional shape. Explain the process by which this occurs.

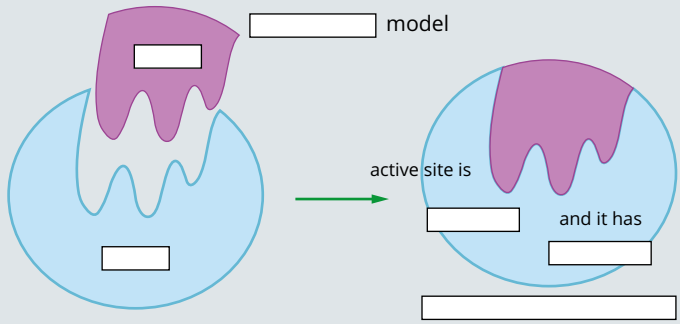
Enzymes

3
- **a** Explain why the action of enzymes justifies the statement 'Enzymes make life possible'.
- **b** Why is the action of an enzyme often described as operating like a lock and key?

4 Indicate whether the following statements summarising the properties of enzymes are true or false.
- **a** Enzymes are made of proteins.
- **b** Enzymes do not change the position of equilibrium.
- **c** Enzymes are consumed by the reaction.
- **d** Enzymes increase the activation energy of a reaction.
- **e** Enzymes increase the rate of reaction.
- **f** Enzymes are sensitive to conditions such as pH changes or temperature increase which denatures the enzyme.
- **g** Enzymes are highly specific for the biochemical reactions they catalyse because of the shapes of their active site.

5 There is a mutation that causes one of the amino acids in the active site of an enzyme to be substituted for another. Although the mutation does not dramatically alter the three-dimensional shape of the protein, it causes a reduction in enzyme activity. Account for this observation.

6 On the following diagram:
- **a** identify the model of enzyme action shown
- **b** use the following words to label the parts of the diagram as indicated to show the first two steps of enzyme action: flexible, changed shape, enzyme, enzyme–substrate complex, substrate, induced fit.
- **c** draw and label a diagram to show the next step in this process.



Enzymes—dependence on pH and temperature

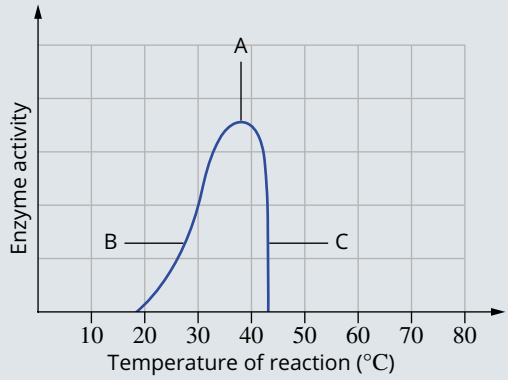
7 Medicinal proteins such as insulin are administered by injection, rather than being ingested. Suggest why insulin cannot be given orally as tablets or capsules.

8 Jellied pineapple dessert 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. Suggest how jellied pineapple might be prepared.

9 Which one of these formulas gives the correct structure of tyrosine ($NH_2CH(C_6H_4OH)COOH$) in the highly acidic conditions present in the human stomach?
- **A** $^+NH_3CH(C_6H_4OH)COOH$
- **B** $NH_2CH(C_6H_4OH)COO^-$
- **C** $^+NH_3CH(C_6H_4OH)COO^-$
- **D** $NH_2CH(C_6H_4OH)COOH$

10 Draw the structure of the zwitterion form of the amino acid valine. You should refer to the table of amino acids (Table 17.1.1, page 460).

11 The graph shows the effect of temperature on the enzyme activity for a metabolic reaction. For each of the parts of the graph labelled A, B and C, explain the variation in enzyme activity with temperature.



Enzymes in industry

12 Give the chemical equation that describes the fermentation of glucose.

13 Describe three differences between the two processes for the formation of ethanol, the fermentation of glucose and the hydration of ethene.

14 The equation for the reaction for the hydration of ethene is:

$CH_2=CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)\ \Delta H = -45\,kJ\,mol^{-1}$

Use your knowledge of Le Châtelier's principle, equilibrium and collision theory to predict how the listed changes will affect both the equilibrium yield and reaction rate.

a Increasing pressure

b Decreasing temperature

15 Give two disadvantages and two advantage of using enzymes as catalysts for industrial processes, rather than inorganic catalysts.

16 In order to purify the ethanol produced by either fermentation of glucose or the hydration of ethene, the process of distillation is used. Explain how distillation can be used to purify ethanol from a mixture of ethanol and water.

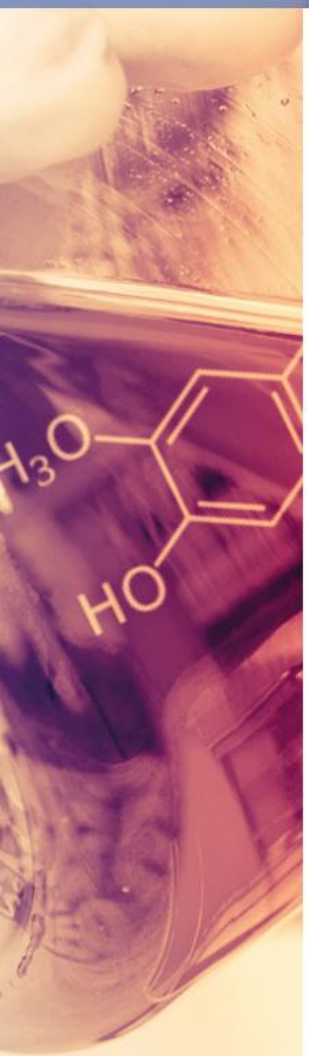
Connecting the main ideas

17 Biological washing powders contain enzymes such as lipases (to break down oil) and proteases (to break down proteins). Evaluate the advantages and disadvantages of using a biological washing powder over a traditional washing powder.

18 Unless distillation is used, beer and wine both have a maximum ethanol content of roughly ~15%. This is because high concentrations of ethanol can cause the enzymes in yeast to denature. Explain this process of denaturation and describe the types of interactions that ethanol is likely to form with the protein.

CHAPTER

19 Science inquiry skills in chemistry



This chapter covers the skills needed to successfully plan, conduct and evaluate results from experiments and investigations in chemistry.

For investigations, you will sometimes need to develop inquiry questions and hypotheses. When conducting experiments and investigations, you will consider risk assessments, ethical concerns and the identification, measurement and control of variables. Uncertainty and error are common to all experimental work, and you will identify causes of random and systematic error, and describe how the effects of these errors can be reduced.

The chapter also describes how best to represent your data, and explains how to analyse your results, including using mathematical models. You will also be shown ways to effectively communicate conclusions using appropriate scientific language, nomenclature and scientific notation.

Science inquiry skills

- identify, research and refine questions for investigation; propose hypotheses; and predict possible outcomes
- design investigations, including the procedure(s) to be followed, the materials required, and the type and amount of primary and/or secondary data to be collected; conduct risk assessments; and consider research ethics
- conduct investigations safely, competently and methodically for the collection of valid and reliable data, including: acid–base properties, using acid–base volumetric analysis techniques, effects of changes to equilibrium systems, and constructing electrochemical cells
- conduct investigations safely, competently and methodically for the collection of valid and reliable data, including properties of organic compounds containing different functional groups and using chemical synthesis processes
- represent data in meaningful and useful ways, including using appropriate graphic representations and correct units and symbols; organise and process data to identify trends, patterns and relationships; identify sources of random and systematic error and estimate their effect on measurement results; and select, synthesise and use evidence to make and justify conclusions
- interpret a range of scientific texts, and evaluate processes, claims and conclusions by considering the quality of available evidence, including confidence intervals in secondary data; and use reasoning to construct scientific arguments
- communicate to specific audiences and for specific purposes using appropriate language, nomenclature and formats, including scientific reports

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19.1 Questioning

DEVELOPING AIMS AND QUESTIONS, FORMULATING HYPOTHESES AND MAKING PREDICTIONS

The inquiry question, aim and hypothesis for an investigation are interlinked (Figure 19.1.1). It is important to note that each of these can be refined as the planning of the investigation continues.

FIGURE 19.1.1 There may be many elements to an investigation. Taking a step-by-step approach will help the process and assist in completing a solid and worthwhile investigation.

Inquiry questions and hypotheses

An inquiry question defines what is being investigated. For example, What is the relationship between the pH of an acidic solution and the rate of reaction with a metal?

A **hypothesis** is a prediction based on previous knowledge and evidence or observations that attempts to answer the inquiry question. For example: Decreasing the pH of the solution will increase the rate of the reaction of hydrochloric acid solution with marble chips.

It is important that you can interpret what an inquiry question is asking you to do. To do this:

- identify a 'guiding' word, such as *who*, *what*, *where*, *why*
- link the guiding word to command verbs that are often used in senior high school such as *identify*, *describe*, *compare*, *contrast*, *distinguish*, *analyse*, *evaluate* and *create*.

Table 19.1.1 gives examples of inquiry questions that could be investigated.

TABLE 19.1.1 How to interpret an inquiry question

Guiding word	Example inquiry questions	What are you being asked to do? What are the command verbs?
What	**What** difference can replacing standard galvanic cells with hydrogen fuel cells make to society and the environment?	Identify and describe specific examples, evidence, reasons and analogies from a variety of possibilities. *Identify* and *describe*.
Where	**Where** would you use redox reactions to treat water supplies?	Identify and describe, giving reasons for a place or location. *Identify* and *describe*.
How	**How** are metals extracted from their ores using redox reactions? **How** do buffer solutions maintain the pH of blood in our bodies? **How** do different types of bonding within proteins respond to changes in the pH of the environment?	Identify and describe in detail a process or mechanism. Give examples using evidence and reasons. *Identify* and *describe*.
Why	**Why** are some acids weak and some strong? **Why** are some industrial processes carried out in conditions that do not produce the fastest possible reaction?	Explain in detail the causes, reasons, mechanisms and evidence. *Identify* and *describe*.
Would	**Would** a weak base react as an acid when mixed with a solution of a strong base?	Evaluate. Justify, giving reasons for and against (using evidence, analogies, comparisons). *Evaluate*, *assess*, *justify*.
Is/are	**Are** all carboxylic acids weak? **Is** potassium metal the strongest reducing agent known?	Evaluate. Justify, giving reasons and evidence. *Evaluate*, *assess*, *justify*.
On what basis	**On what basis** are the strength of acids compared?	Evaluate. Justify using reasons and evidence. Evaluate, assess, justify.
Can	**Can** we use physical methods to protect reactive metals from corrosion?	Evaluate and assess. Is it possible? Give reasons, suggest possible alternatives. *Evaluate*, *assess*, *justify*, *create*.
Do/does	**Does** the rate of corrosion of a metal depend on its group on the periodic table?	Evaluate. Justify using reasons and evidence for and against. *Evaluate*, *assess*, *justify*.
Should	**Should** cars be made from polymers instead of metals?	Evaluate advantages and disadvantages, implications and limitations. Make a judgement. *Evaluate*, *assess*, *justify*, *create*.
Might	What type of power source **might** we use for vehicles in the future?	Evaluate. Justify, giving reasons for and against (using evidence, analogies, comparisons). *Evaluate*, *assess*, *justify*, *compare*, *contrast*, *create*.

Formulating a question

If you are required to formulate a question, it is good practice to research the topic to be investigated. You should become familiar with the relevant scientific concepts and key terms.

During this research, write down questions or correlations as they arise.

Compile a list of possible ideas. Do not reject ideas that initially might seem improbable. Use these ideas to generate questions that are answerable.

Before constructing a hypothesis, formulate a question that needs an answer. This question will lead to a hypothesis when:

- the question is confined to measurable variables
- a prediction is made based on knowledge and experience.

Evaluating your question

Once a question has been chosen, stop to evaluate it before progressing. The question may need further refinement or even further investigation before it is suitable as a basis for investigation. A major planning point is do not attempt something that cannot be completed in the time available or with the resources on hand. For example, it might be difficult to create a specific piece of specialist equipment in the school laboratory, or if experiments take too long it may be impossible to conduct sufficient trials in the time allocated.

To evaluate the question, consider the following:

- Relevance: Is the question related to the appropriate course content?
- Clarity and measurability: Can the question be framed as a clear hypothesis?

If the question cannot be stated as a specific hypothesis, then it is going to be very difficult to complete the investigation.

- Time frame: Can the question be answered within a reasonable period of time? Is the question too broad?
- Knowledge and skills: Do you have a level of knowledge and the laboratory skills needed to allow the question to be explored?
- Practicality: Are resources, such as laboratory equipment and materials, likely to be readily available?
- Safety and ethics: Consider the safety and ethical issues associated with the question you will be investigating. If there are issues, can they be addressed?

Sourcing information

Once you have selected a topic, the next step is to source reliable information. Some of the steps involved in sourcing information are:

- identifying key terms
- sourcing information
- evaluating the credibility of sources
- evaluating experimental data/evidence.

Sources can be:

- **primary sources**—original sources of data and evidence; for example, articles containing research findings that have been published in peer-reviewed scientific journals or research presented at a scientific conference.
- **secondary sources**—analyses and interpretations of primary sources; for example, textbooks, magazine articles and newspaper articles.

Some of the sources that may contain useful information are listed in Table 19.1.2.

TABLE 19.1.2 Useful sources of primary and secondary information

Primary sources of information	Secondary sources of information
Journal articles from peer-reviewed journals, such as *Nature*	Newspaper articles and opinion pieces
Global databases, statistics and surveys	Magazine articles; examples of reputable science magazines include: • *Cosmos* • *Double Helix* (CSIRO) • *New Scientist* • *Popular Science* • *Scientific American*
Laboratory work	Government reports
Computer simulations and modelling	

Hypothesis

A hypothesis is a prediction that is based on evidence and prior knowledge. A hypothesis often takes the form of a proposed relationship between two or more variables in a cause and effect relationship; or in other words, 'If X is done, then Y will occur.'

Here are some examples of hypotheses:

- The buffering capacity of a buffer solution will depend on the relative amounts of the acid and its salt added to make the buffer.
- The pH of a sample of wine is directly related to the concentration of tartaric acid ion the wine.
- The cell potential of a galvanic cell will double if the concentrations of the electrolytes in the half-cells are doubled.

Variables

An investigation can test a good scientific hypothesis and the hypothesis will be supported or refuted. To be a testable hypothesis, it should be possible to measure both what is changed or carried out and what will happen. The factors that are monitored during an experiment or investigation are called the **variables**. An experiment or investigation determines the relationship between variables by measuring the results.

There are three categories of variables:

- The **independent variable** is the variable that is determined by the researcher (the one that is selected and changed).
- The **dependent variable** is the variable that may change in response to a change in the independent variable. This is the variable that will be measured or observed.
- **Controlled variables** are all the variables that must be kept constant during the investigation.

Note that you should only test one variable at a time, otherwise it cannot be stated that the changes in the dependent variable are as a result of changes in the independent variable.

Qualitative and quantitative variables

Variables are either qualitative or quantitative, with further subsets in each category.

- **Qualitative** variables can be observed but not measured. They can only be sorted into groups or categories, such as brightness, type of material, colour of flame.
- **Quantitative** variables can be measured. Mass, volume, temperature, pH and time are all examples of quantitative data.
  - Discrete variables consist of only integer numerical values, not fractions; for example, the number of protons in an atom, the number of atoms of each element in a compound and the number of cells in a battery.
  - Continuous variables allow for any numerical value within a given range; for example, the measurement of temperature, volume, mass, pH and conductivity.

Formulating a hypothesis

Once the inquiry question is confirmed, formulating a hypothesis comes next. A hypothesis requires a proposed relationship between two variables. It should predict that a relationship exists or does not exist.

Identify the two variables in your question. State the independent and dependent variables.

For example: If I do/change this (independent variable), then this (dependent variable) will happen.

A good hypothesis should:

- be a statement
- be based on information contained in the research question (purpose)
- be worded so that it can be tested in the experiment
- include an independent and a dependent variable
- include variables that are measurable.

The hypothesis should also be falsifiable. This means that a negative outcome would disprove it. For example, the hypothesis that all apples are round cannot be proved beyond doubt, but it can be disproved—in other words, it is falsifiable. In fact, only one square apple is needed to disprove this hypothesis. Unfalsifiable hypotheses cannot be proved by science. These include hypotheses on ethical, moral and other subjective judgements.

Worked example 19.1.1

DEVELOPING A HYPOTHESIS

Develop a hypothesis and identify variables for investigating the rate of the reaction between marble chips and hydrochloric acid.	
Thinking	**Working**
Write an inquiry question.	What is the relationship between the concentration of the acid and reaction rate?
Identify the independent variable.	Concentration of hydrochloric acid solution
Identify the dependent variable.	The mass lost during the first 30 seconds of the reaction
Identify the controlled variables.	Starting temperature of hydrochloric acid Volume of hydrochloric acid Mass of the marble chips Surface area of the marble chips
Write a potential hypothesis.	For a constant particle size of marble chips and volume of hydrochloric acid, if the concentration of the hydrochloric acid solution is halved, the rate of reaction will halve.

Worked example: Try yourself 19.1.1

DEVELOPING A HYPOTHESIS

In this example, a student decided to investigate how the cell voltage was related to the concentration of the silver ions in the following galvanic cell. The set-up for the experiment is shown in Figure 19.1.2.

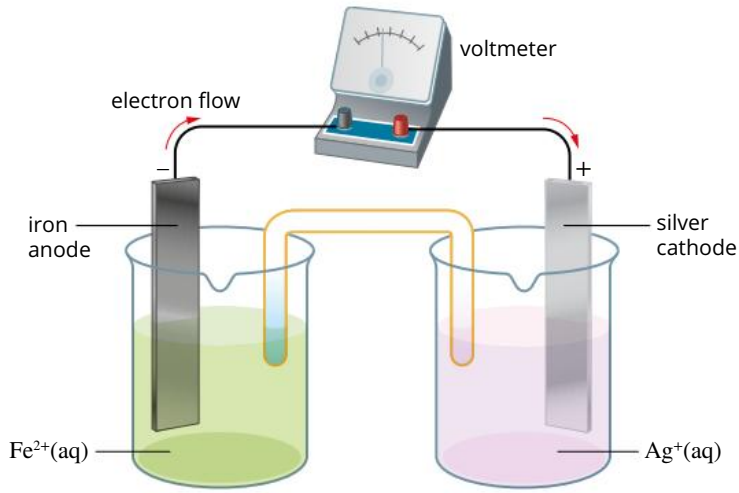


FIGURE 19.1.2 The cell containing Fe/Fe^{2+} and Ag/Ag^{+} half-cells

Develop a hypothesis and identify variables for investigating how the voltage of the galvanic cell is affected by the concentration of the silver ions in the silver nitrate solution.

19.1 Review

SUMMARY

- By utilising data from primary and/or secondary sources, you will better understand the context of your investigation to create an informed inquiry question.
- A hypothesis is a prediction based on previous knowledge and evidence or observations that attempts to answer the research question. For example: If the surface area of magnesium is increased, the rate of reaction of that magnesium and dilute hydrochloric acid will increase.
- Once a question has been chosen, evaluate the question before progressing. The question may need further refinement or even further investigation before it is suitable as a basis for an achievable and worthwhile investigation.
- There are three categories of variables. They are the:
  - independent variable, which is controlled by the researcher
  - dependent variable, which may change in response to a change in the independent variable. This is the variable that will be measured or observed
  - controlled variables, which must be kept constant during the investigation.

KEY QUESTIONS

1 Scientists make observations from which a hypothesis is stated and is then experimentally tested.
- **a** Define 'hypothesis'.
- **b** How are theories and principles different from a hypothesis?

2 For each of the following hypotheses, select the independent variable.
- **a** If more sodium hypochlorite is added to a swimming pool, the pH of the pool water will increase.
- **b** The voltage produced by a commercial cell will decrease over time.
- **c** The amount of dissolved carbon dioxide in the ocean will vary dependent on temperature.
- **d** Hydrogen peroxide solution will decompose more quickly if acid is added.

3 In an experiment a student uses the following range of values to describe colours of indicators: yellow, blue, red and green.
What type of measurement is the variable 'colour'?

4 Which of the following methods is likely to be the most accurate, quantitative method for measuring the pH of water?
- **A** using pH paper (e.g. litmus paper)
- **B** using universal indicator and a colour chart
- **C** using a calibrated pH meter at a particular temperature
- **D** using a conductivity meter

5 Give the correct term that describes an experiment with each of the following conditions.
- **a** The experiment addresses the hypothesis and aims.
- **b** The experiment is repeated and consistent results are obtained.
- **c** Appropriate equipment is chosen for the desired measurements.

19.2 Planning investigations

Once you have formulated your hypothesis, you will need to plan and design your investigation. Taking the time to carefully plan and design a practical investigation before commencing will help you to maintain a clear and concise focus throughout. Preparation is essential. This section is a guide to some of the key steps that should be taken when planning and designing an investigation.

DEVELOPING THE METHOD

The method of your investigation is a step-by-step procedure.

Ensuring accuracy

When designing the method, you must ensure that it ensures a valid, reliable and accurate investigation.

Validity

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

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 effect of each variable in turn.

To ensure validity, carefully determine:

- the independent variable: the variable that will be changed, and how it will change
- the dependent variable: the variable that will be measured
- the controlled variables: the variables that must remain constant, and how they will be maintained.

Reliability

Reliability refers to the notion that if the experiment is repeated many times, the results obtained should be consistent.

It is important to determine how many times the experiment needs to be replicated (Figure 19.2.1). Many scientific investigations lack sufficient repetition to ensure that the results can be considered reliable and repeatable.

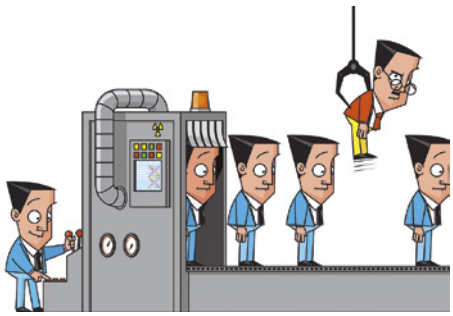


FIGURE 19.2.1 Replication increases the reliability of your investigation. It ensures that if anyone repeats the investigation they will obtain similar data.

- Repeat readings: repeat each reading (at least three times if possible), record each measurement and then average the measurements. This reduces systematic errors and allows random errors to be identified. If a reading differs too much from the rest (known as an outlier), discard it before averaging.
- Sample size: where there might be differences in construction or manufacture of a sample, there should be various samples with the same conditions in the same experiment. The greater the sample size, the more reliable the data.
- Repeats: if possible, repeat the experiment on a different day. Don't change anything. If the results are not the same, think about what could have happened. For example, was the equipment faulty, or were all the controlled variables correctly identified? Repeat the experiment a third time to confirm which run was correct. Repeat an experiment as many times as possible; three is a good number but, if time and resources allow, aim for five.

In some situations, it may be appropriate to conduct a **control experiment**. The control is an identical experiment carried out at the same time, except that in the control experiment the independent variable is not changed.

When the controls do not behave as expected, the data obtained from an experiment or observation is not reliable.

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 firing arrows at an archery target (Figure 19.2.2). Accuracy is being able to hit the bullseye, whereas precision is being able to hit the same spot every time you shoot. If you hit the bullseye every time you shoot, you are both accurate and precise (Figure 19.2.2a). If you hit the same area of the target every time but not the bullseye, you are precise but not accurate (Figure 19.2.2b). If you hit the area around the bullseye each time but don't always hit the bullseye, you are accurate but not precise (Figure 19.2.2c). If you hit a different part of the target every time you shoot, you are neither accurate nor precise (Figure 19.2.2d).

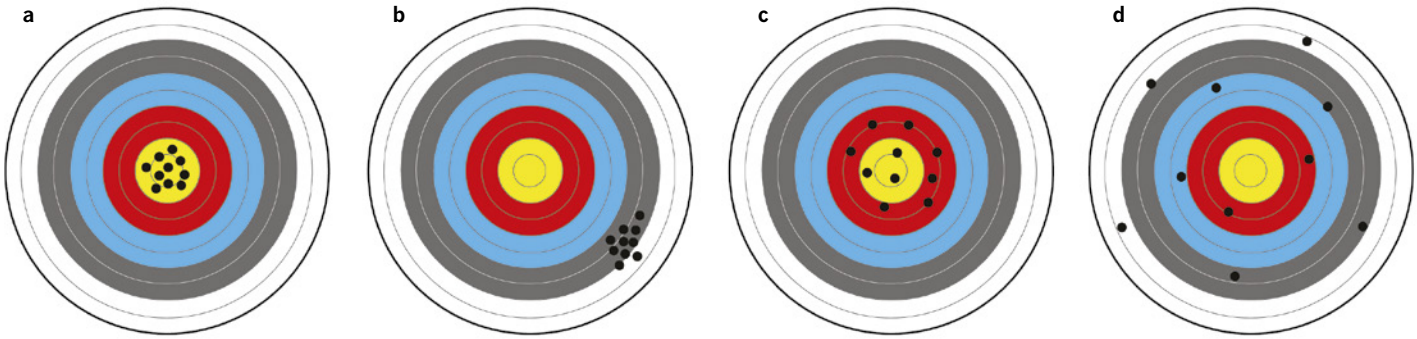


FIGURE 19.2.2 Examples of accuracy and precision: (a) both accurate and precise, (b) precise but not accurate, (c) accurate but not precise, and (d) neither accurate nor precise.

Applying this idea to a chemistry situation, if you are timing the rate of reaction by stopping a stopwatch when 100 mL of gas has been released, and you get consistent results but you are always stopping the stopwatch too early, your results are precise but not accurate.

Uncertainty

When scientists take a measurement, the measurement is always subject to variations in accuracy and precision. The goal when taking measurements is to get as close as possible to 'true' or 'correct value'. The **uncertainty** is how far an experimental quantity might be from the true value. It can be calculated or estimated and is often represented as a percentage. For example, if the uncertainty was described as ±1%, it means that measurement is likely to be no more than 1% above or below the 'true' value of the quantity that is being measured.

In this course you are not required to calculate uncertainties, but it is a good idea to consider uncertainty when planning experiments and later, when you come to evaluate your results.

Confidence intervals

A **confidence interval** is a range of values that are likely to include the 'true' value. This is similar to the uncertainty, which is usually written as a ± number, as shown above. However, the confidence interval is written as a range, such as pH 12.1–12.5. These numbers are called the (upper and lower) confidence limits. Confidence intervals are normally accompanied by a confidence level, expressed as a percentage.

For example, if the confidence interval for the pH is 12.1–12.5 and the confidence level is 95%, this means that the researcher has estimated that there is a 95% change of the true value of the pH being somewhere between 12.1 and 12.5.

Confidence intervals vary, depending on the sample size. The greater the sample size, the smaller the confidence interval. In fact, there is a mathematical relationship—the confidence interval will be inversely proportional to the square root of the sample size. This means, for example, if you were to increase the sample size by a factor of four, the confidence interval would halve. When considering using secondary data, it is useful to consider confidence intervals as they give an indication of the accuracy of the data.

Recording numerical data

Reasonable steps to ensure the accuracy of the investigation include considering:

- the unit in which the independent and dependent variables will be measured
- the instrument that will be used to measure the independent and dependent variables.

Select and use appropriate equipment, materials and methods. For example, select equipment that measures with greater precision to reduce uncertainty and repeat the measurements to confirm them.

When using measuring instruments, the number of significant figures and decimal places you use is determined by how precise your measurements are.

This depends on the scale, accuracy and precision of the instrument and technique you are using. For example, a burette has uncertainties of ±0.02 mL.

Raw data is the information that is recorded directly from observation. When this is processed, for example, calculating a mean or subtracting one value from another, the resulting information is called **processed data**. When you record raw data and report processed data, use the number of significant figures available from your equipment or observation. Using either a greater or smaller number of significant figures can be misleading. For example, Table 19.2.1 shows measurements of 3 titres to two decimal place (three significant figures). The data was entered into a spreadsheet to calculate the **mean**, which was displayed with three decimal places. You would record the mean as 19.52 mL, not 19.517 mL, because two decimal places is the precision limit of the instrument. Recording 19.517 g would be an example of false precision.

TABLE 19.2.1 An example of false precision in a data calculation

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

Data analysis

Data analysis is part of the method. Consider how the data will be presented and analysed. A wide range of analysis tools are available. For example, tables organise data so that patterns can be established and graphs can show relationships and comparisons. In fact, preparing an empty table showing the data that needs to be obtained will help in planning the investigation.

Sourcing appropriate equipment and materials

When designing your investigation, you will need to decide on the materials, technology and instrumentation that will be used to carry it out. It is important to find the right balance between items that are easily accessible and those that will give you accurate results. When conducting your investigation, it will be important to take note of the precision of your chosen instrumentation and how this affects the accuracy and validity of your results.

Modifying the method

The method may need modifying as the investigation is carried out. The following actions will help to determine any issues in the method and how to modify them:

- Record everything.
- Be prepared to make changes to the approach.
- Note any difficulties encountered and the ways in which 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.

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 are identified and further investigations proposed, the work is worthwhile.

COMPLYING WITH ETHICAL AND SAFETY GUIDELINES

Ethical considerations

When planning an investigation, researchers should always identify all possible ethical considerations and evaluate their necessity or ways that can reduce or mitigate them.

Ethical issues might include:

- 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?
- How can this impact on future ethical decisions or issues?
- Does the research cause damage to the environment?
- Does the research cause harm to other living things?

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

Safety in practical experiments and investigations

While planning for an investigation, it is important for your safety and the safety of others, that the potential risks are considered (Figure 19.2.3).

Everything we do has some risk involved. Risk assessments are performed to identify, assess and control hazards. Always identify the risks and control them to keep everyone safe.

FIGURE 19.2.3 When planning an investigation, you need to identify, assess and control hazards.

To identify risks, think about the:

- activity that will be carried out
- equipment or chemicals that will be used.

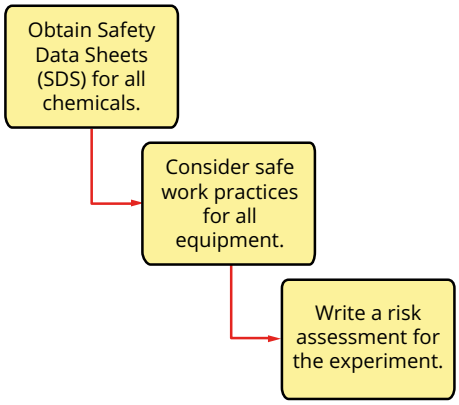


FIGURE 19.2.4 Steps involved in identifying risks

The following hierarchy of risk controls is organised from the most effective to least effective:

1. *Elimination:* Eliminate dangerous equipment, procedures or substances.
2. *Substitution:* Find different equipment, procedures or substances to use that will achieve the same result, but have less risk associated.
3. *Isolation:* Ensure there is a barrier between the person and the hazard. Examples include physical barriers such as guards in machines, or fume hoods to work with volatile substances.
4. *Administrative controls:* Provide guidelines, special procedures, warning signs and safe behaviours for any participants.
5. *Personal protective equipment (PPE):* Wear safety glasses, lab coats, gloves and respirators or other safety equipment where appropriate, and provide these to other participants.

Figure 19.2.4 shows a flow chart of how to consider and assess the risks involved in a research investigation.

Chemical codes

The chemicals at schools or hardware shops have a warning symbol on the label. These are **chemical (HAZCHEM) codes**. Some common codes and their meanings are shown in Figure 19.2.5.

HAZCHEM INTERPRETATION

NUMBER			
1		Water Jets	
2		Water Fog	
3		Foam	
4		Dry Agent	
FIRST LETTER			
P	V	Full Protective Clothing*	DILUTE
R		Full Protective Clothing*	DILUTE
S	V	Breathing Apparatus	DILUTE
S	V	Breathing Apparatus for Fire Only	DILUTE
T		Breathing Apparatus	DILUTE
T		Breathing Apparatus for Fire Only	DILUTE
W	V	Full Protective Clothing*	CONTAIN
X		Full Protective Clothing*	CONTAIN
Y	V	Breathing Apparatus	CONTAIN
Y	V	Breathing Apparatus for Fire Only	CONTAIN
Z		Breathing Apparatus	CONTAIN
Z		Breathing Apparatus for Fire Only	CONTAIN
SECOND LETTER			
E		Consider Evacuation	

Note V: Danger of violent reaction or explosion
* Full Protective Clothing includes Breathing Apparatus

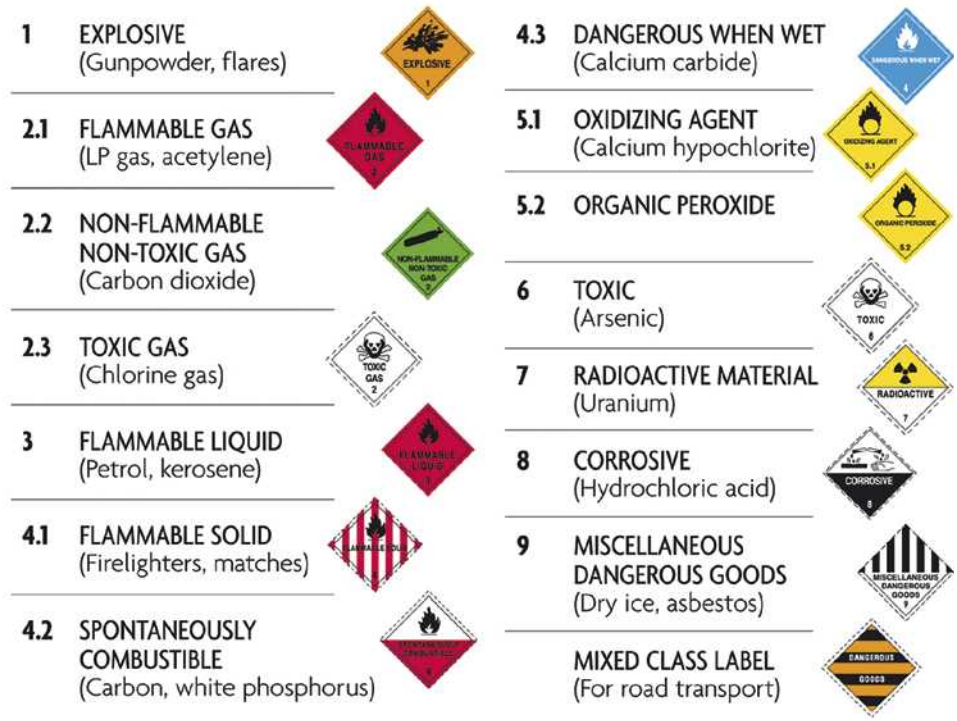


FIGURE 19.2.5 HAZCHEM signs

Safety Data Sheets

Each chemical substance has an accompanying document called a **Safety Data Sheet (SDS)** (Figure 19.2.6), which was previously called a Material Safety Data Sheet (MSDS). 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).

Safety Data Sheet

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 19.2.6 Extracts of 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.

Personal protective equipment

Everyone who works in a laboratory wears items that help keep them safe. This is called **personal protective equipment (PPE)** and includes:

- safety glasses
- shoes with covered tops
- disposable gloves when handling certain chemicals
- a disposable apron or a lab coat if there is risk of damage to clothing.

CHEMFILE

A new system of chemical classification

In all states (apart from Western Australia and Victoria), chemicals in laboratories must be labelled according to the Globally Harmonised System of Classification and Labelling of Chemicals (GHS). This ruling forms part of the labelling provisions of the Work Health and Safety Act, which became fully effective on 1 January 2017. The GHS replaces national systems, such as Hazchem symbols, in order to create a global system for hazard identification. A selection of GHS labels is shown in Figure 19.2.7.

FIGURE 19.2.7 New labels used in the Globally Harmonised System of Classification and Labelling of Chemicals (GHS)

Schools that store, handle, generate, use or dispose of chemicals classified under the new GHS system will be required to train staff in relation to chemical and hazard identification and risk minimisation. Western Australia has not yet adopted the use of the GHS, but is likely to do so in the future.

19.2 Review

SUMMARY

- The method of your investigation is a step-by-step procedure. When detailing the method, ensure it is a valid, reliable and accurate investigation.
- Determine how many times the experiment needs to be replicated. Many scientific investigations lack sufficient repetition to ensure that the results can be considered reliable and repeatable.
- Risk assessments must be carried out before conducting an investigation to make sure that when you carry out your investigation you and others are kept safe. If elements of your investigation are too high a risk, you will need to revise your design.
- Choose appropriate equipment for your experiment. This includes not only personal protective equipment (PPE) that will help keep you safe, but also instrumentation that will give you accurate results.

KEY QUESTIONS

1 A journal article reported the materials and method used in order to conduct an experiment. The experiment was repeated three times, and all values were reported in the results section of the article. Repeating an experiment and reporting results supports:
- **A** validity
- **B** reliability
- **C** credibility
- **D** systematic errors

2 **a** Explain what is meant by the term 'control experiment'.
b Using an example, distinguish between independent and dependent variables.

3 You are conducting an experiment to determine the acidity of different samples of seawater. Identify:
a the independent variable
b the dependent variable
c at least one controlled variable.

4 You are conducting an experiment to determine the pH of a buffer solution. Discuss the accuracy of your results if you are:
a using litmus paper or universal indicator
b recording the pH using a calibrated pH meter.

19.3 Reducing uncertainty in data

During the planning and conducting of an experiment or investigation, minimising potential error is an important consideration.

ERRORS

Most practical experiments have errors associated with them. Errors can occur for a variety of reasons. Being aware of potential errors helps you to avoid or minimise them. For an investigation to be accurate, it is important to identify and record any errors.

There are two types of errors:

- systematic errors
- random errors.

When considering whether an error is random or systematic, you have to consider the measurement that is made compared to the true value of the value being measured.

Systematic errors

A **systematic error** will cause the measured error to always be above, or always below, the true value. It is an error that it will occur again if the investigation is repeated in the same way.

An example of a systematic error is if you were measuring the mass of a substance, and on a piece of filter paper you did not take into account the mass of the filter paper. The mass recorded will always be higher than the true mass of just the substance being weighed. Another example would be if you were making up a standard solution from a primary standard, and when you transferred the initial solution from a beaker to a volumetric flask you did not ensure that all the solution was transferred. In this case, the concentration of the stock solution would always be less than the calculated value.

Systematic errors are usually as a result of instruments that are not calibrated correctly or methods that are flawed.

Random errors

Random errors occur in an unpredictable manner and are generally small. They could give a value higher, or one that is lower than the true value. Whenever a measuring device is used, whether it is a burette or an electric balance, random error will occur.

Note that mistakes are classified as avoidable errors. Mistakes could include misreading the numbers on a scale or spilling a portion of a sample. A measurement that involves a mistake must be rejected and not included in any calculations, or averaged with other measurements of the same quantity.

Techniques for reducing error

Designing the method carefully, including selection and use of equipment, will help to reduce errors. Determining the units of the data being collected and at what scale will help you select the correct equipment. Using the right unit and scale will ensure that measurements are more accurate and precise.

Significant figures

Significant figures are the numbers that convey meaning and precision. The number of significant figures used depends on the scale of the instrument. It is important to record data to the number of significant figures available from the equipment or observation. Using either a greater or smaller number of significant figures can be misleading.

Review the following examples to learn more about significant figures:

- 15 has two significant figures
- 3.5 has two significant figures
- 3.50 has three significant figures
- 0.037 has two significant figures
- 1401 has four significant figures.

Significant figures in processed data

When adding or subtracting the sum or difference of a set of numbers, there should be as many numbers after the decimal as the least accurate number in the set.

Adding: $5.0 + 3.21 + 1.2345 = 9.445 = 9.4$ (because 5.0 has only one figure after the decimal point)

Subtracting: $19.8765 - 1.23 = 18.6465 = 18.64$ (because 1.23.0 has only one figure after the decimal point)

When multiplying or dividing, the answer has no more significant figures than the number with the least significant figures.

Multiplying: $1.234 \times 2.34 = 2.88756 = 2.89$ (because 2.34 has only three significant figures)

Dividing: $34.56 \div 6.7 = 5.158208 = 5.2$ (because 6.7 has only two significant figures)

Calibrated equipment

Some equipment, such as pH meters, needs to be calibrated before use. Before carrying out the investigation, make sure the instruments or measuring devices are properly calibrated and are generally functioning correctly. Record the precision of glassware that you intend to use. If you are preparing a solution of known concentration, you might have access to a volumetric flask which has less uncertainty associated with measurements compared the using a beaker (Figure 19.3.1).

FIGURE 19.3.1 Record the uncertainty for glassware and instruments. This pipette can dispense a volume (aliquot) of 25.00 ± 0.03 mL. When used correctly, the volume dispensed will be between 24.97 mL and 25.03 mL.

Correct use of equipment

Use the equipment properly. Ensure any necessary training has been completed to use the equipment and that you have had an opportunity to practise using the equipment before beginning the investigation. Improper use of equipment can result in inaccurate, imprecise data with large errors, and the validity of the data can be compromised.

Incorrect reading of measurements is a common misuse of equipment. Make sure all of the equipment required in the investigation can be used correctly and record the instructions in detail so they can be referred to if the data does not appear correct.

Repeat trials

As discussed in Section 19.2, reliability is improved by repeating your experiment. Note that repeating trials will only reduce the effect of random errors. Repeating a flawed method will not reduce the effect of the systematic error within that method. Therefore, modifications to your procedure may need to be looked at before repeating the investigation to ensure all variables are being tested under the same conditions.

19.3 Review

SUMMARY

- It is essential that during the investigation the following are recorded in the logbook:
  - all quantitative and qualitative data collected
  - the methods used to collect the data
  - any incident, feature or unexpected event that may have affected the quality or validity of the data.
- A systematic error will cause the measured error to always above, or always below, the true value.
- Random errors could give a value higher, or lower than the true value.
- The number of significant figures used depends on the scale of the instrument used. It is important to record data to the number of significant figures available from the equipment or observation.

KEY QUESTIONS

1 What type of error is associated with:
- **a** inaccurate measurements?
- **b** imprecise measurements?

2 Identify whether each of the situations below is a mistake, systematic error or random error.
- **a** A student washed a burette with distilled water immediately before use.
- **b** The volume of a solution of hydrochloric acid used in a titration was measured using a measuring cylinder.
- **c** A student sometimes forgot to re-zero the balance between weighing samples of solid sodium carbonate when making a standard solution.

3 A scientist carries out a set of experiments, analyses the results and publishes them in a scientific journal. Other scientists in different laboratories repeat the experiment, but do not get the same results as the original scientist. Suggest three reasons why this might occur.

19.4 Processing data and information

Once you have conducted your investigation and collected data, you will need to find the best way of collating it. This section is a guide to the different forms of representation that will help you to better understand your data.

Raw data is unlikely to be used directly to validate the hypothesis. However, raw data is essential to the investigation and plans for collecting the raw data should be made carefully. Consider the formulas or graphs that will be used to analyse the data at the end of the investigation. This will help to determine the type of raw data that needs to be collected in order to validate the hypothesis.

Once you have determined the data that needs to be collected, prepare a table in which to record the data.

The raw data that has been obtained should be presented in a way that is clear, concise and accurate. There are a number of ways of presenting data, including tables, graphs, flow charts and diagrams.

GRAPHS

In general, tables provide more detailed data than graphs, but it is easier to observe trends and patterns in data in graphical form than in tabular form.

Graphs are used when two variables are being considered and one variable is dependent on the other. The graph shows the relationship between the variables.

There are several types of graphs that can be used, including line graphs, bar graphs and pie charts. The best one to use will depend on the nature of the data.

General rules to follow when making a graph (Figure 19.4.1) include the following.

- Keep the graph simple and uncluttered.
- Use a descriptive title.
- Represent the independent variable on the *x*-axis and the dependent variable on the *y*-axis.
- Make axes proportionate to the data.
- Clearly label axes with both the variable and the unit in which it is measured.

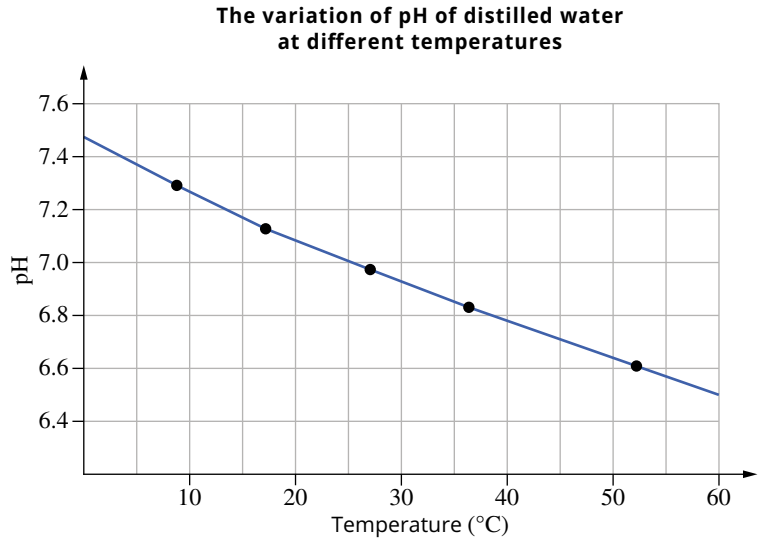


FIGURE 19.4.1 A graph is a better way to observe trends and patterns in data form.

Line graphs

Line graphs are a good way of representing continuous quantitative data. In a line graph, the values are plotted as a series of points on the graph. There are two ways of joining these points:

- A line can be ruled from each point to the next. It shows the overall trend; it is not meant to predict the value of the points between the plotted data.
- The points can be joined with a single smooth straight or curved line (Figure 19.4.2). This creates a **trend line**, also known as a line of best fit. The line of best fit does not have to pass through every point, but should go close to as many points as possible. It is used when there is an obvious trend between the variables.

Sometimes when the data is collected, there may be one point that does not fit with the trend and is clearly an error. This is called an **outlier**. An outlier is often caused by a mistake made in measuring or recording data. If there is an outlier, include it on the graph, but ignore it when adding a line of best fit.

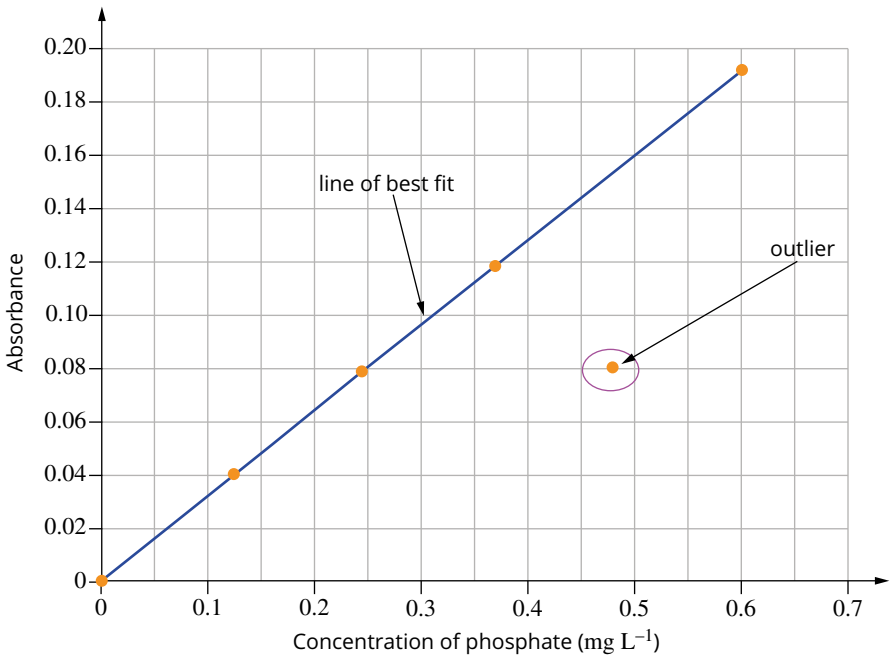


FIGURE 19.4.2 The outlier in this graph is ignored when the line of best fit is drawn.

19.4 Review

SUMMARY

- Consider how the data will be presented and analysed. A wide range of analysis tools could be used. For example, tables organise data so that patterns can be established and graphs can show relationships and comparisons.
- The simplest form of a table is a two-column format in which the first column contains the independent variable and the second column contains the dependent variable.
- General rules to follow when making a graph include the following.
  - Keep the graph simple and uncluttered.
  - Use a descriptive title.
  - Represent the independent variable on the *x*-axis and the dependent variable on the *y*-axis.
  - Make axes proportionate to the data.
  - Clearly label axes with both the variable and the unit in which it is measured.

KEY QUESTIONS

1 How can the general pattern (trend) of a graph be represented once the points are plotted?

2 **a** Use the following values to plot a calibration curve to determine the concentration of nickel (as Ni^{2+}) in solutions of nicke(II) chloride using a colorimeter. The absorbance values were obtained during an experiment using a wavelength of light of 635 nm.

Standard concentration (mol L^{-1})	Absorbance of light at 635 nm
0.00	0.000
0.12	0.038
0.24	0.079
0.36	0.159
0.48	0.154
0.60	0.191

b From the graph you have drawn, select the data point that is an outlier.

c Define the term 'outlier'.

19.5 Analysing data and information

Now that the investigation has been conducted and data collected, it is time to draw it all together. You will now analyse your results to better understand the chemical processes behind them.

ANALYSING AND EVALUATING DATA

In the discussion, the findings of the investigation need to be analysed and interpreted.

- 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.
- Were there discrepancies, deviations or anomalies in the data? If so, these should be acknowledged and explained.
- Identify any limitations in the data you have collected. Perhaps a larger sample or further variations in the independent variable would lead to a stronger conclusion.

Trends in line graphs

Graphs are drawn to show the relationship, or trend, between two variables.

- Variables that change in linear or direct proportion to each other produce a straight, sloping trend line (Figure 19.5.1).
- Variables that change exponentially in proportion to each other produce a curved trend line (Figure 19.5.2).
- When there is an inverse relationship, one variable increases as the other variable decreases (Figure 19.5.3).
- When there is no relationship between two variables, one variable will not change even if the other changes (Figure 19.5.4).

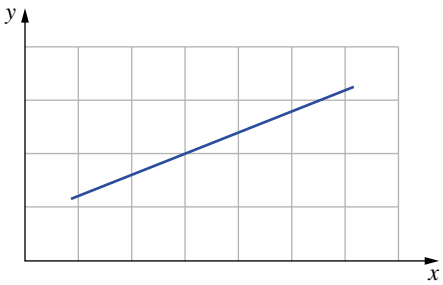


FIGURE 19.5.1 Trend line for variables that change in direct response to each other

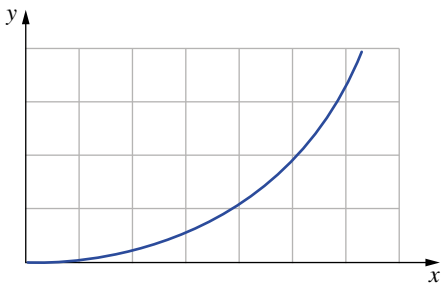


FIGURE 19.5.2 Variables that change in response to each other in a non-linear way

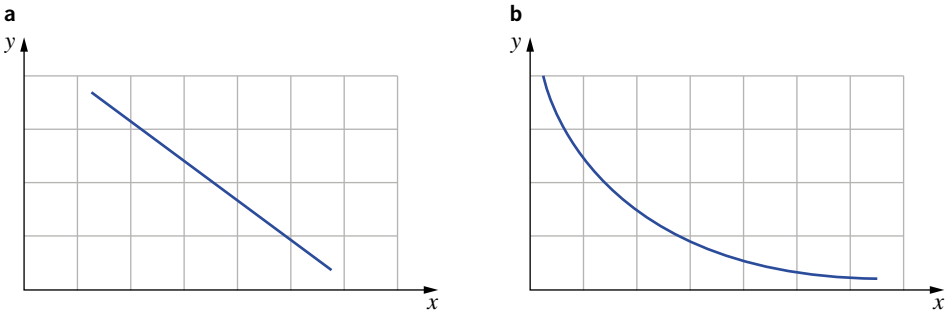


FIGURE 19.5.3 An inverse relationship in which one variable decreases in response to the other variable increasing. It may be (a) direct or (b) non-linear.

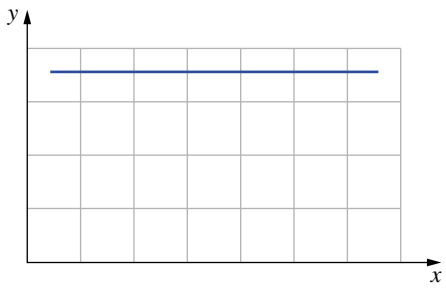


FIGURE 19.5.4 When two variables show no relationship, there is no trend in the data

Remember that the results might be unexpected. This does not make the investigation a failure. However, the findings must be related to the hypothesis, aims and method.

Table 19.5.1 lists the types of graphs used for various examples.

TABLE 19.5.1 Examples of the types of graphs that could be used in your report

Type of graph	When to use	Example
Scatter graph	When showing quantitative data where one variable is dependent on another variable; draw a line of best fit to show the relationship between the two variables	Showing the relationship between the rate of a reaction and the concentration of acid.
Line graph	Used for continuous quantitative data	Concentration of dissolved oxygen at a particular location of a creek over a period of time
Bar graphs	When comparing data in an investigation with a qualitative independent variable	pH of water of seawater various locations
Pie diagrams	When summarising qualitative data; to display proportions	Relative proportion of different pesticides in a sample of water

EVALUATING THE METHOD

It is important to discuss the limitations of the investigation method. Evaluate the method and identify any issues that could have affected the validity, accuracy, precision or reliability of the data. Sources of errors and uncertainty must also be stated in the discussion.

Once any limitations or problems in the methodology have been identified, recommend improvements on how the investigation could be conducted if repeated; for example, suggest how the authors of a journal article could report minimising or eliminating materials.

Bias

Bias may occur 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 or motivations. There are many types of bias, including:

- poor definitions of both concepts and variables (for example, not defining pH)
- incorrect assumptions (for example, measuring pH of a solution without also measuring the temperature of the solution)
- errors in the investigation design and methodology (for example, taking water samples from more than one site).

Some biases cannot be eliminated, but should be addressed in the discussion.

Accuracy and precision

In the discussion, evaluate the degree of accuracy and precision of the measurements for each variable of the hypothesis. Comment on the uncertainties obtained.

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.

Reliability

When discussing 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 short timeframes and scarce resources might have prevented multiple sets of data from being collected. Discuss whether the results of the investigation have been limited by the sample size.

The control group is important to the reliability of the investigation. A control group helps determine if a variable that should have been controlled has been overlooked and might explain any unexpected results.

Error

Discuss any source of systematic or random error and suggest ways of improving the investigation.

CRITICALLY EVALUATING SOURCES OF INFORMATION

Not all sources are **credible**. When you have used primary of secondary data from information sources, it is essential to critically evaluate the content and its origin. Questions you should always ask when evaluating a source include:

- Who created this source? What are the qualifications, expertise, reputation and affiliation of the authors?
- Why was it written?
- Where was the information published?
- When was the information published?
- Are conclusions supported by data or evidence?
- What is implied?
- What is omitted?
- Are any opinions or values being presented in the piece?
- Is the writing objectively and accurately describing a scientific concept or phenomenon?
- How might other people understand or interpret this message differently from me?

  When evaluating the validity or bias of websites consider its domain extension:

  - .gov stands for government
  - .edu stands for education
  - .org stands for non-profit organisations
  - .com stands for commercial/business.

19.5 Review

SUMMARY

- After completing your investigation you will need to analyse and interpret your data. A discussion of your results is required where the findings of the investigation need to be analysed and interpreted.
- 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.
- Where possible, create a mathematical model, for example, using Excel.
- You can describe or calculate a trend line or determine gradients of curves, to describe your data.
- Were there discrepancies, deviations or anomalies in the data? If so, these should be acknowledged and explained.
- Identify any limitations in the data collected. Perhaps a larger sample or further variations in the independent variable would lead to a stronger conclusion.
- It is important to discuss the limitations of the investigation method. Evaluate the method and identify any issues that could have affected the validity, accuracy, precision or reliability of the data. Sources of errors and uncertainty must also be stated in the discussion.
- When discussing the results, indicate the range of the data obtained from replicate results. 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.

KEY QUESTIONS

1 What relationship between the variables is indicated by a sloping linear graph?

2 What relationship exists if one variable decreases as the other increases?

3 What relationship exists if both variables increase or both decrease at the same rate?

4 What might cause a sample size to be limited in an investigation?

19.6 Conclusions

Having analysed your results, you can then apply them to chemical concepts in order to evaluate your conclusions. In this section you will learn how analysing your investigation leads to a better understanding of the underlying scientific principles of your research.

DISCUSSING RELEVANT CHEMICAL CONCEPTS

To make the 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 the hypothesis. For example, if you were studying the impact of dissolved carbon dioxide on the pH of sea water, you could include the information in Table 19.6.1 in your discussion.

TABLE 19.6.1 Examples of how to include chemical concepts in your discussion

Key ideas	Example
Definitions of key terms	'pH', 'dissolved carbon dioxide' and 'sea water'
The source of carbon dioxide	Product from the combustion of fossil fuels
Relationship between variables	Dissolved carbon dioxide and pH of water, temperature was controlled in the experiment
Chemical principles	Dissolved carbon dioxide and formation of carbonic acid (H_2CO_3), including relevant equations
Sources of error	Reducing random error, by repeating measurements and calculating average

Relating your findings to a chemical concept

During the analysing stage of your investigation (section 19.5), you were able to find trends, patterns and mathematical models of your results. This is the framework needed to discuss whether the data supported or refuted the hypothesis. Ask questions such as:

- Was the hypothesis supported?
- Has the hypothesis been fully answered? (If not, give an explanation of why this is so 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 and must be based on the results and previous evidence.)

Be sure to discuss the broader implications of the findings. Implications are the bigger picture. Outlining them for the audience is an important part of the investigation. Ask questions such as:

- Do the findings lead to further questions?
- Can the findings be extended to another situation?
- Are there any practical applications for the findings?

DRAWING EVIDENCE-BASED CONCLUSIONS

A conclusion is usually written as a paragraph that links the collected evidence to the hypothesis and provides a justified response to the research question.

Indicate whether the hypothesis was supported or refuted and the evidence on which this decision is based (that is, the results). Do not provide irrelevant information. Only refer to the specifics of the hypothesis and the research question and do not make generalisations.

Read the examples of poor and better conclusions in Table 19.6.2 and Table 19.6.3 for the hypothesis and research question shown.

TABLE 19.6.2 Examples of strong and weak conclusions to the hypothesis

Hypothesis: An increase in the temperature of pond water will result in a decrease in the measured pH of the water sample.

Strong conclusion	Weak conclusion
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.	The pH of water decreased as temperature increased.

TABLE 19.6.3 Examples of strong and weak conclusions in response to the research question

Research question: Does temperature affect the pH of water?

Strong conclusion	Weak conclusion
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 6.7. These results support the current knowledge that an increase in water temperature results in a decrease in its pH.	The results show that temperature does affect the pH of water.

19.6 Review

SUMMARY

- To make the 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 the hypothesis.
- Indicate whether the hypothesis was supported or refuted and on what evidence this decision is based (that is, the results). Do not provide irrelevant information. Only refer to the specifics of the hypothesis and the research question and do not make generalisations.

KEY QUESTIONS

1 Which of the following would **not** support a strong conclusion to a report?
The concluding paragraphs:
A are relevant and provide evidence.
B are written in emotive language.
C include reference to limitations of the research.
D include suggestions for further avenues of research.

2 A procedure was repeated 30 times. How should the following step in the method be rewritten?
'Many repeats of the procedure were conducted.'

19.7 Communicating

How you approach communicating your results will depend on the audience you want to reach. If you are communicating with a general audience you may want to discuss your investigation in the style of a news article or blog post. These types of communication do not use too much scientific language as you need to assume that your audience does not have a science background.

Throughout this course you will need to present your research using appropriate scientific language and notation. There are many different presentation formats that you can use, such as posters, oral presentations and reports. This section covers the main characteristics of effective science communication and report writing, including objectivity, clarity, conciseness and coherence.

STRUCTURING A REPORT

Your report should have a clear, logical structure.

Introduction:

The first paragraph should introduce your topic and define key terms.

Body paragraphs:

- Each subsequent paragraph should cover one main idea.
- Use evidence to support statements.
- Avoid very long or very short paragraphs.

Conclusion:

- The final section should summarise the main findings.
- It should relate to the aim of the investigation.
- The conclusion should include limitations and discuss implications and applications of the research and potential future research.

Analysing information relevant to your research investigation

Scientific research should always be objective and neutral. Any premise presented must be supported with facts and evidence to allow the audience to make its own decision. Identify the evidence supporting or contradicting each point you want to make. Be sure to explain connections between ideas, concepts, theories and models. Figure 19.7.1 lists the questions you need to consider when writing your investigation report.

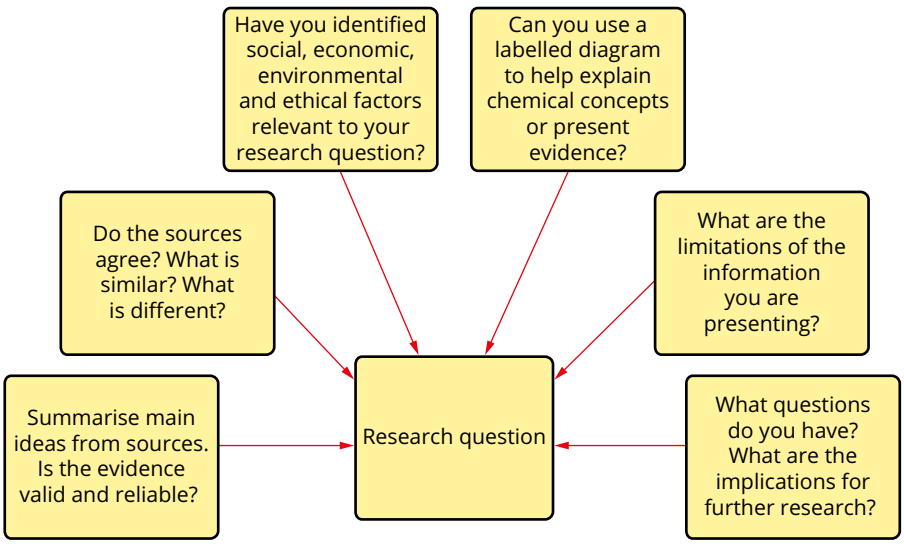


FIGURE 19.7.1 Discuss relevant information, ideas, concepts and implications and make sure your discussion is relevant to the question under investigation.

WRITING FOR SCIENCE

Scientific reports are usually written in an objective or unbiased style. This is in contrast with English writing, which most often uses the subjective techniques of rhetoric or persuasion. Read Table 19.7.1, which contrasts persuasive and scientific writing styles.

TABLE 19.7.1 Persuasive writing versus scientific writing styles

Persuasive writing examples	Scientific writing equivalent examples
Use of biased and subjective language Examples: The results were extremely bad, atrocious, wonderful etc. This is terrible because ... This produced a disgusting odour. Health crisis	**Use of unbiased and objective language** Examples: The results showed ... The implications of these results suggest ... The results imply ... This produced a foul odour. Health issue
Use of exaggeration Example: The object weighed a colossal amount, like an elephant.	**Use of non-emotive language** Example: The object weighed 256 kg.
Use of everyday or colloquial language Examples: The bacteria passed away. The results don't ... The researchers had a sneaking suspicion ...	**Use of formal language** Examples: The bacteria died. The results do not ... The researchers predicted/hypothesised/theorised ...

Consistent reporting narrative

Scientific writing can be written either in first-person or in third-person narrative. Your teacher may advise you about which to select. In either case, ensure that you keep the narrative point of view consistent. Read the examples of first-person and third-person narrative in Table 19.7.2.

TABLE 19.7.2 Examples of first-person and third-person narrative

First person	Third person
I put 50.0 g marble chips in a conical flask and then added 10.0 mL of 2.0 mol L^{-1} hydrochloric acid.	First, 50.0 g of marble chips was weighed into the conical flask and then 10.0 mL of 2.0 mol L^{-1} hydrochloric acid was added.
After I observed the reaction, I found that ...	After the reaction was completed, the results showed ...
My colleagues and I found ...	Researchers found ...

Qualified writing

Be careful of words that are absolute, such as *always*, *never*, *shall*, *will* and *proven*. Sometimes it may be more accurate and appropriate to use qualifying words, such as *may*, *might*, *possible*, *probably*, *likely*, *suggests*, *indicates*, *appears*, *tends*, *can* and *could*.

Concise writing

It is important to write concisely, particularly if you want to engage and maintain the interest of your audience. Use shorter sentences. Read Table 19.7.3, which shows some examples of more concise wording.

TABLE 19.7.3 Examples of verbose and concise language

Verbose example	Concise example
Due to the fact that ...	Because ...
Smith undertook an investigation into ...	Smith investigated ...
It is possible that the cause could be ...	The cause might be ...
A total of five experiments ...	Five experiments ...
End result	Result
In the event that ...	If ...
Shorter in length	Shorter

REFERENCES AND ACKNOWLEDGEMENTS

All the quotations, documents, publications and ideas used in the investigation need to be acknowledged in the 'references and acknowledgments' section in order to avoid accusations of plagiarism and to ensure authors are credited for their work. References and acknowledgements also give credibility to the study and allow the audience to locate information sources, should they wish to study it further. The standard referencing style used is the Amercian Psychological Association (APA) academic referencing style.

When referencing a book, include in this order:

- author's surname and initials
- date of publication
- title
- publisher's name
- place of publication.

For example: Rickard, Greg, et al. (2016), *Pearson Science SB9* (2nd ed.), Pearson Education, Melbourne, Australia.

When referencing a website, include in this order:

- author's surname and initials, or name of organisation, or title
- year website was written or last revised
- title of webpage
- date website was accessed
- website address.
- For example: National Geographic (2015), 'Killer fungus that's devastating bats may have met its match', accessed 29 May 2015, from http://news.nationalgeographic.com/2015/05/150527-bats-white-nose-syndrome-treatment-conservation-animals-science.

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). List the full details in your list of references.

The following examples show the use of in-text citation.

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).

Or

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.

The bibliographic details of the example above would be:

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.

MEASUREMENT AND UNITS

In every area of chemistry we have attempted to quantify the phenomena we study. In practical demonstrations and investigations, we generally make measurements and process them in order to come to some conclusions. Scientists have a number of conventional ways of interpreting and analysing data from their investigations. There are also conventional ways of writing numerical measurements and their units.

Table 19.7.4 presents the main quantities and units used in chemistry.

TABLE 19.7.4 Quantities and units used in chemistry

Quantity	Symbol for quantity	Unit
Mass	m	gram (g)
Volume	V	litre (L)
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
Density	d	$g\,mL^{-1}$, $kg\,L^{-1}$
Molarity	c	moles per litre ($mol\,L^{-1}$)

Correct use of unit symbols

The correct use of unit symbols removes ambiguity, as symbols are recognised internationally. The symbols for units are not abbreviations and should not be followed by a full stop unless they are at the end of a sentence.

Upper-case letters are only used 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. We do this because a lower-case '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 19.7.5 provides some examples of correct and incorrect use of symbols for derived units.

TABLE 19.7.5 Some examples of the use of symbols for derived units

Preferred	Incorrect
$g\,mol^{-1}$	$gmol^{-1}$
kPa	K Pa

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. It is acceptable to say 'two kilojoules' but it is wrong to write 2 kJs.

Numbers and symbols should not be mixed with words for units and numbers. For example, thirty grams and 30 g are correct, but thirty g is incorrect.

Scientific notation

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

Examples of some values written in scientific notation are:

6.022×10^{23} particles

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

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

You should be routinely using scientific notation to express 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 frequently 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 to the nearest (that is, somewhere between 239.5 g and 240.5 g) or it could have been rounded up to the nearest 10 g. Writing this quantity as 2.40×10^2 g makes the accuracy of the value clear (in this case three significant figures).

Prefixes and conversion factors

Conversion factors should be used carefully. You should be familiar with the prefixes and conversion factors in Table 19.7.6. Note that the table gives all conversions as a multiplying factor.

TABLE 19.7.6 Prefixes and conversion factors

Multiplying factor		Prefix	Symbol
1 000 000 000 000	10^{12}	tera	T
1 000 000 000	10^{9}	giga	G
1 000 000	10^{6}	mega	M
1 000	10^{3}	kilo	k
0.01	10^{-2}	centi	c
0.001	10^{-3}	milli	m
0.000 001	10^{-6}	micro	μ
0.000 000 001	10^{-9}	nano	n
0.000 000 000 001	10^{-12}	pico	p

Do not put spaces between prefixes and unit symbols.

It is important to give the symbol the correct case (upper or lower case). There is a big difference between 1 mm and 1 Mm.

19.7 Review

SUMMARY

- A scientific report must include an introduction, body paragraphs and conclusion.
- The conclusion should include a summary of the main findings, a conclusion related to the issue being investigated, limitations of the research, implications and applications of the research, and potential future research.
- Scientific writing uses unbiased, objective, accurate, formal language. it should also be concise and qualified.
- Visual support can assist in conveying scientific concepts and processes efficiently.
- Ensure you edit your final report.
- Scientific notation needs to be used when communicating your results.

KEY QUESTIONS

1 The variables molar mass, and molarity each have different units. Write the units for each of the following in correct notation.

a molar mass; grams per mole

b molarity; mole per litre

2 **a** Show how to convert mL into L.

b Discuss why you might need to convert between different multiplying factors, for example, litres to millilitres.

Chapter review

19

KEY TERMS

accuracy
chemical (HAZCHEM) codes
confidence interval
control experiment
controlled variable
credible
dependent variable
hypothesis
independent variable
mean
outlier
personal protective equipment (PPE)
phenomenon
precision
primary source
processed data
qualitative
quantitative
random error
raw data
reliability
Safety Data Sheet (SDS)
secondary source
significant figures
systematic error
trend line
uncertainty
validity
variable

1 Consider the following research question:
'Is the pH of water sampled from the Ningaloo Reef within acceptable limits?'
Identify each of the following as independent, dependent or controlled variables.
- **a** pH
- **b** Analytical technique, temperature of water sample, type of sampling container
- **c** Source and location of water.

2 Match the following command verbs with their definitions:
describe, analyse, apply, create, identify, reflect, investigate.
- **a** Think deeply about.
- **b** Produce or make new.
- **c** Identify connections and relationships, interpret to reach a conclusion.
- **d** Observe, study, examine, inquire systematically in order to establish facts or derive conclusions.
- **e** Use knowledge and understanding in a new situation.
- **f** Recognise or indicate what or who.
- **g** Give a detailed account.

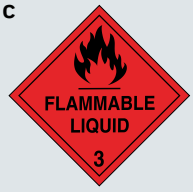
3 Consider the following hypothesis:
'The concentration of calcium ions in drinking water from the Perth desalination plant is greater than that of drinking water sourced from the Perth Hills.'
Name the independent, dependent and controlled variables for an experiment with this hypothesis.

4 What are the meanings of the following chemical codes?

a

b

c



5 Explain the terms 'accuracy' and 'validity.'

6 Identify whether the following are mistakes, systematic errors or random errors.
- **a** A student spills some solution during an experiment.
- **b** The reported measurements are above and below the true value.
- **c** A weighing balance has not been calibrated.

7 What relationship between variables is indicated by a straight trend line?

8 What factors should you consider to ensure you discuss the limitations of your method?

9 Explain the meaning of the term 'trend' in a scientific investigation and describe the types of trends that might exist.

10 What is meant by the 'limitations' of the investigation method?

11 What is the purpose of referencing and acknowledging documents, ideas and quotations in your investigation?

12 For the following source, what is the correct way to make an in-text citation in APA style?
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), 3796–3777.
- **A** However, Selke et al. (2015) did not find any significant difference in biodegradability.
- **B** However, Selke et al. did not find any significant difference in biodegradability[1].
- **C** However, Selke et al. did not find any significant difference in biodegradability (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).
- **D** However, Selke et al. (2015) did not find any significant difference in biodegradability (Evaluation of biodegradation-promoting additives for plastics. *Environmental Science & Technology*).

13 Convert 23.0 mL into L.

14 A scientist designed and completed an experiment to test the following hypothesis:
'Increasing the concentration of the electrolyte in a hydrogen fuel cell would result in an increase in the voltage generated by the cell.'

- **a** What would be the independent, dependent and controlled variables in this investigation?
- **b** What data would be collected? Would it be qualitative or quantitative?
- **c** List the equipment that could be used and the type of precision expected for each item.
- **d** Explain the difference between raw data and processed data, using this hypothesis as an example. Sketch what you expect the graph of the results to look like if the scientist's hypothesis was correct.

UNIT 4 • ORGANIC CHEMISTRY AND CHEMICAL SYNTHESIS

REVIEW QUESTIONS

Section 1: Multiple choice

1 The systematic name for $CH_3CH_2CH_2CH(CH_3)_2$ is:
- **A** 1,1-dimethylbutane.
- **B** 2-methylpentane.
- **C** 2-methylpentene.
- **D** propyldimethylmethane.

2 Oxidation of a secondary alcohol produces:
- **A** an aldehyde.
- **B** a ketone.
- **C** a carboxylic acid.
- **D** an ester.

3 Which of the following compounds would be expected to have the highest boiling point?
- **A** $CH_3CH_2CH_2OH$
- **B** $CH_3CH_2CH_2CH_3$
- **C** $CH_3CH_2CH_2Cl$
- **D** $CH_3CH_2CH_3$

4 Which of the following statements 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** II and III
- **C** I and III
- **D** I, II and III

5 Chloroform (trichloromethane, $CHCl_3$) is synthesised commercially by the chlorination of methane. Reaction occurs according to the equation:
$CH_4 + 3Cl_2 \rightarrow CHCl_3 + 3HCl$
The final mixture contains hydrogen chloride and chloroform, along with chloromethane, dichloromethane and tetrachloromethane. Distillation allows separation of the chloroform, and at one plant yields of 75% are obtained. What mass of methane (in g) would be needed to generate 1.0 kg of chloroform, assuming 75% yield?
- **A** 101
- **B** 134
- **C** 179
- **D** 197

6 The ester methyl ethanoate could be made by reacting together which of the following?
- **A** CH_3CH_2OH and CH_3COOH
- **B** CH_3CH_2OH and $HCOOH$
- **C** CH_3OH and CH_3CH_2COOH
- **D** CH_3OH and CH_3COOH

7 The volume of carbon dioxide (in L) collected at STP when 6.32 g of ethane undergoes complete combustion is:
- **A** 4.77
- **B** 9.25
- **C** 9.55
- **D** 18.5

8 Which of the following molecules is most likely to undergo an addition polymerisation reaction?
- **A** FCH_2CH_2COOH
- **B** $HOCH_2CONH_2$
- **C** $C_6H_5CHCHOH$
- **D** $CH_3COCH_2CH_3$

9 Listed below are the names of groups found in some organic compounds.
- **I** alcohol
- **II** amide
- **III** aldehyde
- **IV** ketone

Which of these groups are always found at the end of a hydrocarbon chain?
- **A** I and II only
- **B** III only
- **C** I, II and III only
- **D** I, III and IV only

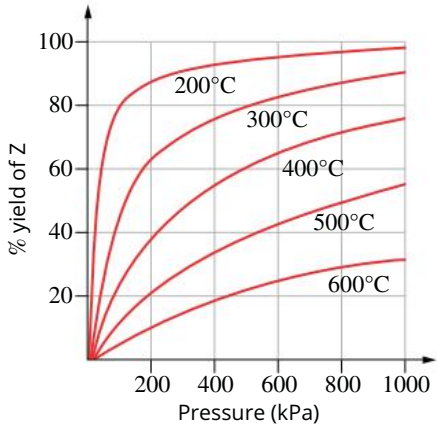
10 Consider the following reaction pathway:
ethene $\xrightarrow{I}$ chloroethane $\xrightarrow{II}$ ethanol $\xrightarrow{III}$ ethanoic acid
The reactions that occur in steps I, II and III of the pathway are:
- **A** substitution, addition, hydrolysis.
- **B** chlorination, substitution, addition.
- **C** addition, substitution, oxidation.
- **D** addition, reduction, hydrolysis

11 A triglyceride molecule with a molar mass of 878 g mol^{-1}, when fully hydrolysed, yields a single type of fatty acid molecule. The molar mass of this fatty acid (g mol^{-1}) is closest to:
- **A** 262
- **B** 280
- **C** 292
- **D** 310

12 The industrial production of chemical Z proceeds in the presence of a catalyst according to the equation:

$$X(g) + 2Y(g) \rightarrow zZ(g)$$

The graph below shows the variation in the equilibrium yield of Z with pressure at a range of temperatures.



It can be deduced that the production of Z is an:

A endothermic reaction and the value of *z* could be 2.
B endothermic reaction and the value of *z* could be 4.
C exothermic reaction and the value of *z* could be 2.
D exothermic reaction and the value of *z* could be 4.

Section 2: Short answer

1 Enzymes are biological catalysts, some of which can be used for industrial-scale synthesis reactions. One example is the synthesis of ethanol from glucose, using enzymes derived from yeast. Ethanol can also be produced by the catalysed hydration of ethene. Ethanol can be used as a fuel in modified vehicles, or mixed with petrol for use in existing vehicles.

a Write a balanced equation, using molecular formulae for organic compounds, for the enzyme-catalysed reaction of glucose to produce ethanol.

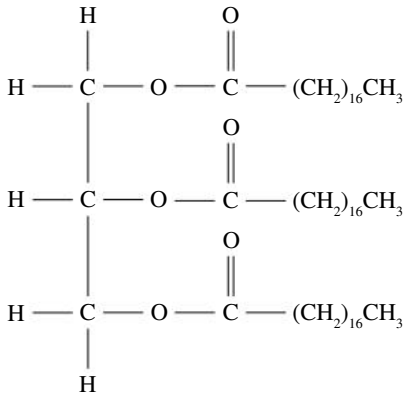
b i Write a balanced equation, using semistructural formulae for organic compounds, for the catalysed hydrolysis of ethene. Include the name of a suitable catalyst.

ii Which one or more of the following terms could be used to describe the type of reaction occurring in part **b(i)**: substitution, addition, acid–base, redox, condensation?

iii The synthesis reaction in part **b(i)** takes place in industry at pressures of around 60 times atmospheric pressure, and a temperature near 300°C. In terms of the rate and extent of the reaction, account for the use of such high pressure.

c Suggest two reasons why the enzyme catalysed synthesis reaction in part **a** may be the preferred method for large-scale, long-term synthesis of ethanol for use as a fuel.

2 A triglyceride molecule found in a fat is shown in the following diagram.

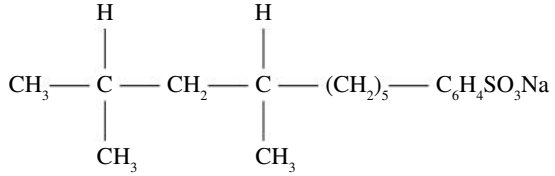


triglyceride

a i Draw the structures of the glycerol molecule and the anionic form of the long-chain fatty acid produced by the base-catalysed hydrolysis of this triglyceride.

ii The saponification reaction in part **a(i)** produces soap. Name the functional group in the anionic particle drawn in part **a(i)**.

b The semistructural formula of a synthetic detergent that can be used in place of soap is shown below.



i Is the detergent shown cationic, anionic or polar?

ii Name the type of bonding that occurs between the detergent ions and water molecules.

iii Name the type of bonding that occurs between the detergent ions and oil molecules from a greasy plate.

c Synthetic detergents have replaced natural detergents, such as soap, for many cleaning purposes.

i State one advantage of detergents over soap.

ii State one disadvantage of detergents over soap.

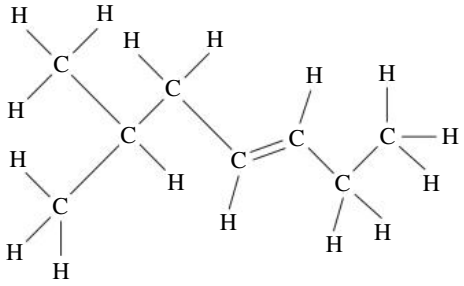
d Biodiesel is an increasingly important alternative fuel which is synthesised from triglycerides and methanol using either a hydroxide catalyst or a lipase catalyst.

i Draw the structure of a biodiesel molecule containing a total of 18 carbon atoms.

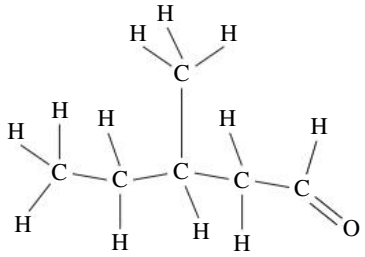
ii Name the types of bonding that exist between biodiesel molecules.

3 **a** For each of the following structures, write a condensed (semistructural) formula.

i



ii



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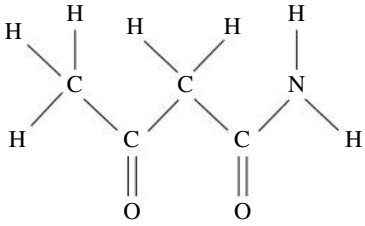
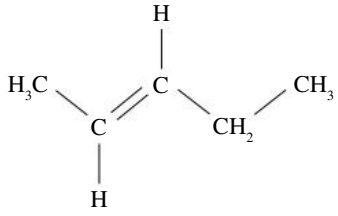


b Give the correct IUPAC names for each of the following structures.

i



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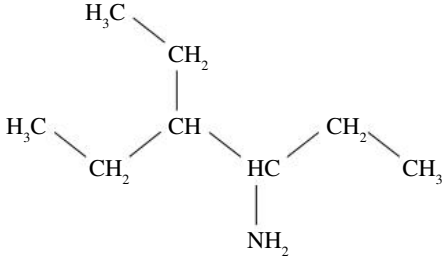

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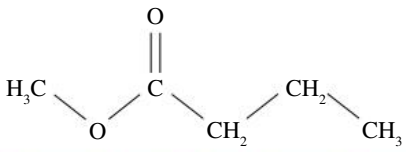


c State appropriate reagents and conditions to effect the conversion of:

i butan-2-ol to butanone

ii cyclohexene to cyclohexane.

d Write balanced chemical equations (excluding states) using semi-structural formulae for the:

i condensation reaction of ethanol and propanoic acid

ii acid–base reaction between ethanamine and propanoic acid.

4 An experiment was conducted to synthesise ethanal. When 3.00 g of ethanol was treated with 25.0 mL of a 1.00 mol L^{-1} solution of acidified potassium dichromate under appropriate conditions, 2.42 g of ethanal was obtained. The reaction is represented by the equation:

$$3CH_3CH_2OH(l) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3CH_3CHO(l) + 2Cr^{3+}(aq) + 7H_2O(l)$$

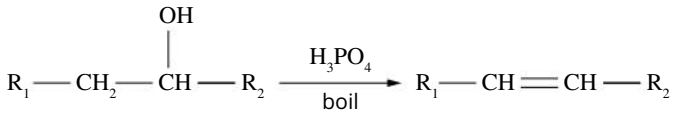
a **i** State the oxidation number of carbon in ethanal.

ii Write a balanced half-equation for the oxidation process occurring in the reaction.

b **i** Calculate the percentage yield for the synthesis experiment.

ii Suggest two reasons why the percentage yield is less than 100%.

5 Alcohols can be dehydrated by heating in acid to produce alkenes, as shown in the following generalised reaction.



When hexan-3-ol was heated with acid, the resultant mixture was found to contain four distinct isomeric products.

a **i** Draw a structural formula for hexan-3-ol.

ii What type of alcohol (primary, secondary or tertiary) is hexan-3-ol?

iii Hexan-3-ol has a very low solubility in water compared with ethanol, which is completely miscible in water. Account for this difference in solubilities.

b Two of the products of the dehydration of hexan-3-ol are structural isomers, differing only in the position of the functional group. Draw and name these two isomers.

c Each of the isomers drawn in part **b** can exhibit *cis–trans* isomerism. For one of the compounds drawn in part **b**, draw and label the *cis* and *trans* isomers.

6 A number of reactions involving sulfur-containing compounds are shown in the equations K–O. Some of these reactions occur during the production of sulfuric acid by the contact process.

K $S(l) + O_2(g) \rightarrow SO_2(g)$

L $H_2SO_4(aq) + MgO(s) \rightarrow MgSO_4(aq) + H_2O(l)$

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

N $SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$

O $H_2SO_4(l) + 3H_2S(aq) \rightarrow 4S(s) + 4H_2O(l)$

a Select the letter K–O corresponding to a reaction:

i showing sulfuric acid acting as an oxidising agent

ii in which the oxidation number of sulfur is unchanged

iii in which the substance called oleum appears.

b Reaction M is an important step in the manufacture of sulfuric acid by the contact process.

i To improve the yield of SO_3 in this reaction, should the temperature be raised or lowered? Explain your choice.

ii State one disadvantage of using the temperature chosen in part **b(i)**.

iii The yield of SO_3 in this reaction would be improved by the use of high pressure. Explain why the reaction is carried out at near atmospheric pressure during industrial production of sulfuric acid.

c Reaction M is conducted in the presence of a catalyst. Does the presence of this catalyst increase, decrease or not change each of the following characteristics of the reaction?

i ΔH value

ii Equilibrium yield of SO_3

iii Rate of reverse reaction

Section 3: Extended answer

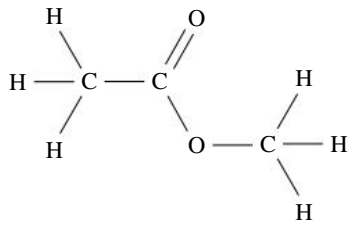
1 A 6.500 g sample of an organic compound ($C_xH_yO_z$) was burnt in excess oxygen. 4.74 g of water, and 11.60 g of carbon dioxide were produced.

In a separate experiment, a 5.01 g sample of the compound was vaporised. The vapour occupied 2.22 L at 200°C and 1.20×10^2 kPa.

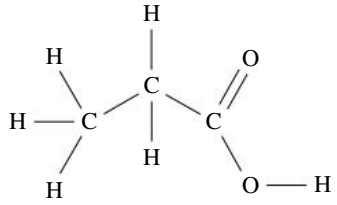
a Show that the molecular formula of the compound is $C_3H_6O_2$.

b Two possible molecular structures for the compound are shown below.

isomer I



isomer II

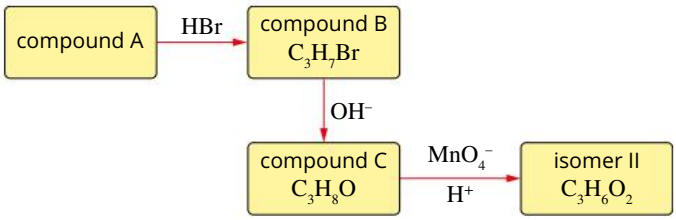


i Give the systematic name of isomer I.

ii Describe a simple laboratory test, including the results of the test, which could distinguish between samples of the isomers I and II above.

iii Draw a structural formula for, and give the name of, another isomer of $C_3H_6O_2$.

c Isomer II may be produced using the reaction sequence shown below.



i Draw the structural formula for compound B.

ii Compound C, C_3H_8O, has a molar mass of 60 g mol^{-1} and a boiling point of 97°C.

Propanone (C_3H_6O) has a molar mass of 58 g mol^{-1} and a boiling point of 56°C.

Account for the difference in the boiling point of these two compounds of similar molar mass.

iii Write the expected observations that could be made when substance C reacts with an acidified solution of potassium permanganate to produce isomer II. Include the appearance of reactants and products in your answer.

2 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 residue, is shown below. Met-enkephalin may undergo acid catalysed hydrolysis to release the four different amino acids.

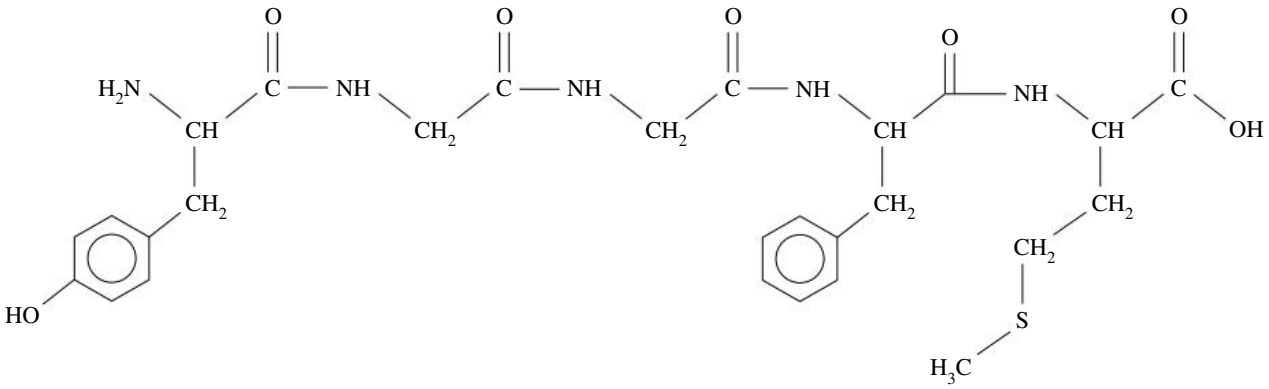
a i Refer to a table of amino acids in your Chemistry Data Booklet and use it to name the amino acids (other than methionine) present in met-enkephalin.

ii On the structure shown below, circle and label two peptide linkages.

iii On the structure shown below, circle and label the terminal carboxyl and amino groups.

iv Draw the structure of the methionine amino acid as it would exist in the acidic hydrolysis solution.

v At a particular pH, an amino acid has both a positive and negative charge and is known as a zwitterion. Draw the zwitterion structure for one of the amino acids in met-enkephalin other than methionine.



b Enkephalins are short polypeptides. Much longer polypeptides form proteins, whose structure may be described in terms of primary, secondary and tertiary structures.

Give explanations for the following facts relating to protein structure and function.

i Formation of the primary structure of proteins produces water as a by-product, but formation of secondary, tertiary and quaternary structures do not.

ii Despite having unique and very different amino acid sequences, almost all proteins are able to form α-helical and β-pleated regions.

iii All proteins are denatured by extreme pH changes, but some enzymes can lose their activity as a result of even relatively small pH changes without being fully denatured.

iv The tertiary structures of some proteins are more easily disrupted by an increase in temperature than are those of others.

c Proteins are formed by condensation polymerisation of amino acids. Another similar condensation polymer is nylon. The structure of one nylon molecule is shown below.

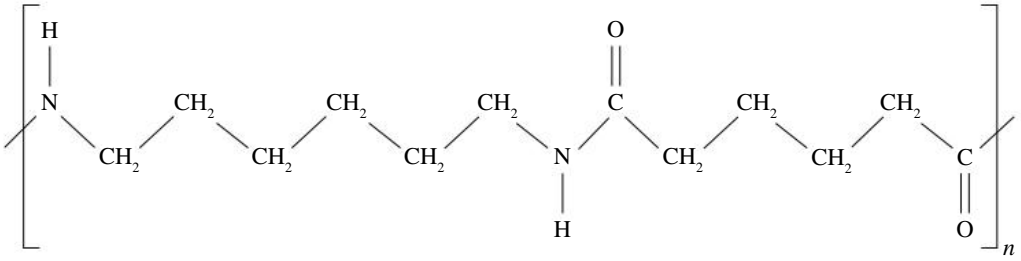
This nylon is composed of two alternating monomers. One of these monomers shows a strongly basic character.

i Draw the structural formula of this basic monomer.

ii Write an equation to show the reaction of this monomer with excess hydrochloric acid (states are not required).

iii State one structural similarity between proteins and nylon.

iv State one structural difference between proteins and nylon.



APPENDIX A Symbols, units and fundamental constants

TABLE 1 Units and symbols based on the SI system. Units listed in red are the arbitrarily defined fundamental units of the SI system

Quantity	Symbol for physical quantity	Corresponding SI unit	Symbol for SI unit	Definition of SI unit
Mechanics				
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 potential difference	V	volt	V	J A^{-1} s^{-1}
Nuclear and chemical quantities				
Atomic number	Z	—	—	—
Neutron number	N	—	—	—
Mass number	A	—	—	$Z + N$
Amount of substance	n	mole	mol	fundamental unit
Relative atomic mass	A_r	—	—	—
Relative molecular mass	M_r	—	—	—
Molar mass	M	—	—	kg mol^{-1}
Molar volume	V_m	—	—	m^3 mol^{-1}
Concentration	c	—	—	mol m^{-3}
Thermal quantities				
Temperature	T	kelvin	K	fundamental unit
Specific heat capacity	C	—	—	J K^{-1} kg^{-1}

TABLE 2 SI prefixes, their symbols and values

SI prefix	Symbol	Value
pico	p	10^{-12}
nano	n	10^{-9}
micro	μ	10^{-6}
milli	m	10^{-3}
centi	c	10^{-2}
deci	d	10^{-1}
kilo	k	10^{3}
mega	M	10^{6}
giga	G	10^{9}
tera	T	10^{12}

TABLE 3 Some physical constants

Description	Symbol	Value
Avogadro's constant	N_A	6.022×10^{23} mol^{-1}
Charge of an electron	e	-1.60×10^{-19} C
Mass of electron	m_e	9.109×10^{-31} kg
Mass of proton	m_p	1.673×10^{-27} kg
Mass of neutron	m_n	1.675×10^{-27} kg
Gas constant	R	8.31 J K^{-1} mol^{-1}
Ionic product for water	K_w	1.00×10^{-14} at 298 K
Molar volume of an ideal gas	V_m	
at 273 K, 100 kPa		22.71 L mol^{-1}
Specific heat capacity of water	c	4.18 J^{-1} g^{-1} K^{-1}
Density of water	d	1.00 g mL^{-1} at 298 K

APPENDIX B Significant figures and standard form

SIGNIFICANT FIGURES

The number of significant figures a piece of data has indicates the precision of a measurement. For example, compare the following data:

- A jogger takes 20 minutes to cover 4 kilometres.
- A sprinter takes 10.21 seconds to cover 100.0 metres.

The sprinter's data has been measured more precisely than that of the jogger. This is indicated by the greater number of significant figures in the second set of data.

Which figures are significant?

A significant figure is an integer or a zero that follows an integer.

In the data above, the:

- distance '4 kilometres' has one significant figure
- time '20 minutes' has two significant figures (the zero follows the integer 2)
- 10.21 seconds and 100.0 metres each have four significant figures.

A zero that comes before any integers, however, is not significant. For example:

- the value 0.0004 has only one significant figure, whereas the value 0.0400 has three significant figures. The zeros that come before the integer 4 are not significant, whereas those that follow the integer are significant.

Using significant figures

In chemistry you will often need to calculate a value from a set of data. It is important to remember that the final value you calculate is only as precise as your *least precise piece of data*.

Addition and subtraction

When adding or subtracting values, the answer should have no more digits to the right of the decimal place than the value with the least number of digits to the right of the decimal place.

Example

12.78 mL of water was added to 10.0 mL of water. What is the total volume of water?

12.78 mL + 10.0 mL = 22.78 = 22.8 mL

Because one of the values (10.0 mL) has only one digit to the right of the decimal place, the answer will need to be adjusted so that it too has only one digit to the right of the decimal place.

Multiplication and division

When multiplying and dividing values, the answer should have no more significant figures than the value with the least number of significant figures.

Example

An athlete takes 3.5 minutes to complete four laps of an oval. What is the average time taken for one lap?

$$\text{Average time} = \frac{3.5 \text{ minutes}}{4} = 0.875 = 0.88 \text{ minutes}$$

Because the data (3.5 minutes) has only two significant figures, the answer will need to be adjusted to two significant figures so that it has the same degree of precision as the data. (Note: The 'four' is taken to indicate a precise number of laps and so is considered to have as many significant figures as the calculation requires. This applies to values that describe *quantities* rather than *measurements*.)

Rounding off

When adjusting the number of significant figures, if the integer after the last significant figure is equal to or greater than '5', then the last significant integer is rounded up. Otherwise, it is rounded down.

STANDARD FORM

A value written in standard form is expressed as a number equal to or greater than 1 and less than 10 multiplied by 10^x, where x is an integer. For example, when written in standard form:

- 360 becomes 3.6×10^2
- 0.360 becomes 3.60×10^{-1}
- 0.000456 becomes 4.56×10^{-5}.

Sometimes you will need to use standard form to indicate the precision of a value.

APPENDIX C Table of relative atomic masses*

TABLE 1 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	—	Hafnium	Hf	72	178.49	Praseodymium	Pr	59	140.9077
Aluminium	Al	13	26.9815	Hassium	Hs	108	—	Promethium	Pm	61	—
Americium	Am	95	—	Helium	He	2	4.00260	Protactinium	Pa	91	231.0359
Antimony	Sb	51	121.76	Holmium	Ho	67	164.9303	Radium	Ra	88	—
Argon	Ar	18	39.948	Hydrogen	H	1	1.0080	Radon	Rn	86	—
Arsenic	As	33	74.9216	Indium	In	49	114.82	Rhenium	Re	75	186.21
Astatine	At	85	—	Iodine	I	53	126.9045	Rhodium	Rh	45	102.9055
Barium	Ba	56	137.33	Iridium	Ir	77	192.22	Roentgenium	Rg	111	—
Berkelium	Bk	97	—	Iron	Fe	26	55.845	Rubidium	Rb	37	85.468
Beryllium	Be	4	9.01218	Krypton	Kr	36	83.80	Ruthenium	Ru	44	101.07
Bismuth	Bi	83	208.9804	Lanthanum	La	57	138.9055	Rutherfordium	Rf	104	—
Bohrium	Bh	107	—	Lawrencium	Lr	103	—	Samarium	Sm	62	150.4
Boron	B	5	10.81	Lead	Pb	82	207.2	Scandium	Sc	21	44.9559
Bromine	Br	35	79.904	Lithium	Li	3	6.94	Seaborgium	Sg	106	—
Cadmium	Cd	48	112.41	Livermorium	Lv	116	—	Selenium	Se	34	78.97
Caesium	Cs	55	132.9055	Lutetium	Lu	71	174.967	Silicon	Si	14	28.086
Calcium	Ca	20	40.08	Magnesium	Mg	12	24.305	Silver	Ag	47	107.868
Californium	Cf	98	—	Manganese	Mn	25	54.9380	Sodium	Na	11	22.9898
Carbon	C	6	12.011	Meitnerium	Mt	109	—	Strontium	Sr	38	87.62
Cerium	Ce	58	140.12	Mendelevium	Md	101	—	Sulfur	S	16	32.06
Chlorine	Cl	17	35.453	Mercury	Hg	80	200.59	Tantalum	Ta	73	180.9479
Chromium	Cr	24	51.996	Molybdenum	Mo	42	95.95	Technetium	Tc	43	—
Cobalt	Co	27	58.9332	Moscovium	Mc	115	—	Tellurium	Te	52	127.60
Copernicium	Cn	112	—	Neodymium	Nd	60	144.24	Tennessine	Ts	117	—
Copper	Cu	29	63.55	Neon	Ne	10	20.180	Terbium	Tb	65	158.9254
Curium	Cm	96	—	Neptunium	Np	93	—	Thallium	Tl	81	204.384
Darmstadtium	Ds	110	—	Nickel	Ni	28	58.693	Thorium	Th	90	232.038
Dubnium	Db	105	—	Nihonium	Nh	113	—	Thulium	Tm	69	168.9342
Dysprosium	Dy	66	162.50	Niobium	Nb	41	92.9064	Tin	Sn	50	118.71
Einsteinium	Es	99	—	Nitrogen	N	7	14.0067	Titanium	Ti	22	47.87
Erbium	Er	68	167.26	Nobelium	No	102	—	Tungsten	W	74	183.84
Europium	Eu	63	151.96	Oganesson	Og	118	—	Uranium	U	92	238.0289
Fermium	Fm	100	—	Osmium	Os	76	190.2	Vanadium	V	23	50.942
Flerovium	Fl	114	—	Oxygen	O	8	15.9994	Xenon	Xe	54	131.29
Fluorine	F	9	18.9984	Palladium	Pd	46	106.4	Ytterbium	Yb	70	173.05
Francium	Fr	87	—	Phosphorus	P	15	30.9738	Yttrium	Y	39	88.9058
Gadolinium	Gd	64	157.25	Platinum	Pt	78	195.08	Zinc	Zn	30	65.38
Gallium	Ga	31	69.72	Plutonium	Pu	94	—	Zirconium	Zr	40	91.22
Germanium	Ge	32	72.63	Polonium	Po	84	—				
Gold	Au	79	196.9666	Potassium	K	19	39.098				

* Based on the atomic mass of $^{12}C = 12$.
The values for relative atomic masses given in the table apply to elements as they exist in nature, without artificial alteration of their isotopic composition, and, further, to natural mixtures that do not include isotopes of radiogenic origin.

APPENDIX D Common positive and negative ions and solubility of common ionic compounds in water

TABLE 1 Names and formulae of some common positive and negative 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+}	Dihydrogen phosphate	$H_2PO_4^-$	Hydrogen phosphate	HPO_4^{2-}
Potassium	K^+	Copper(II)	Cu^{2+}			Ethanoate	CH_3COO^-	Oxalate	$C_2O_4^{2-}$
Rubidium	Rb^+	Iron(II)	Fe^{2+}	+4		Fluoride	F^-	Oxide	O^{2-}
Silver	Ag^+	Lead(II)	Pb^{2+}	Lead(IV)	Pb^{4+}	Hydrogen carbonate	HCO_3^-	Sulfide	S^{2-}
Sodium	Na^+	Magnesium	Mg^{2+}	Tin(IV)	Sn^{4+}	Hydrogen sulfide	HS^-	Sulfite	SO_3^{2-}
		Manganese(II)	Mn^{2+}			Hydrogen sulfite	HSO_3^-	Sulfate	SO_4^{2-}
		Mercury(II)	Hg^{2+}			Hydrogen sulfate	HSO_4^-		
		Nickel	Ni^{2+}			Hydroxide	OH^-	−3	
		Strontium	Sr^{2+}			Iodide	I^-	Nitride	N^{3-}
		Tin(II)	Sn^{2+}			Nitrite	NO_2^-	Phosphate	PO_4^{3-}
		Zinc	Zn^{2+}			Nitrate	NO_3^-		
						Permanganate	MnO_4^-		

TABLE 2 Solubility of common ionic compounds in water

Soluble ionic compounds		
Soluble in water (>0.1 mol dissolves per L at 25°C)	**Exceptions: insoluble (<0.01 mol dissolves per L at 25°C)**	**Exceptions: slightly soluble (0.01–0.1 mol dissolves per L at 25°C)**
Most chlorides (Cl^-), bromides (Br^-) and iodides (I^-)	AgCl, AgBr, AgI, PbI_2	$PbCl_2$
All nitrates (NO_3^-)	No exceptions	No exceptions
All ammonium (NH_4^+) salts	No exceptions	No exceptions
All sodium (Na^+) and potassium (K^+) salts	No exceptions	No exceptions
All ethanoates (CH_3COO^-)	No exceptions	No exceptions
Most sulfates (SO_4^{2-})	$SrSO_4$, $BaSO_4$, $PbSO_4$	$CaSO_4$, Ag_2SO_4
Insoluble ionic compounds		
Insoluble in water	**Exceptions: soluble**	**Exceptions: slightly soluble**
Most hydroxides (OH^-)	NaOH, KOH, $Ba(OH)_2$, NH_4OH*, AgOH**	$Ca(OH)_2$, $Sr(OH)_2$
Most carbonates (CO_3^{2-})	Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$	No exceptions
Most phosphates (PO_4^{3-})	Na_3PO_4, K_3PO_4, $(NH_4)_3PO_4$	No exceptions
Most sulfides (S^{2-})	Na_2S, K_2S, $(NH_4)_2S$	No exceptions

*NH_4OH does not exist in significant amounts in an ammonia solution. Ammonium and hydroxide ions readily combine to form ammonia and water.
**AgOH readily decomposes to form a precipitate of silver oxide and water.

APPENDIX E Electrochemical series

Half-reaction	E° (volts)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.89
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.76
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.69
$2HClO(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l)$	+1.63
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$HClO(aq) + H^+(aq) + 2e^- \rightleftharpoons Cl^-(aq) + H_2O(l)$	+1.49
$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$	+1.46
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.08
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.70
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(aq)$	+0.17
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0 exactly
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	–0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	–0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	–0.24
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	–0.28
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$	–0.36
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	–0.40
$2CO_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2C_2O_4(aq)$	–0.43
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	–0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	–0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	–0.83
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	–1.18
$Al^{3+} + 3e^- \rightleftharpoons Al(s)$	–1.68
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	–2.36
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	–2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	–2.87
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	–2.90
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	–2.91
$K^+(aq) + e^- \rightleftharpoons K(s)$	–2.94

APPENDIX F Mathematical skills for chemistry ATAR

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 ten notation) is written as:

$$a \times 10^n$$

where a is a number equal to or greater than 1 and less than 10, that is $1 \leq a < 10$.

n is an integer (a positive or negative whole number).

n is the power that 10 is raised to and is called the index value.

To transform a very large or very small number into scientific notation:

Write the original number as a decimal number greater than or equal to 1 but less than 10.

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.

If the decimal point is moved n places to the right, n will be a positive number. For example:

$$51 = 5.1 \times 10^1$$

If the decimal point is moved n places to the left, n will be a negative number. For example:

$$0.51 = 5.1 \times 10^{-1}$$

You will notice from these examples that when large numbers are written in scientific notation, the 10 has a positive index value. When very small numbers are written in scientific notation, the 10 has a negative index value.

Practice questions

1 Match each number with its correct scientific notation.

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

2 Write 7.009×10^{-4} using decimal notation.

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 a set of scales 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, 56.1 g, 56.2 g or 55.8 g.

56 is a number with two 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 two significant figures.

Determining to what number of significant figures to give an answer to depends on what 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.

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

Practice questions

1. Which of the following is written to two significant figures?
   A 30.1
   B 0.000 40
   C 0.5
   D 5.12
2. George multiplied 1.22 by 1.364. Which of the options below shows the result of this multiplication with the correct number of significant figures?
   A 1.66
   B 1.664
   C 1.65
   D 1.7
3. How can 41 be written to four significant figures?
   A 00.41
   B 4100
   C 41.00
   D 4.100
4. Alex is getting ready to go for a bike ride. Alex's mass is 65.3 kg. The bicycle has a mass of 12.92 kg.
   a Calculate the combined mass of Alex and the bicycle. Give your answer to the correct number of significant figures.
      A 78
      B 78.2
      C 78.22
      D 78.3
   b Using the combined mass calculated in part **a** above, and the formula $F_{net} = ma$, calculate the force Alex needs to apply to achieve an acceleration of 1.250 $m s^{-1}$. Give your answer to the correct number of significant figures.

3. Calculating percentages

Scientists use percentages to express a ratio or fraction of a quantity.

To express one quantity as a percentage of another, use the second quantity to represent 100%.

For example, expressing 6 as a percentage of 24 is like saying '6 is to 24 as x is to 100':

$$\frac{6}{24} = \frac{x}{100}$$
$$x = \frac{6}{24} \times 100$$
$$= 25\%$$

To calculate a percentage of a quantity, the percentage is expressed as a decimal then multiplied by the quantity.

For example, to calculate 40% of 20:

$$x = \frac{40}{100} \times 20$$
$$= 0.4 \times 20$$
$$= 8$$

Practice questions

1 What is 9 as a percentage of 12?
- **A** 25%
- **B** 50%
- **C** 75%
- **D** 30%

2 What is 25% of 24?
- **A** 6.6
- **B** 6
- **C** 5
- **D** 0.5

3 Which of the following values expresses 15 as a percentage of 120?
- **A** 8%
- **B** 5%
- **C** 12.5%
- **D** 0.125%

4 Converting between percentages and fractions

To write a percentage as a fraction, divide the percentage by 100.

For example:

$$25\% = \frac{25}{100}$$
$$= \frac{1}{4}$$

$\frac{25}{100}$ is not the simplest form of this fraction. If you divide both the numerator and the denominator by 25 (their highest common factor) then the fraction simplifies to $\frac{1}{4}$.

Whenever you give a fraction as an answer, always try and simplify it by dividing the numerator and denominator by the highest common factor.

To write a fraction as a percentage, multiply the fraction by 100%. In many cases it is easier to convert the fraction to a decimal number first.

For example:

$$\frac{1}{4} = 0.25 \times 100$$
$$= 25\%$$

The value of the fraction or percentage has not changed. It is just being represented in a different way.

Practice questions

1 Choose the option that expresses $\frac{1}{5}$ as a percentage.
A 25%
B 20%
C 30%
D 50%

2 Match each percentage with its corresponding fraction.

Percentage	Fraction
0.2%	$\frac{7}{20}$
2.5%	$\frac{7}{40}$
17.5%	$\frac{1}{40}$
35%	$\frac{111}{250}$
44.4%	$\frac{1}{500}$

5. Changing the subject of an equation

Scientists use equations to represent relationships between variables. In an equation like $A = \pi r^2$, A is called the subject of the equation.

Sometimes the subject of the equation has to be changed in order to express the relationship in a more useful way. For example, if you need to find the radius of a circle, you would want r to be the subject of the equation above.

To change the subject of a simple equation, transpose the equation to leave the new subject on its own. In the example above, the equation needs to read

$r = \ldots$

Keep the equation balanced by performing the same operation to both sides of the equation to cancel operations being performed on the desired subject. Inverse operations (the opposite operation; for example dividing is the inverse of multiplying) will allow cancelling.

For example, make r the subject of the equation $A = \pi r^2$.

1 Divide both sides of the equation by π.

$$A = \pi r^2$$

$$\frac{A}{\pi} = \frac{\pi r^2}{\pi}$$

The π in the numerator and denominator on the right side of the equation cancel out, giving

$$\frac{A}{\pi} = r^2$$

2 To cancel the squaring operation of r, take the square root of both sides of the equation.

$$\frac{A}{\pi} = r^2$$

$$\sqrt{\frac{A}{\pi}} = \sqrt{r^2}$$

The square and square root on the right side of the equation cancel out, giving

$$\sqrt{\frac{A}{\pi}} = r$$

3 r is now the subject of the equation.

$$r = \sqrt{\frac{A}{\pi}}$$

Practice questions

1 Rearrange the formula $A = \frac{2}{3}R$ to make R the subject.

A $R = \frac{2A}{3}$

B $R = \frac{A}{3}$

C $R = \frac{3A}{2}$

D $R = 6A$

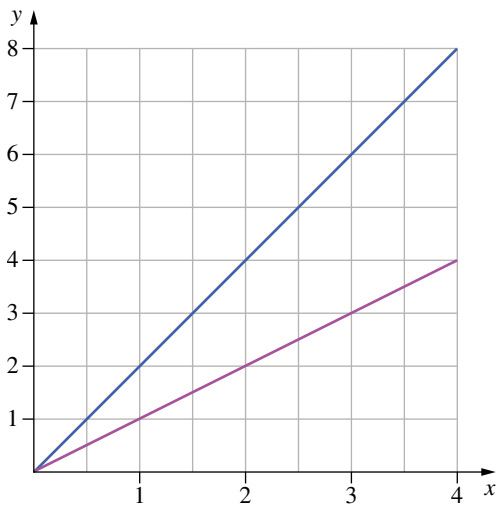
2 Rearrange the formula $y = 3\sqrt{\frac{p}{q}}$ to make p the subject.

6 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).

The graph below has two straight lines with different slopes. The steeper slope (blue line) indicates that the rate of change is higher. This means the change is happening more quickly. On the other hand, the flatter slope (red line) indicates that the rate of change is lower. This means the change is happening more slowly.



Practice questions

1 On a graph with two sloped lines, what does the steeper sloped line indicate?
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.

2 The rate of change of a straight line on a graph is given by the:
A *y*-intercept
B *x*-intercept
C gradient
D area under the graph.

7. Understanding mathematical symbols

Part of the language of science is using symbols to represent quantities or to give meanings. For example, the four symbols <, >, ≤ and ≥ are known as 'inequalities'.

The following mathematical symbols are commonly used in science.

Symbol	Meaning	Example	Explanation
<	less than	$2 < 3$	2 is less than 3
>	greater than	$6 > 1$	6 is greater than 1
≤	less than or equal to	$2x \leq 10$	$2x$ is less than or equal to 10
≥	greater than or equal to	$3y \geq 12$	$3y$ is greater than or equal to 12
$\sqrt{}$	square root	$\sqrt{4} = 2$	The square root of 4 is 2
Δ	change in (difference between)	Δt	change in t (time)
≈	approximately equal to	$\pi \approx 3.14$	π is approximately equal to 3.14
Σ	summation	$\sum_{i=1}^{4} i$	The sum of consecutive integers from 1 to 4, i.e. 1 + 2 + 3 + 4 = 10

Practice questions

1 The symbol that means 'less than' is:
A <
B >
C ≤
D ≥

2 Which of these symbols is an inequality?
A ≈
B Δ
C $\sqrt{}$
D ≤

8 Understanding the difference between discrete and continuous data

Quantitative data forms the backbone of science. Scientists are constantly working with data—measuring, recording, analysing and interpreting it.

Quantitative data consists of numerical values that can either be discrete or continuous.

Discrete data is data that has a set of clearly defined values. For example, the number of students in a class would have a discrete set of possible data.

Continuous data is usually data that is measured in some way and can have an infinite number of values. For example, your height or weight would have a continuous set of possible data.

The easiest way to distinguish between the two types of quantitative data is to ask, 'Is the data measured or counted?' If it is counted, the data set is discrete. If it is measured, the data set is continuous.

Practice questions

1 Which one of these data sets is continuous?
- **A** the number of cars parked in a street
- **B** the temperature of the air over a 24-hour period
- **C** the number of students at a school
- **D** the number of nails used to build a fence.

2 Which one of these data sets is discrete?
- **A** the number of cars parked in a street
- **B** the temperature of the air over 24 hours
- **C** the heights of a team of footballers
- **D** the mass of a team of netballers.

9. Calculating the mean, median and range of a data set

When handling data, scientists often look for ways to describe patterns in the data. Common terms used when analysing a set of data include the mean, median and range.

Mean: the *average* value in the data set. To calculate the mean, sum all the values in the data set and then divide this by the number of data values.

Median: the *middle* value in an ordered data set. To calculate the median, arrange the data set in ascending order and then count the number of data values. If the number of values is odd, the median is the middle value. If the number of values is even, calculate the median by adding the two middle values and dividing by 2, i.e. by calculating the average of the two middle numbers.

Range: the *spread* of values in the data set. To calculate the range, take the largest data value and then subtract the smallest data value.

Practice questions

1 The following set of data is recorded:
44, 17, 21, 26, 42, 18
Find the
- **a** mean
- **b** median
- **c** range.

2 The mass in kilograms of each student in a class of 25 students is recorded below. The combined mass of all the students is 1340 kg.
Find the
- **a** mean
- **b** median
- **c** range.

Students' weights: 67, 60, 41, 52, 39, 60, 42, 55, 55, 50, 46, 62, 48, 48, 56, 64, 55, 56, 59, 61, 41, 63, 53, 62, 45

10. Solving simple algebraic equations

To solve an equation means to find the values that make the equation true. Scientists manipulate equations and substitute in known variables in order to solve for the variable required.

For example, you can solve

$$a = \frac{F_{\text{net}}}{m}$$

where F_{net} is the net force on the car, which is 2400 N
m is the mass of the car, which is 1200 kg
a is the acceleration of the car in $m\,s^{-2}$, which is unknown.

$$a = \frac{2400}{1200}$$
$$= 2\,m\,s^{-2}$$

Practice questions

1 Solve the equation $V = IR$ if $I = 3$ and $R = 9$.
A $V = 3$
B $V = 6$
C $V = 12$
D $V = 27$

2 Solve the equation and find the value of Q if $Q = mc\Delta T$, $m = 1.2$, $c = 4200$ and $\Delta T = 30$.
A $Q = 840$
B $Q = 25\,200$
C $Q = 126\,000$
D $Q = 6$

11. Completing calculations with more than one operation

Scientists often deal with complex calculations that can involve numerous operations within the one calculation. The order in which these operations are performed can affect the result of the calculation.

For example, the calculation $2 + 3 \times 4$ will give an incorrect answer of 20 if you calculate the $2 + 3$ part first, but it will give the correct answer of 14 if you calculate the 3×4 part first.

Scientists and mathematicians have agreed on a set order in which operations are carried out so that calculations are consistent. You can remember this order using the acronym 'BIDMAS':

- brackets
- indices (powers, square roots, etc.)
- division and multiplication
- addition and subtraction.

The operations present in a calculation are performed in the order shown in the list. If there are multiple instances of division and multiplication, or addition and subtraction, work from left to right.

For example, the 3×4 part in the original example would always be performed first, since multiplication is higher in the list than addition.

When dealing with scientific notation, it is important to keep each individual number complete. Use brackets to help do this, especially when dividing.

For example, when dividing 3.01×10^{21} by 6.02×10^{23}, brackets are used to keep the second number together.

If you used a calculator and entered $\frac{3.01 \times 10^{21}}{6.02 \times 10^{23}}$ (i.e. $3.01 \times 10^{21} \div 6.02 \times 10^{23}$), the answer would come out as 5.00×10^{43}. This is not the correct answer.

The correct answer is only obtained by entering $\frac{3.01 \times 10^{21}}{\left(6.02 \times 10^{23}\right)}$. This time, the answer comes out correctly as 5.00×10^{-3}.

Using the calculator's *EXP* button or the $x10^x$ button keeps the number and power of 10 together as one number and avoids the problems of using the number multiplied by 10^x. If your calculator does not have an *EXP* or $x10^x$ button, check the user manual. It may be that it is just labelled differently on your calculator. Alternatively, remember to always use brackets to keep the terms in the denominator together, as shown above.

Practice questions

1 What is 3.4×10^{-4} divided by 1.7×10^{-3}?
A 2×10^{-7}
B 2
C 20
D 0.2

2 Substitute $m = 1.4$, $d = 3.9$ and $c = 2.7$ into $W = 6m - 4(d + c)$ and solve for W.
A –4.5
B –18
C 34.8
D 26.7

12. Understanding the relationship between data, graphs and algebraic rules

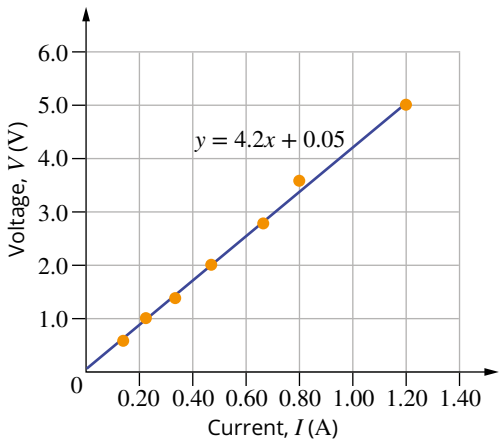
Scientists use graphs to analyse the data they collect from experiments. All graphs tell a story. The shape of the graph shows the relationship between the variables, and this relationship can be written algebraically and numerically. The horizontal axis is known as the *x*-axis and the vertical axis is known as the *y*-axis.

Once the algebraic rule is known, the values for one variable can be substituted and the values for the other variable can be calculated. These values can also be determined by reading them from the graph.

For example, when investigating how current and voltage vary across a light bulb, the following data was collected:

Current, *I* (A)	Voltage, *V* (V)
0.14	0.6
0.22	1.0
0.33	1.4
0.47	2.0
0.66	2.8
0.80	3.6
1.20	5.0

Graphing this data produced:



The numerical values from the experiment are listed in the table and plotted on the graph. The algebraic relationship between the variables is given by the equation of the line:

$$y = 4.2x + 0.05$$

The value of the y-intercept is approximately zero, so assuming that the y-intercept is zero, and labelling the x-axis as current and the y-axis as voltage, the relationship can be written as:

$$y = 4.2 \times \text{current}$$

Using the appropriate symbols this can also be written as: $V = 4.2I$

Practice questions

1 If a graph had L on the y-axis and B on the x-axis and the equation of the straight line was $y = 3.7x$, what is the algebraic form of the graph?
- **A** $L = 3.7x$
- **B** $y = 3.7x$
- **C** $y = 3.7B$
- **D** $L = 3.7B$

2 If a relationship was written as $m = 5.9L$, what shape would the graph be and which variable would be plotted on which axis?
- **A** The graph would be non-linear, with m on the y-axis and L on the x-axis.
- **B** The graph would be non-linear, with m on the x-axis and L on the y-axis.
- **C** The graph would be linear, with m on the y-axis and L on the x-axis.
- **D** The graph would be linear, with m on the x-axis and L on the y-axis.

13. Recognising and using ratios

A ratio is the relationship between two numbers of the same kind. It could be the quantities in a recipe, the division of profits from a sale, or the number of different types of the same thing.

Scientists use ratios to compare quantities. This might be the numbers of atoms of different elements in a compound, or the number of primary and secondary windings of a transformer.

You can also use the principle of ratios to solve problems. For example, if 1 reaction produces 2.5 MeV of energy, then how much energy does 34 reactions produce?

The reaction-to-energy ratio of 1:2.5 should remain constant as the number of reactions increases. So you need to find the factor that 1 needs to be multiplied by to give 34:

$$1 \times 34 = 34$$

You then multiply the energy amount by the same factor:

$$2.5 \times 34 = 85\,\text{MeV}$$

You may also see ratios expressed as fractions.

Practice questions

1 If the primary coil of a transformer has 2400 windings and the secondary coil has 600 windings, what is the simplest ratio of primary to secondary windings?
- **A** 2400:600
- **B** 24:6
- **C** 12:3
- **D** 4:1

14. Understanding pie charts, frequency graphs, and histograms

It is essential in science to collect data and arrange it in an orderly way. Tables are often used to organise data, which can then be displayed in a graph.

Pie charts

A pie chart is a circle that is divided into sectors. Each sector represents one item in the data set and is shown as a percentage or fraction of the total data set.

Frequency graphs and histograms

Frequency graphs and histograms are another way of representing data visually.

If data is discrete (i.e. can be counted), each column in a column graph will represent one category, e.g. 'apples' or 'strawberries'. Often these columns have a gap between them.

If the data is continuous (i.e. can be measured), such as the heights of the students in that class, each column will represent a range of possible heights, e.g. 140 to 160 cm, and there will be no gaps between the columns. These are called histograms.

Practice questions

1 Choose the pie chart that correctly shows the data from Emmanuel's poll of soccer fans.

Number of matches watched	10	12	15	18	21
Relative frequency (%)	25	35	15	15	10

Matches watched:

- = 10
- = 18
- = 12
- = 21
- = 15

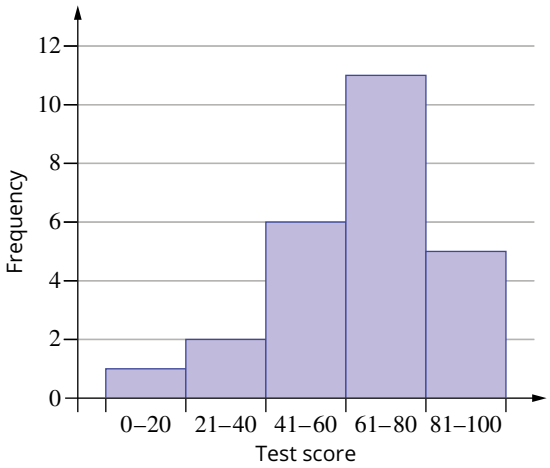
A

B

C

D

2 A class of Year 12 Chemistry students had a test. A histogram of their test scores is shown below.



a How many students scored over 80?
b How many students scored below 40?
c How many student are in this class?

15. Using units in an equation to check for dimensional consistency

Scientists know that each term in an equation represents a quantity. The units used to measure that quantity are not used in the calculations. Units are only indicated on the final line of the solved equation.

For example, this is the equation for the area (A) of a rectangle of length (L) and width (W):

$$A = L \times W$$

If L has a value of 7 m and W has a value of 4 m, it is written:

$$\begin{aligned} A &= L \times W \\ &= 7 \times 4 \\ &= 28\,\text{m}^2 \end{aligned}$$

Note that the units are left out of the actual calculation on the second line and only included at the end, after the numerical answer.

You can use units to check the dimensional consistency of the answer. In the example above, the two quantities of L (length) and W (width) both have to be expressed in consistent units, in this case metres (m), to give an answer that is expressed in square metres ($\text{m} \times \text{m} = \text{m}^2$).

If you had made a mistake, and used the formula $A = L + W$ instead, the answer would be expressed in metres only. This is not the correct unit to express area, so you would know that was wrong.

Practice questions

1 Which formula has the correct dimensions for calculating volume in m^3?
A $\text{m} \times \text{m}$
B $\text{m} \times \text{s}$
C $\text{m} \times \text{m} \times \text{s}$
D $\text{m} \times \text{m} \times \text{m}$

2 Which of these shows the correct substitution into $p = 2L + 2W$ using consistent units for $L = 3.5\,\text{cm}$ and $W = 240\,\text{cm}$?
A $P = 2 \times 3.5 + 2 \times 240$
B $P = 2 \times 3.5 + 2 \times 24$
C $P = 2 \times 35 + 2 \times 240$
D $P = 2 \times 3.5 + 2 \times 2.4$

3 By using the equation $p = mv$ as a guide, select the correct units in which to measure momentum, p (where velocity, v, has the units m s^{-1} and mass, m, has the units kg).
A m s
B m s^{-1}
C kg m s^{-1}
D kg m s^{-2}

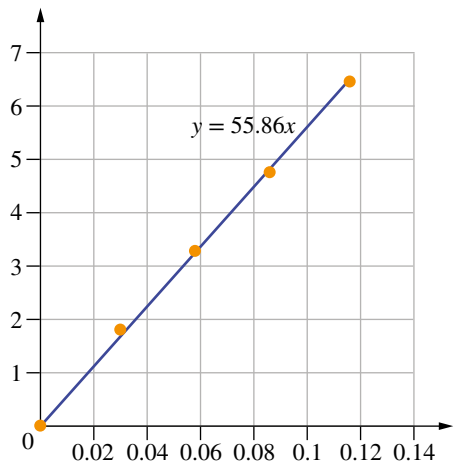
16. Understanding lines of best fit

When scientists observe that the points on a graph seem to form a straight line, then a line of best fit (or trendline) can be drawn through them. Computer programs such as Excel can fit a trendline to a data set; lines of best fit can also be drawn by hand onto a printed or drawn graph.

The line of best fit should pass as closely as possible to as many of the points as possible (i.e. it should 'fit' the data closely). It may not pass exactly through any of the points, but once the line of best fit is drawn, the points should be spaced equally on each side, above and below the line. There should be no points very far away from the line, unless they are considered to be unreliable. Unreliable points are called 'outliers' and can be disregarded for the purposes of creating a line of best fit.

The gradient and y-intercept of the line (not the points) can be determined to find the relationship between the variables using the general equation for a straight line: $y = mx + c$.

For example:



Practice questions

1 Are the following statements true or false?
a All the points on a scatter plot must lie on the line of best fit.
b The line of best fit may pass through none of the points.
c The points of the scatter plot should lie close to the line of best fit.

2 Are the following statements true or false?
a A trendline is the same as a line of best fit.
b A line of best fit can only be drawn using a computer program such as Excel.
c Outliers should be included as normal points when considering where to draw a line of best fit.

Answers to practice questions

1. Transforming decimal notation to scientific notation

1

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

0.002: Move the decimal point 3 places to the right which gives an index of –3, so 0.002 is written as 2×10^{-3}.
2000: Move the decimal point 3 places to the left which gives an index of +3, so 2000 is written as 2×10^{3}.
0.1234: Move the decimal point 1 place to the right which gives an index of –1, so 0.1234 is written as 1.234×10^{-1}.
12.34: Move the decimal point 1 place to the left which gives an index of +1, so 12.34 is written as 1.234×10^{1}.
123.4: Move the decimal point 2 places to the left which gives an index of +2, so 123.4 is written as 1.234×10^{2}.

2 The –4 index shows the decimal point has been moved 4 places to the right. Move it back 4 places to the left to give 0.000 700 9.

2. Identifying significant figures

1 B. 0.000 40

2 A. 1.66
When two numbers are multiplied, use the smallest number of significant figures in the initial values to give your answer. In George's multiplication, the answer is 1.66408, but as 1.22 has 3 significant figures, the correct answer is 1.66.

3 C. 41.00
The zeroes to the right of the decimal point are significant. When writing an answer to a 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, you round up. 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.

4 **a** B. 78.2
When 65.3 is added to 12.92, the answer is 78.22, but only if it is assumed that 65.3 is actually 65.30. When adding or subtracting with significant figures, use the smallest number of significant figures provided in the initial values. As there is no way of knowing the accuracy of beyond 65.3, the answer should only be given to 3 significant figures, which is 1 decimal place, 78.2.

b When multiplying or dividing, use the smallest number of significant figures in the initial values to give your answer.

$$F_{net} = ma$$
$$= 78.2 \times 1.250$$
$$= 97.8$$

Since the mass value only has 3 significant figures, the answer should also only have 3 significant figures. Therefore, even though the calculated answer is 97.75, the answer to 3 significant figures is 97.8 m s^{-1}.

3. Calculating percentages

1 C. 75%

$$\frac{9}{12} = \frac{x}{100}$$
$$x = \frac{9}{12} \times 100$$
$$= 75\%$$

2 B. 6

$$x = \frac{25}{100} \times 24$$
$$= 0.25 \times 24$$
$$= 6$$

3 C. 12.5%

$$\frac{15}{120} = \frac{x}{100}$$
$$x = \frac{15}{120} \times 100$$
$$= 12.5\%$$

4. Converting between percentages and fractions

1 B. 20%
To write a fraction as a percentage, multiply the fraction by 100.

$$\frac{1}{5} = 0.2 \times 100$$
$$= 20\%$$

2

0.2%	$\frac{1}{500}$
2.5%	$\frac{1}{40}$
17.5%	$\frac{7}{40}$
35%	$\frac{7}{20}$
44.4%	$\frac{111}{250}$

To change a percentage to a fraction, divide by 100.

$$0.2\% = \frac{0.2}{100} = \frac{2}{1000} = \frac{1}{500}$$
$$2.5\% = \frac{2.5}{100} = \frac{25}{1000} = \frac{1}{40}$$
$$17.5\% = \frac{17.5}{100} = \frac{175}{1000} = \frac{35}{200} = \frac{7}{40}$$
$$35\% = \frac{35}{100} = \frac{7}{20}$$
$$44.4\% = \frac{44.4}{100} = \frac{444}{1000} = \frac{222}{500} = \frac{111}{250}$$

5. Changing the subject of an equation

1 C

$R = \frac{3A}{2}$

Multiply both sides of the equation by 3:

$3A = 3 \times \frac{2}{3}R$

$= 2R$

Divide both sides of the equation by 2:

$\frac{3A}{2} = R$

Rewrite the equation so it reads:

$R = \frac{3A}{2}$

2 $p = \frac{y^2q}{9}$

Divide both sides of the equation by 3:

$\frac{y}{3} = \sqrt{\frac{p}{q}}$

Square both sides:

$\left(\frac{y}{3}\right)^2 = \frac{p}{q}$

Expand the brackets on the left:

$\frac{y^2}{9} = \frac{p}{q}$

Multiply both sides by q:

$\frac{y^2q}{9} = p$

Rewrite the equation so it reads:

$p = \frac{y^2q}{9}$

6. Interpreting the slope of a linear graph

1 A. The steepness of the slope indicates the rate of change. A line with a steeper slope indicates a faster rate of change.

2 C. The gradient or slope of a linear graph indicates the rate of change.

7. Understanding mathematical symbols

1 A <. One way is to remember that the smaller end of the shape points toward the smaller number. For example, 3 < 6 means 3 is less than 6.

2 D ≤. The symbols <, >, ≤ and ≥ are all inequalities.

8. Understanding the difference between discrete and continuous data

1 B. The temperature of the air over a 24-hour period.
If the data can be counted, the data set is discrete. If the data can be measured, the data set is continuous. The temperature of the air can be measured with a thermometer, so the data set is continuous.

2 A. The number of cars parked in a street.
If the data can be counted, the data set is discrete. If the data can be measured, the data set is continuous. The number of cars parked in a street can be counted, so the data set is discrete.

9. Calculating the mean, median and range of a data set

1 **a** $44 + 17 + 21 + 26 + 42 + 18 = 168$

$\frac{168}{6} = 28$

b Place the numbers in ascending order: 17, 18, 21, 26, 42, 44
As there is an even number of values, add the two middle values and divide by 2

$\frac{21+26}{2} = 23.5$

c $44 - 17 = 27$

2 **a** $\frac{1340}{25} = 53.6$ kg

b 55 kg

c $67 - 39 = 28$ kg

10. Solving simple algebraic equations

1 D $V = 27$

Substitute the values and solve the equation.

$V = 3 \times 9$

$= 27$

2 B $Q = 25\,200$

Substitute the values and solve the equation.

$Q = 0.2 \times 4200 \times 30$

$= 25\,200$

11. Completing calculations with more than one operation

1 D 0.2

The correct calculation, using brackets, is:

$\frac{3.4 \times 10^{-4}}{(1.7 \times 10^{-3})} = 0.2$

2 B −18

$W = 6 \times 1.4 - 4 \times (3.9 + 2.7)$

$= 6 \times 1.4 - 4 \times 6.6$

$= 8.4 - 26.4$

$= -18$

12. Understanding the relationship between data, graphs and algebraic rules

1 D. $L = 3.7B$

Substituting L for y and B for x gives $L = 3.7B$.

2 C. The graph would be linear, with m on the y-axis and L on the x-axis.

The graph would be linear as the equation is written in the form $y = mx + 0$ with m on the y-axis and L on the x-axis.

13. Recognising and using ratios

1 D. 4:1

The primary to secondary ratio is 2400:600. Dividing both sides of the ratio by 600 simplifies it to 4:1.

14. Understanding pie charts, frequency graphs, and histograms

1 A

The largest sector of the pie chart is purple, representing the percentage of people who watched 12 matches (35%). The next in size is blue (10 matches, 25%), then green (18 matches, 15%) and yellow (15 matches, 15%). The smallest sector is red (21 matches, 10%).

2 **a** 5
b 3
c 25
The height of the 81–100 column is 5. This shows 5 students scored over 80.
The heights of the 0–20 and 21–40 columns are 1 and 2. This shows that 3 students scored below 40.
If you add up the heights of all the columns ($1 + 2 + 6 + 11 + 5 = 25$), it tells you that there are 25 students in the class.

15. Using units in an equation to check for dimensional consistency

1 D. $m \times m \times m$

2 D. $P = 2 \times 3.5 + 2 \times 2.4$
Both units must be consistent.
Since 100 cm = 1 m the consistent units must be either
$L = 3.5$ m and W = 240 cm
or
$L = 350$ cm and $W = 240$ cm
The only correct combination is $P = 2 \times 3.5 + 2 \times 2.4$.

3 C. $kg\,m\,s^{-1}$
The unit for momentum is taken from the unit for mass (kg) multiplied by the unit for velocity ($m\,s^{-1}$). Therefore, momentum is measured in $kg\,m\,s^{-1}$.

16. Understanding lines of best fit

1 **a** false
b true
c true

2 **a** true
b false
c false

Answers

Comprehensive answers and fully worked solutions for all section review questions, try yourself worked examples, chapter review questions and unit review questions are available via Pearson Chemistry 12 Western Australia Reader+.

Chapter 1 Rate of chemical reactions

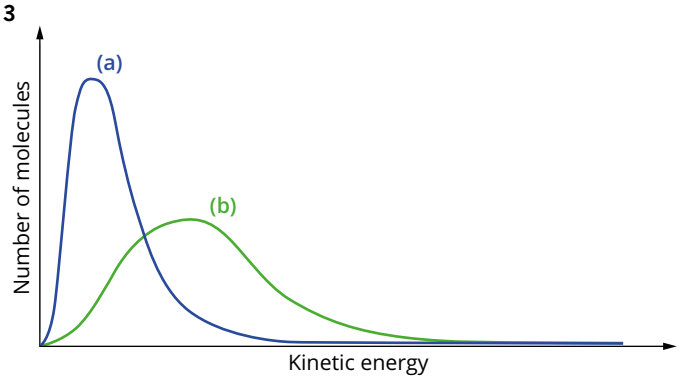
Section 1.1 Rate of chemical reactions

1.1 Key questions

1 C

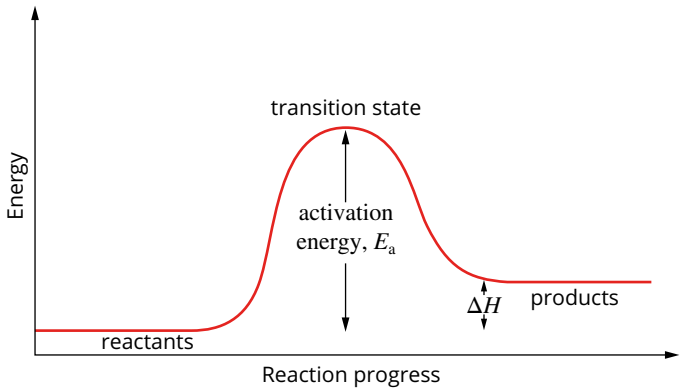
2 Correct orientation and sufficient energy (to meet the required activation energy).

3



4 The minimum energy required to break existing chemical bonds in a collision and allow the formation of products.

5



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

b If there are remaining solid marble chips in the conical flask, the hydrochloric acid must be the limiting reagent. If the marble chips have completely dissolved, the marble chips must be the limiting reagent.

c The mass lost by the reaction vessel is the mass of carbon dioxide gas escaping from the reaction vessel and thus not being weighed.

Section 1.2 Factors that influence reaction rate

1.2 Key questions

1 D **2** A **3** D

4 **a** A faster reaction rate

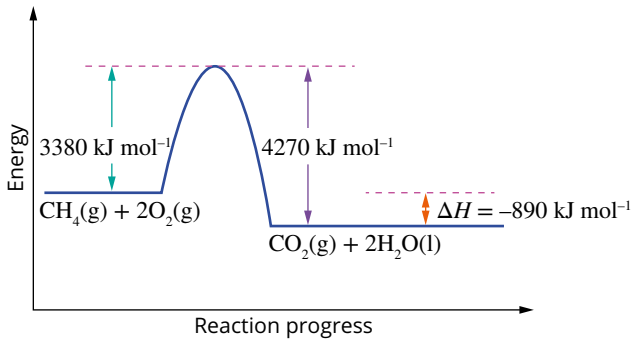
b The reaction has stopped, time is passing and no more volume of gas is produced.

c This is the maximum amount of carbon dioxide that can be produced for these reagents.

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

b $-890\ kJ\ mol^{-1}$

c



6 $139\ kJ\ mol^{-1}$

7 **a** exothermic **b** activation energy

c change of enthalpy **d** change of enthalpy

e activation energy

8 They don't differ; they are the same. Adding a catalyst reduces the required activation energy; it does not change the energy distribution of the particles.

Chapter 1 Review

1 Particles must collide with correct orientation and sufficient energy to overcome the activation energy barrier.

2 C **3** B **4** D

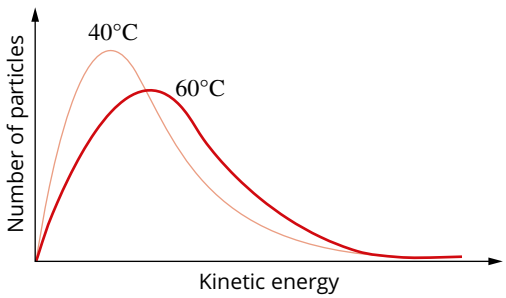
5 Reaction rate is measured by how quickly reactants are consumed or products generated over time. The duration only measures the time taken to consume all of the given reagents; it does not indicate how quickly, i.e. the rate, that those reagents were consumed.

6 As the mixture does not have a constant composition throughout, stirring increases the frequency of collisions between reactant particles leading to an increased reaction rate.

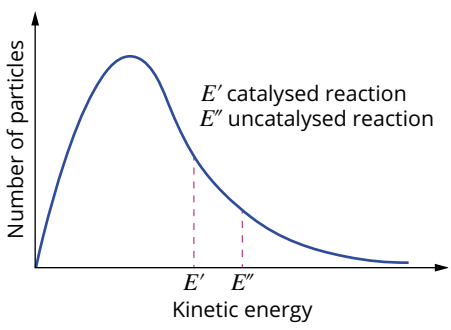
7 The temperature is high enough to provide the required activation energy for the combustion of the substance in oxygen provided by the atmosphere.

8 The low temperatures slow down the chemical reaction that cause food to rot because fewer of the molecules present have sufficient energy to overcome the activation energy. Lowering the temperature does not stop the reaction; it only slows it significantly. Food will still go rotten eventually.

9 **a**



b



c When a catalyst is present, the reaction proceeds by an alternative reaction pathway with a lower activation energy (E') than in the uncatalysed reaction (E''). At a given temperature, there will be a greater proportion of reacting particles that have a kinetic energy equal to or greater than the activation energies (E' than E''). As more reactants have sufficient energy to react, the rate of reaction increases.

10 **a** Surface area, concentration, gas pressure, temperature and the presence of catalysts

b **i** Surface area, concentration and gas pressure (assuming constant T)

ii Temperature and the presence of catalysts

11 A

12 The time is unchanged. Adding a greater volume of acid does not change the concentration of the acid and will not generate a greater number of collisions per unit of time, thus the reaction rate remains the same.

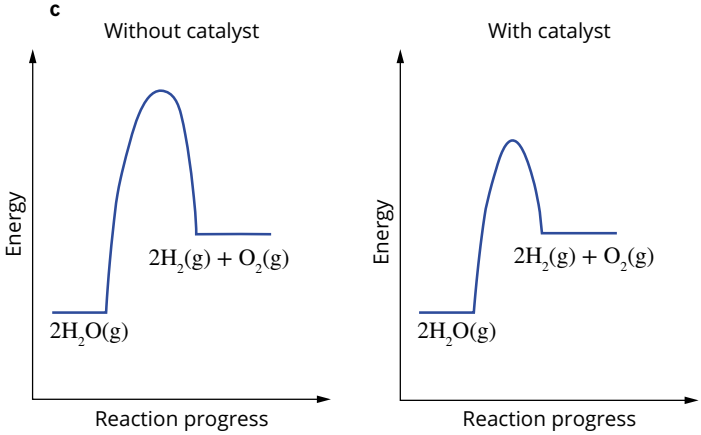
13
- Grind up the sugar crystals or use caster sugar.
- Use a cup of hot water to dissolve the sugar.
- Gently heat the sugar and water mixture while the sugar was dissolving.
- Stir the sugar and water mixture while the sugar was dissolving.

14 C

15 **a** 1370 kJ mol^{-1}

b –572 kJ mol^{-1}

c

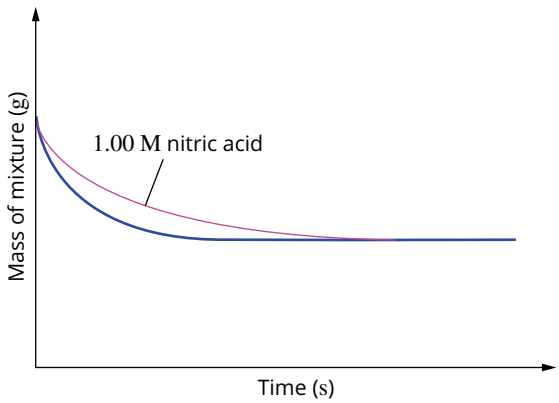


d +572 kJ mol^{-1}

16 **a** Initially the rate was high due to the highest concentration of nitric acid present. Over time, as the nitric acid was consumed, its concentration began to decrease; this is associated with a gradually decreasing reaction rate. Once all the limiting reagent has been consumed, the reaction stops and there is no more mass change.

b The copper is all used up so the reaction stops.

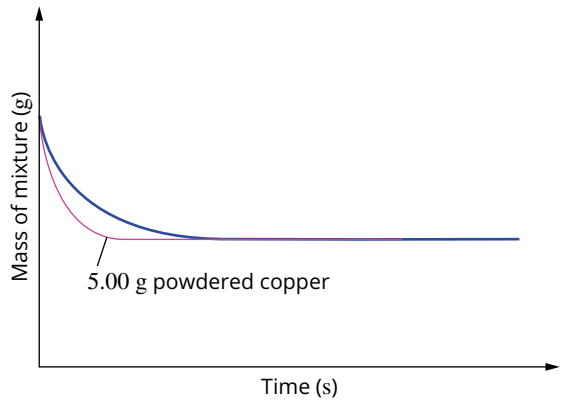
c



Decreased rate of mass loss due to lower nitric acid concentration.

Copper is still limiting, so final mass remains the same.

d



Increased rate of mass loss due to increased copper surface area.

Copper is still limiting, so final mass remains the same.

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

b $n(CaCO_3) = 10.0\,g/100.1\,g\,mol^{-1} = 0.0999\,mol$

$n(HCl) = 0.1\,mol\,L^{-1} \times 0.1\,L = 0.01\,mol$

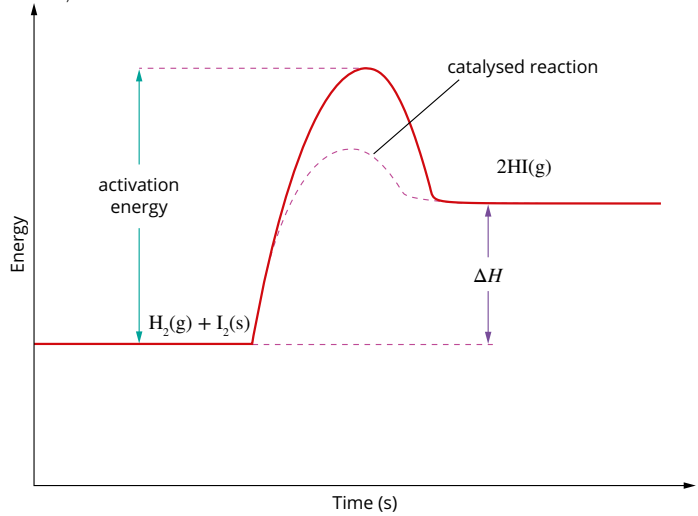
$\therefore$ $CaCO_3$ is in excess because only 0.005 mol of $CaCO_3$ is required to react with 0.01 mol of HCl.

c
- A decrease in mass of reaction mixture as $CO_2(g)$ escapes to the atmosphere.
- An increase in pH with a pH probe as acid is consumed.

d The reaction with the smaller lumps will be faster. The smaller lumps have a larger surface area so more collisions can occur per second.

e Increase temperature to increase the proportion of successful collisions; increase the concentration of hydrochloric acid so more collisions can occur per second.

18 **a, c**



b endothermic

19 **a** The temperature of the new process is much lower.

b $2Fe(s) + O_2(g) \rightarrow 2FeO(s)$

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

c No. The reaction of iron with water is different to the reaction of iron with dry oxygen and proceeds at a different rate.

d exothermic

e High surface area of iron pellets, high temperature caused by trapped heat that was unable to escape rapidly.

f Water would have caused the production of more hydrogen and increased the fire. The firefighters floodeds the hold with liquid nitrogen, which extinguished the surface fire but did not stop the deeper burning. A crane and clamshell bucket was then used to unload the iron into piles less than 1 m deep so the heat could escape.

Chapter 2 Equilibrium

Section 2.1 Chemical systems

2.1 Key questions

1 B

2 **a** closed **b** open
c closed **d** open

3 reversible, energy, matter, rates, remains constant

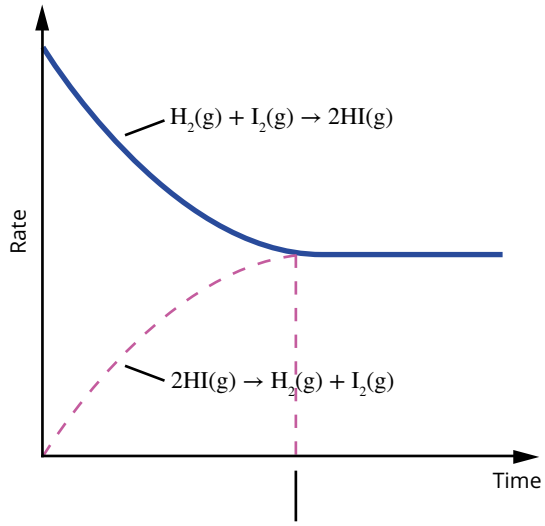
4 130 kJ mol^{-1}

Section 2.2 Dynamic equilibrium

2.2 Key questions

1 C

2



Equilibrium first established

3 closed, decreases, less, reverse, increases, equal

4 **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 There is no change in concentration of NO_2 or N_2O_4. This is when the system is at equilibrium and both the forward and reverse reactions are occurring at the same rate.
g 6 s
h The intensity of the brown colour will increase as the concentration of NO_2 increases until equilibrium is reached. Once equilibrium is reached, the colour of the reaction mixture will remain constant.

Section 2.3 The equilibrium law

WE 2.3.1 $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

2.3 Key questions

1 $K_c = \frac{[HCl]^2}{[H_2][Cl_2]}$

2 **a** A system where all the species are in the same state
b A system where some of the species are in different states
c Is equal to K_c at equilibrium
d Is always equal to K_c

3 **a** $[NH_3][H_2S]$ **b** $[Ag^+][Cl^-]$
c $\frac{1}{[Ag^+]^2[CO_3^{2-}]}$ **d** $\frac{[H_2O]^2[Cl_2]}{[HCl]^4[O_2]}$

4 D

Section 2.4 Working with equilibrium constants

2.4 Key questions

1 equal to, both the reactants and products, negligible

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

b This is the reverse of the reaction in the question, where the equilibrium constant of 100 indicates a high concentration of products compared to reactants. In the reverse reaction, it will be the reactants that will have the relatively high concentration, resulting in a low value for the equilibrium constant.

3 **a** $K_c = \frac{[HCl]^2[O_2]^{\frac{1}{2}}}{[H_2O][Cl_2]}$

b $K_c = \frac{[H_2O][Cl_2]}{[HCl]^2[O_2]^{\frac{1}{2}}}$

4 B

5 **a** increased
b decreased
c increased
d decreased

Section 2.5 Le Châtelier's principle

WE 2.5.1

Because of the higher rate of the reverse reaction initially when the CO molecules were added, a net reverse reaction has occurred.

2.5 Key questions

1 **a** net forward reaction
b net reverse reaction
c net forward reaction

2 **a** Concentration of H_2 molecules increases. So, more frequent collisions between the H_2 molecules and other molecules. The forward reaction occurs faster than the reverse reaction. 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 and equilibrium is re-established. Therefore, there is a net forward reaction.
b Concentration of H_2 molecules increases. So, more frequent collisions between H_2 molecules and other molecules. The reverse reaction occurs faster than the forward reaction. As the reverse reactions proceeds, there is a decrease in the rate of the reverse reaction and an increase in the rate of the forward reaction. The rates of the forward and revers reactions become equal and equilibrium is re-established. Therefore, there is a net reverse reaction.

3 **a** net reverse reaction
b net forward reaction

4 B

Section 2.6 Further applications of Le Châtelier's principle

WE 2.6.1 The Cl_2 concentration and partial pressure will be higher than it was at the initial equilibrium.

WE 2.6.2 This results in a net reverse reaction, with higher concentrations of CO_2 and H_2 and lower concentrations of CH_4 and H_2O.

2.6 Key questions

1 B. This gaseous equilibrium contains two particles on both sides of the equation. In such a situation, a volume decrease causes a pressure increase, resulting in an increase in the number of collisions between all molecules. Because there is an equal chance of reactant molecules colliding and forming a product or of product molecules colliding and forming the reactants (2 moles of reactants and 2 moles of products), there is no overall net reaction. The system is unable to oppose the change applied.

2 **a** Shifts to the right
b No effect
c Shifts to the right

3 **a** Doubling the pressure causes increased frequency of collisions and an increased rate of both the forward and reverse reactions. However, because there are more particles on the left-hand side, there will be more successful collisions in the forward direction, so a net forward reaction results.
b Increasing the pressure causes increased frequency of collisions and an increased rate of both the forward and reverse reactions. Because there is an equal chance of reactant molecules colliding and forming a product or of product molecules colliding and forming the reactants (2 moles of reactants and 2 moles of products), there is no overall net reaction.
c A temperature increase means all reactant and product molecules have more energy and move faster. There will be more collisions and more molecules will have the necessary activation energy. An increased temperature favours an endothermic reaction because a higher proportion of molecules at the higher temperature will have the necessary activation energy than for the exothermic reaction. Hence, there will be a net reaction in the direction of the endothermic reaction—a net forward reaction.

4 **a** **i** increase
ii increase
iii decrease
b **i** cannot cause forward reaction
ii increase
iii cannot cause forward reaction

5 **a** decrease
b higher

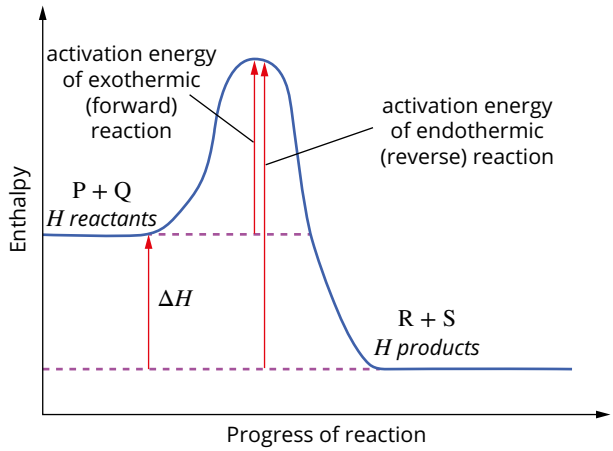
6 **a** Decreasing the temperature would favour the forward exothermic process because there is a net forward reaction.
b There are five particles on the reactant side and three particles on the product side. A decrease in volume would increase the pressure of the system. This would cause the system to favour the forward reaction in order to reduce the overall number of particles.

Chapter 2 Review

1 C

2 C

3 **a**

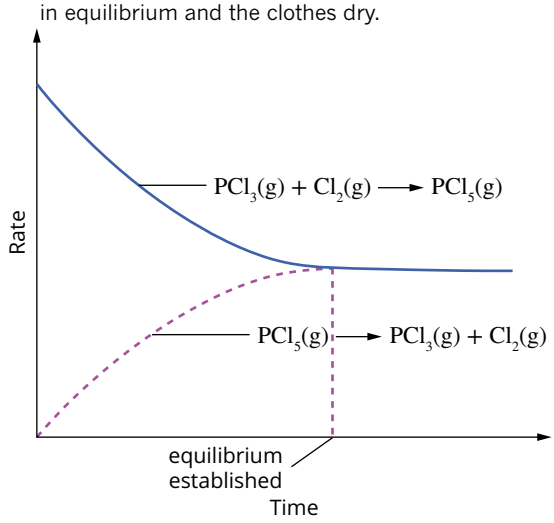


b If particles of R and S have energies greater than the activation energy of the reverse reaction, when they collide they can react to form P and Q.

4 Reactants and products must all be in the same state. Reaction must be reversible and have reached a state where the rate of the forward reaction is equal to the rate of the reverse reaction. There will be no observable change in concentration of the reactants or the products.

5 **a** Both forward and reverse reactions occur at the same rate. An equilibrium develops between water vapour and water when wet clothes are in a sealed bag, with water evaporating as rapidly as water vapour condenses, so the clothes remain wet.
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.

6



7 $K_c = \frac{[Fe^{2+}]^2[Sn^{4+}]}{[Fe^{3+}]^2[Sn^{2+}]}$

8 **a** $CH_3OH(g) \rightleftharpoons 2H_2(g) + CO(g)$
b $S_2(g) + 2H_2(g) \rightleftharpoons 2H_2S(g)$
c $NO_2(g) \rightleftharpoons \frac{1}{2}N_2O_4(g)$

9 **a** $\frac{1}{[Cu^{2+}][CO_3^{2-}]}$
b $[Cu^{2+}][CO_3^{2-}]$
c $\frac{[PCl_5]^4}{[Cl_2]^{10}}$
d $\frac{[Cl_2]^{20}}{[PCl_5]^8}$

10 The reaction quotient is the ratio of the concentrations of the products to the concentration of the reactants, with the index of each concentration the same as the coefficient of the substance in the reaction equation. The value of the reaction quotient becomes equal to the equilibrium constant at equilibrium.

11 **a** less than
b $\frac{[H_2O]^2[N_2]}{[H_2]^2[NO]^2}$
c moves to the right

12 **a** No; K_c is very small.

b Yes; K_c is very large (provided the rate is sufficiently fast).

13 $K_c = \frac{[Br_2][Cl_2]}{[BrCl]^2}$

14 If an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of that change.

For the equilibrium:

$A + B \rightleftharpoons C + D$

when the products, C and D, are removed, a net forward reaction occurs. Applying Le Châtelier's principle, the system can be regarded as opposing the change and trying to restore equilibrium.

15 **a** net forward reaction

b net reverse reaction

c net forward reaction

16 **a** More $H_2(g)$ has been added, causing a net forward reaction.

b Some $H_2(g)$ could have been removed, lowering the partial pressure of $H_2(g)$ and causing a net reverse reaction.

17 C

18 **a** A is NO_2. B is N_2O_4.

b A

19 D

20 **a** Reaction **i**: increase
Reaction **ii**: decrease

b A temperature increase means all reactant and product molecules have more energy and move faster. An increased temperature favours an endothermic reaction because a higher proportion of molecules will have the required activation energy for the endothermic reaction (at the higher temperature).

Since reaction **i** is exothermic, the reverse reaction, the endothermic reaction, will be favoured and so the hydrogen gas concentration will increase. Since reaction **ii** is endothermic, the forward reaction will be favoured. Hence, the reaction moves toward the right and the hydrogen gas concentration will increase.

21 **a** net reverse reaction

b net forward reaction

c no effect

22 If Ca^{2+} ions are inefficiently absorbed from food, decreased concentrations of these ions can occur in body fluids. As a consequence, a net forward reaction would occur, raising the concentration of dissolved Ca^{2+} ions and resulting in decreased amounts of calcium phosphate in bones.

23 **a** **i** net forward reaction
ii no change
iii net forward reaction
iv net reverse reaction

b **i** increase
ii no change
iii no change
iv no change

c likely to be large

24

	Colour change	Explanation using Le Châtelier's principle and collision theory
a The temperature is increased to 450°C at constant volume.	Lighter	Le Châtelier's principle: The forward reaction is exothermic, so K_c will decrease as temperature increases, so a net reverse reaction occurs. Collision theory: A higher temperature causes all molecules to have more energy and there are more frequent collisions. The increase in temperature affects the rate of the endothermic (reverse) reaction more than the exothermic reaction because this reaction has a higher activation energy to overcome. So the net reaction will be the reverse, endothermic reaction, producing more colourless NO and O_2.
b The volume of the container is increased at constant temperature.	Lighter	Le Châtelier's principle: An increase in volume causes a decrease in pressure. The system will oppose the change by increasing the pressure, so the equilibrium position moves in the direction of the most particles, producing more NO and O_2. Collision theory: Decreased pressure means there will be less frequent collisions. The rate of the reaction involving the smaller number of particles (the reverse reaction) will be less affected by the change and so it won't be slowed down as much as the forward reaction. Therefore the equilibrium shifts to the left.
c A catalyst is added at constant volume and temperature.	No change	Le Châtelier's principle: The system cannot adjust to oppose the addition of a catalyst. There is therefore no net reaction. Collision theory: Addition of a catalyst increases the rate of the forward and back reactions equally. There is no net reaction because the change in the number of collisions is equal in both directions.
d More oxygen is added at constant volume and temperature.	Darker	Le Châtelier's principle: The reaction opposes the change by consuming the added O_2 and shifts toward the right to produce more brown NO_2. Collision theory: Addition of O_2 increases its concentration and causes the number of collisions with NO to increase. As O_2 is consumed, the rate of the forward reaction decreases and the rate of the reverse reaction increases until a new equilibrium is established. Overall, there is a net forward reaction.

25 **a** $2SO_3(g) + CO_2(g) \rightleftharpoons CS_2(g) + 4O_2(g)$

b $K_c = \frac{[CS_2][O_2]^4}{[SO_3]^2[CO_2]}$

c **i** increase
ii increase
iii no effect
iv decrease
v no effect

26 **a** $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

b 15–20 minutes; 25–30 minutes, 35–40 minutes.

c 10 minutes; before 10 minutes the concentrations were changing slowly but the catalyst caused equilibrium to be reached more rapidly.

d increased pressure by reducing volume

e addition of O_2

Chapter 3 Equilibrium systems in the environment

Section 3.1 Carbon dioxide in the atmosphere

3.1 Key questions

1 carbon dioxide

2 $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$

3 A gas in the atmosphere that absorbs and emits radiation within the infrared range: vapour, carbon dioxide, methane, nitrous oxide and ozone.

4 The enhanced greenhouse effect, or global warming, is caused by additional heat being retained due to the increased amounts of carbon dioxide and other greenhouse gases that have been released into the Earth's atmosphere in the last 200 years. The impact on the Earth's climate is shifting weather patterns and more extreme weather events.

Section 3.2 Carbon dioxide in the oceans

3.2 Key questions

1 $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$
$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$
or:
$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$
$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$

2 increase, decrease, decrease, increase

3 $CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq)$
or:
$CO_3^{2-}(aq) + H_3O^+(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$
hydrogen/hydronium ions react with carbonate ions forming hydrogencarbonate ions.

4 calcium carbonate, calcification

5 **a** Krill eggs will not hatch at lower pH, therefore there will be a lower number of krill.

b Krill are a food source for many marine animals. If the number of krill cannot sustain organisms that feed directly on them, such as seals, penguins and small fish, then organisms such as killer whales and larger fish would also die off. This would lead to an overall decrease in the number of large species that live within specific ecosystems.

Section 3.3 Modelling and responding to climate change

3.3 Key questions

1
- The average global temperature is expected to rise by 0.3–4.8°C over the next century.
- The amount of rainfall is expected to increase.
- Tropical storms are likely to increase in wind strength and amount of rainfall.
- Sea levels are expected to rise by 0.3–1.2 metres in the next century.
- Sea ice and snow are expected to decrease.

2 B

3
- The stimulation of many national policies
- The creation of an international market for carbon
- The development of emissions trading schemes

4 **a** International Panel for Climate Change

b To stabilise greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous human-induced effects on the global climate.

5 Kyoto Protocol, reduce, greenhouse gas, stabilised, greenhouse emissions, 26–28%, 2030, solar energy.

6 **a** Burning coal to generate electricity produces greenhouse gas emissions, which would not help Australia meet its Paris Agreement obligations. However, the cost of electricity could rise if other energy sources are required to replace coal, which is relatively abundant and cheap.

b The use of biofuels (if harvested and produced using renewable energy) could potentially reduce carbon dioxide emissions. The carbon dioxide produced from the combustion of the fuels is offset by the carbon dioxide absorbed to grow the crops, which are used to make the fuels. This would help Australia meet its Paris Agreement obligations.

Chapter 3 review

1 Combustion of fossil fuels and plant decay

2 **a** A number of atmospheric gases, including carbon dioxide, are capable of absorbing some of the infrared radiation re-radiated from the surface of the Earth. This warms the air nearer the Earth to a higher temperature than it would be without the atmosphere. This has meant that, over millions of years, life on Earth has been able to evolve at temperatures much warmer than would otherwise have been the case.

b Carbon dioxide, methane, water vapour, nitrogen oxides and ozone

3 $2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$

4 The enhanced greenhouse effect is an increase in the temperature of the Earth's surface due to an increased concentration of greenhouse gases, resulting from human activities. Less heat is radiated back into space, which results in an increase in the temperature of the Earth—global warming. This affects the weather patterns, creating more extreme weather events.

5 D **6** D **7** D

8 Carbon dioxide combines with water to produce carbonic acid, as shown in reaction 2. This weak acid produces hydrogen ions in water, as shown by equation 3, hence increasing the concentration of hydrogen ions and reducing the pH.

9 Calcification: b, c.
Acidification: a, d, e

10 C

11 absorbed, reduces, decreases, right, lower, dissolve, left, decreasing

12 **a** Decalcification

b As the concentration of dissolved carbon dioxide in sea water increases, the concentration of H_3O^+ increases. Applying Le Châtelier's principle, this affects the position of the equilibrium:
$H^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq)$
or:
$H_3O^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + H_2O(l)$
The free carbonate ion concentration decreases, causing a net forward reaction in the equilibrium:
$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$
As a consequence, solid calcium carbonate dissolves. The rate of growth of corals can reduce, since they are composed of calcium carbonate.

13 C **14** C

15 stabilise, concentrations, human-induced, climate

16 **a** An increase in the average temperature of the Earth, causing a change in the rainfall patterns, a rise in the sea levels flooding of low-lying countries and coastal land.

b Use alternative energy sources, reduce the amount of energy generated by fossil fuels, use more efficient technologies.

17 $CO_2(g) \rightleftharpoons CO_2(aq)$
$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$
$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$
$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$
$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$

Chapter 4 Acids and bases

Section 4.1 Introducing acids and bases

4.1 Key questions

1 $HBr(g) + H_2O(l) \rightarrow H_3O^+(aq) + Br^-(aq)$
2 H_2SO_4/HSO_4^- and $H_2NO_3^+/HNO_3$
3 **a** H_2O
b H_3O^+
c CH_3NH_2
4 **a** NH_4^+
b CH_3COOH
c $H_2PO_4^-$
d HCO_3^-
5 Brønsted–Lowry acid–base reactions are those involving the exchange of a proton (H^+ ion). The acid donates the proton to the base. In the reaction below, 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.
$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
6 Acting as an acid, whereby the reactant donates one proton:
a $HCO_3^- + H_2O(l) \rightarrow CO_3^{2-}(aq) + H_3O^+(aq)$
b $HPO_4^{2-} + H_2O(l) \rightarrow PO_4^{3-}(aq) + H_3O^+(aq)$
c $HSO_4^- + H_2O(l) \rightarrow SO_4^-(aq) + H_3O^+(aq)$
d $H_2O(l) + H_2O(l) \rightarrow OH^-(aq) + H_3O^+(aq)$
Acting as a base, whereby the reactant accepts one proton:
a $HCO_3^- + H_2O(l) \rightarrow H_2CO_3(aq) + OH^-(aq)$
b $HPO_4^{2-} + H_2O(l) \rightarrow H_2PO_4^-(aq) + OH^-(aq)$
c $HSO_4^- + H_2O(l) \rightarrow H_2SO_4(aq) + OH^-(aq)$
d $H_2O + H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq)$

Section 4.2 Strength of acids and bases

4.2 Key questions

1 **a** $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$
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 Stage 1: $H_3AsO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + H_2AsO_4^-(aq)$
Stage 2: $H_2AsO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HAsO_4^{2-}(aq)$
Stage 3: $HAsO_4^{2-}(aq) + H_2O(l) \rightarrow H_3O^+(aq) + AsO_4^{3-}(aq)$
3 A
4 Stronger acids more readily ionise, forming ions in solution. As perchloric acid is stronger, more hydronium ions would be present in solution than in a solution of ethanoic acid, making it a better conductor of electricity.
5 **a** $K_a = \frac{[H_3O][F^-]}{[HF]}$
b $K_a = \frac{[H_3O^+][ClO^-]}{[HClO]}$
c $K_a = \frac{[H_3O^+][HS^-]}{[H_2S]}$
d $K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$

Section 4.3 Acidity of solutions

WE 4.3.1 $[H_3O^+] = 5.6 \times 10^{-6}\,mol\,L^{-1}$
$[OH^-] = 1.8 \times 10^{-9}\,mol\,L^{-1}$
WE 4.3.2 pH = 8.2
WE 4.3.3 pH = 12.3
WE 4.3.4 pH = 12.3
WE 4.3.5 $[H_3O^+] = 3.98 \times 10^{-11}\,mol\,L^{-1}$
WE 4.3.6 pH = 11.8

4.3 Key questions

1 $1.00 \times 10^{-11}\,mol\,L^{-1}$
2 $1.75 \times 10^{-6}\,mol\,L^{-1}$
3 $1.0 \times 10^{-9}\,mol\,L^{-1}$
4 pH = 2
5 pH = 3
6 $[H_3O^+] = 1.0 \times 10^{-6}$ (or 0.0000010) $mol\,L^{-1}$
7 pH = 1.3
8 pH = 11.5

Section 4.4 Dilution of acids and bases

WE 4.4.1 $1.00\,mol\,L^{-1}$
WE 4.4.2 60.0 mL
WE 4.4.3 pH = 1.5
WE 4.4.4 pH = 11.7

4.4 Key questions

1 $0.075\,mol\,L^{-1}$
2 30 mL
3 100 mL
4 increases the pH by one unit
5 pH = 12.6
6 **a** **i** $0.001\,mol\,L^{-1}$
ii $1 \times 10^{-11}\,mol\,L^{-1}$
iii 3
b **i** $0.03\,mol\,L^{-1}$
ii $3.33 \times 10^{-13}\,mol\,L^{-1}$
iii 1.5
c **i** $1.0 \times 10^{-12}\,mol\,L^{-1}$
ii $0.010\,mol\,L^{-1}$
iii 12
d **i** $3.16 \times 10^{-5}\,mol\,L^{-1}$
ii $3.16 \times 10^{-10}\,mol\,L^{-1}$
iii 4.5
e **i** $1.0 \times 10^{-12}\,mol\,L^{-1}$
ii $0.01\,mol\,L^{-1}$
iii 12

Section 4.5 pH of salt solutions

WE 4.5.1 The salt is basic.

4.5 Key questions

1

Reactants	Name of salt formed	Formulae of ions present in the salt solution
Hydrochloric acid + magnesium hydroxide	Magnesium chloride	$Mg^{2+}(aq) + Cl^-(aq)$
Sulfurous acid + zinc hydroxide	Zinc sulfite	$Zn^{2+}(aq) + SO_3^{2-}(aq)$
Phosphoric acid + potassium hydroxide	Potassium phosphate	$K^+(aq) + PO_4^{3-}(aq)$
Ethanoic acid + calcium hydroxide	Calcium ethanoate	$Ca^{2+}(aq) + CH_3COO^-(aq)$
Ammonia + nitric acid	Ammonium nitrate	$NH_4^+(aq) + NO_3^-(aq)$
Phosphoric acid + sodium hydroxide	Sodium dihydrogenphosphate	$Na^+(aq) + H_2PO_4^-(aq)$

2 **a** $S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + OH^-(aq)$
b $ClO_2^-(aq) + H_2O(l) \rightleftharpoons HClO_2(aq) + OH^-(aq)$
c $PH_4^+(aq) + H_2O(l) \rightleftharpoons PH_3(aq) + H_3O^+(aq)$
d $F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$

3 **a** Neutral
b Acidic
$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
c Basic
$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
d Neutral

Chapter 4 Review

1 B **2** D

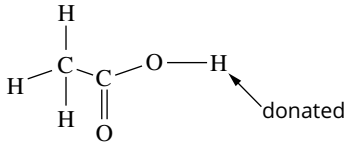
3 **a** NH_4^+
b HCl
c HCO_3^-
d H_3O^+
e $CH_3COOH(aq)$

4 **a** $PO_4^{3-}(aq) + H_2O(l) \rightarrow HPO_4^{2-}(aq) + OH^-(aq)$
b The $H_2PO_4^-$ accepts a proton from water, and acts as a base:
$H_2PO_4^-(aq) + H_2O(l) \rightarrow H_3PO_4(aq) + OH^-(aq)$
The $H_2PO_4^-$ donates a proton to the water, and acts as an acid:
$H_2PO_4^-(aq) + H_2O(l) \rightarrow HPO_4^{2-}(aq) + H_3O^+(aq)$
c $H_2S(aq) + H_2O(l) \rightarrow HS^-(aq) + H_3O^+(aq)$

5 **a** Cl^-
b $H_2OH_2OH_2OH_2O$
c OH^-
d SO_4^{2-}

6 **a** Sulfuric acid (H_2SO_4) is a diprotic acid because each molecule can donate two protons to a base:
i.e. $H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$
$HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)$
The HSO_4^- ion, however, is amphiprotic because it can act as either an acid or a base, depending on the environment. In water it will undergo both acid and base reactions. For example:
As an acid: $HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)$
As a base: $HSO_4^-(aq) + H_2O(l) \rightarrow OH^-(aq) + H_2SO_4(aq)$
b A strong acid is one that ionises completely in solution (e.g. HCl). A concentrated acid is one in which there is a large amount of acid dissolved in a given volume of solution; for example, 5 mol L^{-1} HCl and 5 mol L^{-1} CH_3COOH are concentrated acids.

7



8 **a** This is a Brønsted–Lowry acid–base reaction. H^+ donated to OH^-.
b This is an acid reacting with a metal, not a Brønsted–Lowry acid–base reaction.
c This a precipitation reaction.
d This is a Brønsted–Lowry acid–base reaction. H^+ donated to O^{2-}.

9 D
10 C
11 $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$
12 $HClO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO_3^-(aq)$
13 $NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$
14 $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3PO_4(aq) + OH^-(aq)$

15 **a** 10^{-11} mol L^{-1}
b 10^{-9} mol L^{-1}
c 1.8×10^{-6} mol L^{-1}
d 2.9×10^{-3} mol L^{-1}
e 1.5×10^{-13} mol L^{-1}
f 4.48×10^{-2} mol L^{-1}

16 **a** $[H_3O^+]$
$= 0.1$ mol L^{-1}
$[OH^-] = \frac{1.00 \times 10^{-14}}{[H_3O^+]}$
$= \frac{1.00 \times 10^{-14}}{0.10 \text{ mol L}^{-1}} = 1.0 \times 10^{-13}$ mol L^{-1}
b $[H_3O^+] = 10^{-3}$ mol L^{-1}
$[OH^-] = 10^{-11}$ mol L^{-1}
c $[H_3O^+] = 10^{-7}$ mol L^{-1}
$[OH^-] = 10^{-7}$ mol L^{-1}
d $[H_3O^+] = 2 \times 10^{-12}$ mol L^{-1}
$[OH^-] = 5 \times 10^{-3}$ mol L^{-1}

17 basic
18 100

19 **a** $[H^+] = 0.001$ mol L^{-1}
$[OH^-] = 1.0 \times 10^{-11}$ mol L^{-1}
b $[H^+] = 10^{-10}$ mol L^{-1}, $[OH^-] = 10^{-4}$
c $[H^+] = 3.16 \times 10^{-9}$ mol L^{-1}, $[OH^-] = 3.16 \times 10^{-6}$ mol L^{-1}
d $[H^+] = 1.58 \times 10^{-6}$ mol L^{-1}, $[OH^-] = 6.3 \times 10^{-9}$ mol L^{-1}
e $[H^+] = 2.5 \times 10^{-10}$ mol L^{-1}, $[OH^-] = 4.0 \times 10^{-5}$ mol L^{-1}
f $[H^+] = 3.16 \times 10^{-14}$ mol L^{-1}, $[OH^-] = 0.316$ mol L^{-1}

20 2.0×10^{-9} mol L^{-1}

21 Remember to use $[OH^-] \times [H_3O^+] = 1 \times 10^{-14}$ at 25°C and $pH = -\log_{10}[H_3O^+]$.
a pH = 2, $\therefore [H_3O^+] = 10^{-2}$ or 0.01 mol L^{-1}
b The formula for amounts of substance in solution is $n = c \times V$ (where n is the amount in moles, c the concentration in mol L^{-1} and V the volume of the solution in litres).
$n = 0.01 \times 0.500 = 0.005$ mol

22 **a** 1.3
b 10.3
c 3

23 111 mL
24 1000 mL
25 increase
26 B

27 **a**

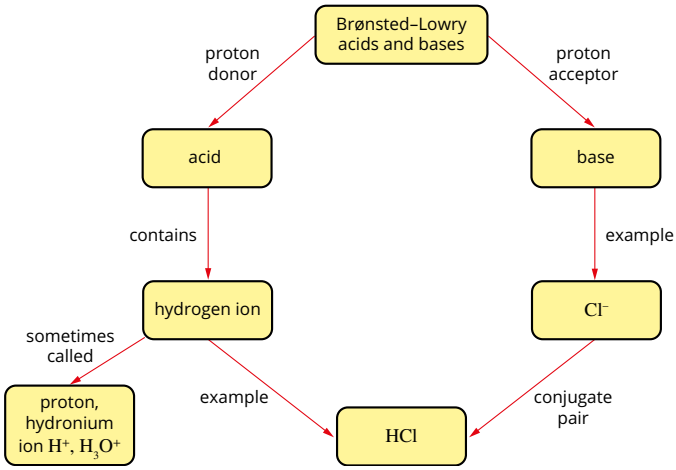
Salt dissolved	Approximate pH (5, 7 or 9)
Potassium nitrate	7
Ammonium chloride	5
Sodium phosphate	9
Potassium hydrogensulfate	5

b $PH_4^+(aq) + H_2O(l) \rightleftharpoons PH_3(aq) + H_3O^+(aq)$ equation 1
$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$ equation 2
Since pH < 7, $[H^+]$ must be greater than $[OH^-]$
And so, the position of equilibrium in equation 1 must be further over to the right hand side than in equation 2.

28 Solution A: weaker base, few freely moving charged particles—ammonia
Solution B: neutral, no freely moving charged particles—glucose
Solution C: strong base, many freely moving charged particles—sodium hydroxide
Solution D: strong acid, many freely moving charged particles—hydrochloric acid
Solution E: weaker acid, few freely moving charged particles—ethanoic acid

29 **a** **i** A Brønsted–Lowry acid is a proton donor.
ii A strong base is a substance that readily accepts hydrogen ions.
iii Molarity is a measure of concentration of a solution expressed in mol L^{-1}.
iv The conjugate acid of a base contains one more hydrogen ion (proton) than the base.
b An amphiprotic substance can act as an acid (proton donor) or a base (proton acceptor).
Acting as an acid: $HCO_3^-(aq) + H_2O(l) \rightarrow CO_3^{2-}(aq) + H_3O^+(aq)$
Acting as a base: $HCO_3^-(aq) + H_2O(l) \rightarrow H_2CO_3(aq) + OH^-(aq)$

30



31 **a** $NH_3(l) + NH_3(l) \rightleftharpoons NH_4^+(am) + NH_2^-(am)$
acid 1 base 2 acid 2 base 1
b endothermic

Chapter 5 Buffers

Section 5.1 Introducing buffers

5.1 Key questions

1 D
2 $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
3 $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
4 $HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$
5 alkaline, acidic, acidic

Section 5.2 How buffers work

5.2 Key questions

1 C
2 CH_3COO^-, left, H_3O^+, small, CH_3COOH, H_3O^+.
3 C

Section 5.3 Applications of buffers

5.3 Key questions

1 $H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq)$
$H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq)$
$H_6C_8O_7(aq) \rightleftharpoons H_5C_8O_7^-(aq)$
2 **a** $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$
b When acid is added the concentration of H_3O^+ increases and the equilibrium is disturbed. In accordance with Le Châtelier's principle, the equilibrium moves to the left to re-establish equilibrium.
3 decrease
4 $H_6C_8O_7(aq) + H_2O(l) \rightleftharpoons H_5C_8O_7^-(aq) + H_3O^+(aq)$

Chapter 5 review

1 A near equimolar solution of either a weak acid and its conjugate or a weak base and its conjugate.
2 A conjugate acid is a species formed when a base accepts a proton; a conjugate base is a species formed when a proton is removed from an acid.
3 $CH_3COOH(aq)/CH_3COO^-(aq)$, $NH_3(aq)/NH_4^+(aq)$
4 A cannot be a buffer because the NaOH is a strong base. Hence, the reverse reaction cannot occur. In B, the acetate ion readily accepts a proton to form acetic acid.
5 $H_2PO_4^-(aq)$ (acid) $\rightleftharpoons HPO_4^{2-}(aq)$ (base)
6 HPO_4^{2-}, left, H_3O^+, small, $H_2PO_4^-$, H_3O^+
7 The number of moles of acid or base that can be added to a buffer before a significant change in pH is observed (usually one pH unit).
8 D
9 **a** Carbonic acid/hydrogencarbonate, dihydrogen phosphate/monohydrogen phosphate
b Carbonic acid/hydrogencarbonate, citric acid/citrate
10 E numbers are a system of labelling used to classify food additives. E numbers between E330 and E340 represent a group of antioxidants, food additives that can also act as buffers.
11 $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$. Increases, decreases, returns to almost the original value
12 The phosphate buffer system ($H_2PO_4^-/HPO_4^{2-}$) is described by the chemical equation: $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$. If the hydronium ion concentration rises the equilibrium is disturbed. In accordance with Le Châtelier's principle, the equilibrium moves to the left to re-establish equilibrium. In a more alkaline environment, the equilibrium is disturbed and moves to the right.
13 The buffer can be summarised as: $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$
Because both species are present, the equation can move to the RHS (right-hand side) or the LHS (left-hand side) depending on the $[H_3O^+(aq)]$. Thus it is a buffer.
14 Lactic acid $C_3H_6O_3$ is a monoprotic acid. It ionises: $C_3H_6O_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_3H_5O_3^-(aq)$. This causes a drop in pH with a rise in $[H_3O^+]$ in the blood, which affects the hydrogen carbonate/bicarbonate buffer. $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$. In accordance with Le Châtelier's principle, the rise in $[H_3O^+(aq)]$ causes the buffer to move to the LHS and absorb the excess H_3O^+.
15 **a** With no removal of carbon dioxide the blood pH will fall.
b $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$. The basic HCO_3^- reacts with the additional hydronium ions to raise the pH.
16 **a** $C_6H_8O_7(aq) + H_2O(l) \rightleftharpoons C_6H_7O_7^-(aq) + H_3O^+(aq)$
b $C_6H_7O_7^-(aq)$
c $C_6H_8O_7(aq) + H_2O(l) \rightleftharpoons C_6H_7O_7^-(aq) + H_3O^+(aq)$
If the hydronium ion concentration rises the equilibrium is disturbed. In accordance with Le Châtelier's principle, the equilibrium moves to the LHS to re-establish equilibrium. In a more alkaline environment, the equilibrium is disturbed and the equilibrium moves to the right.
17 The buffer can be summarised as: $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$. In accordance with Le Châtelier's principle, when acidity is increased the equilibrium moves to the LHS to re-establish equilibrium. In a more alkaline environment the equilibrium is disturbed and the equilibrium moves to the RHS
18 **a** $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$
$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$
Excess $OH^-(aq)$ would decrease the $[H_3O^+(aq)]$. In accordance with Le Châtelier's principle, this will cause the third equation to move to the right. Thus the $[H_2CO_3(aq)]$ will fall. This decrease will, in accordance with Le Châtelier's principle, cause the second equation to move to the RHS and decrease $[CO_2(aq)]$. There would be less $CO_2(aq)$ than in pure water.
b Atmospheric CO_2 reacts with ocean water, as shown in three equations:
$CO_2(g) \rightleftharpoons CO_2(aq)$
$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$
$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$
Calcium carbonate is sparing soluble in water. $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$. Coral uses the reverse reaction to make coral reefs. By increasing the $[CO_2(g)]$ in the atmosphere, the first, second and third reactions are moved to the right in accordance with Le Châtelier's principle. Thus the ocean becomes more acidic. This increase in $[H_3O^+(aq)]$ causes a decrease in $[CO_3^{2-}(aq)]$ thus:
$CO_3^{2-}(aq) + H_3O^+(aq) \rightleftharpoons HCO_3^-(aq) + H_2O(l)$
and limits the formation of calcium carbonate solid. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$

Chapter 6 Indicators

Section 6.1 Characteristics of indicators

6.1 Key questions

1 C

2 **a** 0–1.7
b 8.2–14
c Approximately 4.6

Section 6.2 Common indicators

6.2 Key questions

1 The ammonia and sodium hydroxide solutions change colour because they are both basic.

2 **a** HIn, In^-
b The concentration of HIn is much greater than the concentration of In^-, and the colour of the solution is red.

3 B

4 **a** violet
b violet
c yellow

Section 6.3 pH range of an indicator

6.3 Key questions

1 The end point is the point in the titration at which the indicator changes colour. 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.

2 C

3 **a** Cgr^-, H_3O^+
b **i** purple
ii red
iii blue
iv red

Chapter 6 Review

1 $HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$

2 C

3 **a** yellow
b colourless
c intermediate between blue and yellow

4 **a** dynthetic
b natural; litmus is derived from lichens
c synthetic

5 Universal indicator is a mixture of several indicators and so it changes through a range of colours.

6 **a** yellow
b The addition of an acid solution of pH 5 will shift the equilibrium to the left. The concentration of HBB (acidic form) molecules is now much greater than the concentration of BB^- ions (conjugate base) and the solution is yellow.

7 pH 8.3 and very pale pink (practically colourless)

8 The end point is when the indicator changes colour. The equivalence point is the point during a neutralisation reaction when the amounts of acid and base are in the stoichiometric ratio represented by the reaction equation.

9 Near the equivalence point, a very small addition of either the acid or the base in the burette can cause a large change in pH. A sharp end point is one at which the indicator changes colour (due to a large change in pH) with just one additional drop of the solution being added from the burette. Selecting the indicator based on the expected equivalence point enables a sharp end point to be seen.

10 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.

Chapter 7 Volumetric analysis

Section 7.1 Acids and bases in water

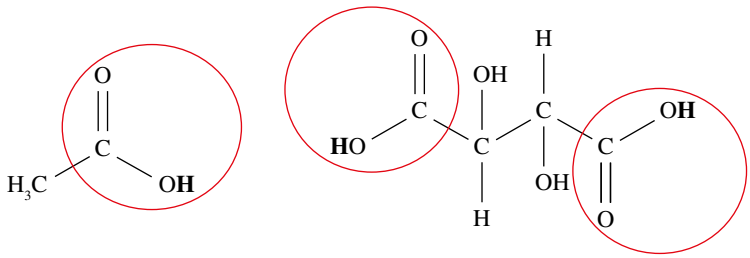
7.1 Key questions

1 non-metal oxides

2 Nitrogen oxides produced by the reaction of nitrogen and oxygen from the air in internal combustion engines contribute to the formation of acid rain. Acid rain is more acidic than pure water (pH of 7); therefore, nitrogen oxides lower the pH.

3 $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$

4 Ethanoic acid can donate only one proton from its single carboxylic acid group; therefore, it is a monoprotic acid. Tartaric acid can donate two protons from its two carboxylic acid groups; therefore, it is a diprotic acid.



ethanoic acid tartaric acid

Section 7.2 Calculations involving acids and bases

WE 7.2.1 10.0 mL

WE 7.2.2 0.218 mol L^{-1}

7.2 Key questions

1 **a** $H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$
b 15.0 mL

2 **a** $2HNO_3(aq) + Ca(OH)_2(aq) \rightarrow Ca(NO_3)_2(aq) + 2H_2O(l)$
b 0.133 mol L^{-1}

3 **a** $HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$
b 0.001985 mol
c 0.001985 mol
d 0.1087 mol L^{-1}

Section 7.3 Standard solutions

WE 7.3.1 0.539 mol L^{-1}

7.3 Key questions

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 0.2000 mol L^{-1}

3 13.3 g

Section 7.4 Volumetric analysis

7.4 Key questions

1 A

2

Indicator	Colour after adding indicator
Alizarin yellow	Yellow
Bromothymol blue	Yellow
Methyl red	Orange
Methyl orange	Yellow
Phenolphthalein	Colourless

3 25.42 mL

Section 7.5 Calculations in volumetric analysis

WE 7.5.1 0.108 mol L^{-1}
WE 7.5.2 12.88 mol L^{-1}
WE 7.5.3 0.0938 g

7.5 Key questions

1 0.770 mol L^{-1}
2 **a** $CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$
b 0.02145 mol
c 0.02145 mol
d 0.858 mol L^{-1}
3 10.45 mol L^{-1}
4 0.118 mol L^{-1}

Chapter 7 Review

1 Acid rain is rainfall made acidic when pollutant gases generated by smelters, the internal combustion engine and the burning of fossil fuels dissolve in rain. These gases contain SO_2 and NO_2 and they dissolve in rain to form sulfuric, nitrous and nitric acids respectively.
2 D
3 Any two of tartaric acid, malic acid, citric acid
4 If a wine is too acid, it will taste tart and sour, while too little acid will cause the wine to taste flat.
5 15.0 mL
6 40 mL
7 C
8 0.8003 mol L^{-1}
9 21.2 g
10 **a** A burette delivers a precise variable volume of solution.
b A pipette delivers a precise known volume of solution.
c A volumetric flask is used to prepare a solution of known concentration.
11 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.
12 Near the equivalence point, a very small addition of either the acid or the base in the burette can cause a large change in pH. A sharp end point is one where the indicator changes colour (due to a large change in pH) with just one additional drop of the solution being added from the burette. Selecting the indicator based on the expected equivalence point enables a sharp end point to be seen.
13 **a** $H_2SO_4(aq) + K_2CO_3(aq) \rightarrow K_2SO_4(aq) + H_2O(l) + CO_2(g)$
b 0.03557 mol L^{-1}
c 0.0315 mol L^{-1}
14 **a** $2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$
b 0.05125 mol L^{-1}
c 0.1013 mol L^{-1}
d Sulfuric acid is a diprotic acid so only half as much acid would be required to neutralise an equivalent amount of sodium carbonate. Since the two acids have the same concentration, half the volume of sulfuric acid is required.
15 $2HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2NaNO_3(aq) + H_2O(l) + CO_2(g)$
a 0.04166 mol L^{-1}
b 0.007100 mol L^{-1}
16 0.114 mol L^{-1}
17 **a** 0.003815 mol
b 0.100 mol
c 3.0953 g
d 80.2%
18 **a** Sodium carbonate or potassium carbonate could be used as they are both good primary standards. They are also both bases, so they will neutralise the hydrochloric acid.
b 1 Weigh the pure solid on an electronic balance.
2 Transfer the solid into the volumetric flask using a clean, dry funnel.
3 Rinse any remaining solid particles into the flask using deionised water.
4 Half-fill the flask with deionised water and swirl vigorously to dissolve the solid.
5 Add deionised water up to the calibration line on the neck of the flask. The bottom of the meniscus of the solution should be on the mark when viewing at eye level.
6 Stopper and shake the solution to ensure an even concentration throughout.
c Rinse the burette with the acid solution, rinse the pipette with the base and rinse the conical flask with the deionised water.
d 13.56 mol L^{-1}
e The concentration calculated should not be different if using a different base in the titration. The volume of base titrated and the concentration of the base may be different and therefore the mole ratio in the equation might be different, but the concentration of HCl in the concrete cleaner would be the same. If there were errors evident in either titration then there would be slight inaccuracies in the results and potentially a different concentration calculated.
19 **a** $MgO + 2HCl \rightarrow MgCl_2 + H_2O$
b $HCl + NaOH \rightarrow NaCl + H_2O$
c This is a titration of a strong acid and a strong base, so most indicators could be used. Phenolphthalein has an easily observed endpoint – colourless to pink
d 0.001860 mol
e 0.02325 mol
f 0.06675 mol
g 1.345 g
h 76.9%

Chapter 8 Redox reactions

Section 8.1 Oxidation and reduction

WE 8.8.1 $Na(s) \rightarrow Na^+(s) + e^-$
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$
WE 8.1.2 $Cu(s) \rightarrow Cu^{2+}(aq)$
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Electrons are lost, so this is oxidation.
The Cu(s) is being oxidised.
WE 8.1.3 $O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$
$K(s) \rightarrow K^+(s) + e^-$
$4K(s) + O_2(g) \rightarrow 2K_2O(s)$

8.1 Key questions

1 I_2, loses, oxidised, gains, reduced, I^-
2 **a** oxidation
b oxidation
c reduction
d oxidation
e reduction
f reduction
3 **a** Fe(s) has been oxidised to $Fe^{2+}(aq)$.
b $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

c $H^+(aq)$
d $H^+(aq)$ has been reduced to H_2
e $2H^+(aq) + 2e^- \rightarrow H_2(g)$
f Fe(s)

4 **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 $O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$ (reduction)

5 **a** Zn(s)
b Ca(s)
c I^- ions

6 **a** Oxidant O_2, reductant Zn
b Oxidant Cl_2, reductant Ca
c Oxidant Cl_2, reductant I^- ions

7 $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$
As the nickel metal goes from solid metal to a positive ion it must be losing electrons, therefore being oxidised.

8 $Al(s) \rightarrow Al^{3+}(l) + 3e^-$ (oxidation)
$S(l) + 2e^- \rightarrow S^{2-}(l)$ (reduction)

9 **a** $Ag^+(aq) + e^- \rightarrow Ag(s)$
$M(s) \rightarrow M^{3+}(aq) + 3e^-$
$M(s) + 3Ag^+(aq) \rightarrow M^{3+}(aq) + 3Ag(s)$
b The silver half-equation is reduction, the unknown metal half-equation is oxidation.
c M(s) is the reducing agent, $Ag^+(aq)$ is the oxidising agent.

10 **a** Magnesium is oxidised, copper ions are 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 Oxidant Cu^{2+}; reductant Mg
f Blue Cu^{2+} ions are reduced to salmon salmon pink Cu(s).

11 **a** Cu^{2+}
b Cu

12 **a** CaO
b Ca(s)
c $Ca(s) \rightarrow Ca^{2+}(s) + 2e^-$
d $O_2(g)$
e $O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$
f $2Ca(s) + O_2(g) \rightarrow 2CaO(s)$
g oxidised, oxygen, oxygen, calcium, reduced, calcium, calcium, oxygen

Section 8.2 Oxidation numbers

WE 8.2.1 $\overset{+1}{Na}\overset{+5}{N}\overset{-2}{O_3}$

WE 8.2.2 Copper in CuO has been reduced.
H_2 has been oxidised.

8.2 Key questions

1 **a** +2
b +4
c –4
d 0
e +4

2 K_2MnO_4: the oxidation state of K is +1, O is –2
$2 \times +1 + x + 4 \times -2 = 0$; hence $x = +6$

3 **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

4 **a** Oxidant Cl_2; reductant Mg
b Oxidant O_2; reductant SO_2
c Oxidant Fe_2O_3; reductant CO
d Oxidant H_2O_2; reductant Fe^{2+}

5

Redox reaction	Conjugate redox pair (oxidation process)	Conjugate redox pair (reduction process)
$Na(s) + Ag^+(aq) \rightarrow Na^+(aq) + Ag(s)$	$Na(s)/Na^+(aq)$	$Ag^+(aq)/Ag(s)$
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$	$Zn(s)/Zn^{2+}(aq)$	$Cu^{2+}(aq)/Cu(s)$
$2K(s) + Cl_2(g) \rightarrow 2K^+(s) + 2Cl^-(s)$	$K(s)/K^+(s)$	$Cl_2(g)/Cl^-(s)$

Section 8.3 More complex redox equations

WE 8.3.1 $MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$

WE 8.3.2 $SO_3^{2-}(aq) + 8H^+(aq) + 6e^- \rightarrow H_2S(g) + 3H_2O(l)$
$ClO^-(aq) + 2H_2O(l) \rightarrow ClO_3^-(aq) + 4H^+(aq) + 4e^-$
$2SO_3^{2-}(aq) + 4H^+(aq) + 3ClO^-(aq) \rightarrow 2H_2S(g) + 3ClO_3^-(aq)$

8.3 Key questions

1 **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 $SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$

2 **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 $3Zn(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 3Zn^{2+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

3 **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 $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$
$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
$MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Cl_2(g)$

4 **a** **i** Ce^{4+} is reduced to Ce^{3+} and H_2S is oxidised to S.
ii $Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$
$H_2S(aq) \rightarrow S(s) + 2H^+(aq) + 2e^-$
iii $2Ce^{4+}(aq) + H_2S(aq) \rightarrow 2Ce^{3+}(aq) + S(s) + 2H^+(aq)$
b **i** NO_3^- is reduced to NO and Cu is oxidised to Cu^{2+}.
ii $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
iii $2NO_3^-(aq) + 8H^+(aq) + 3Cu \rightarrow 2NO(g) + 4H_2O(l) + 3Cu^{2+}(aq)$
c **i** H_2O_2 is reduced to H_2O and Br^- is oxidised to Br_2.
ii $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$
$2Br^-(aq) \rightarrow Br_2(l) + 2e^-$
iii $H_2O_2(aq) + 2H^+(aq) + 2Br^-(aq) \rightarrow 2H_2O(l) + Br_2(l)$
d **i** MnO_2 is reduced to Mn^{2+} and S is oxidised to SO_2.
ii $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$
$S(s) + 2H_2O(l) \rightarrow SO_2(g) + 4H^+(aq) + 4e^-$
iii $2MnO_2(s) + 4H^+(aq) + S(s) \rightarrow 2Mn^{2+} + 2H_2O(l) + SO_2(g)$

Section 8.4 The reactivity series of metals

WE 8.4.1 There will be a reaction.
$2(aq) + 3Cu(s) \rightarrow 2Au(s) + 3Cu^{2+}(aq)$

8.4 Key questions

1 For reactions to occur spontaneously, the aqueous cation in the solution must be a stronger oxidant than the cation of the metal added.
a no **b** no **c** yes
d yes **e** yes **f** yes
g no

2 **a** $3Cu^{2+}(aq) + 2Al(s) \rightarrow 3Cu(s) + 2Al^{3+}(aq)$
b no reaction
c $2Ag^{+}(aq) + Zn(s) \rightarrow 2Ag(s) + Zn^{2+}(aq)$

3 iron and lead

Chapter 8 review

1 **a** Oxidation is the gain of oxygen; reduction is the loss of oxygen.
b Oxidation is the loss or donation of electrons; reduction is the gain or acceptance of electrons.

2 **a** false
b false
c true
d false

3 loses, positive, loses, gains, negative, gains, 7, gains, bromide

4 Oxidation half-equation: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^{-}$
Reduction half-equation: $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$
Overall: $Pb(s) + 2Ag^{+}(aq) \rightarrow Pb^{2+}(aq) + 2Ag(s)$

5 **a** oxidation
b oxidation
c reduction
d oxidation
e reduction
f reduction

6 **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: $Na^{+}(aq) + e^{-} \rightarrow Na(s)$

7 **a** Cu(s) **b** $Br^{-}(l)$
c Zn(s) **d** Ni(s)

8 **a** $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$
b $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$
c $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$

9 C

10 **a** +4 **b** –2
c +6 **d** +6
e +4 **f** +2

11

Compound	Element	Oxidation number
$CaCO_3$	Ca	+2
HNO_3	O	–2
H_2O_2	O	–1
HCO_3^-	C	+4
HNO_3	N	+5
$KMnO_4^-$	Mn	+7
H_2S	S	–2
Cr_2O_3	Cr	+3
N_2O_4	N	+4

12 K_3N, N_2, N_2O, NO, N_2O_3, N_2O_4, $Ca(NO_3)_2$
Oxidation states for nitrogen are as follows:
K_3N: –3
N_2: 0
N_2O: +1
NO: +2
N_2O_3: +3
N_2O_4: +4
$Ca(NO_3)_2$: +5

13 Reactions b, c, e, f and h are redox reactions because the elements in the reactions undergo changes in oxidation number during the course of the reaction.

14 **a** $\underline{Cu}O$ +2 **b** $\underline{Fe}(OH)_3$ +3
c $H\underline{Cl}O_2$ +3 **d** $\underline{Mn}O_4^-$ +7
e $\underline{Cr}_2O_7^{2-}$ +6

15 **a** **i** 0
ii +2
b **i** +5
ii +4
c oxidising agent HNO_3; reducing agent Cu

16

Equation	Conjugate redox pair (oxidation)	Conjugate redox pair (reduction)
$Fe(s) + I_2(aq) \rightarrow FeI_2(aq)$	$Fe(s)/Fe^{2+}(aq)$	$I_2(aq)/I^{-}(aq)$
$Mg(s) + FeCl_2(aq) \rightarrow MgCl_2(aq) + Fe(s)$	$Mg(s)/Mg^{2+}(aq)$	$Fe^{2+}(aq)/Fe(s)$
$10Br^{-}(aq) + 2MnO_4^{-}(aq) + 16H^{+}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Br_2(aq)$	$Br^{-}(aq)/Br_2(aq)$	$MnO_4^{-}(aq)/Mn^{2+}(aq)$
$Cu(s) + 2NO_3^{-}(aq) + 4H^{+}(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$	$Cu(s)/Cu^{2+}(aq)$	$NO_3^{-}(aq)/NO_2(g)$

17

Step	Task	How it's done	Half-equation
1	Balance nitrogens.	Already balanced	$NO_3^- \rightarrow NO_2$
2	Balance oxygens by adding H_2O.	Add one H_2O molecule(s) to the right-hand side of the equation.	$NO_3^- \rightarrow NO_2 + H_2O$
3	Balance hydrogens by adding H^+.	Add $2H^+$ ion(s) to the left-hand side of the equation.	$NO_3^- + 2H^+ \rightarrow NO_2 + H_2O$
4	Balance charge by adding electrons.	Charge on left-hand side = –1 + 2 = +1 Charge on right-hand side = 0 Add one e^- to the left-hand side of the equation.	$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$
5	Add state symbols to give the final half equation.	Give the appropriate states for each reactant and product in the equation.	$NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$

18 $2IO_3^-(aq) + 12H^+(aq) + 10e^- \rightarrow I_2(aq) + 6H_2O(l)$

19 Oxidation half-equation: $SO_2(g) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$
Reduction half-equation: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
Overall equation: $3SO_2(g) + Cr_2O_7^{2-}(aq) + 2H^+(aq) \rightarrow 3SO_4^{2-}(aq) + 2Cr^{3+}(aq) + H_2O(l)$

20 Half-equations:
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
$2MnO_2(s) + 2H^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + H_2O(l)$
Overall equation:
$Zn(s) + 2MnO_2(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + H_2O(l)$

21 **a** $2H_3AsO_4(aq) + 4H^+(aq) + 4e^- \rightarrow As_2O_3(s) + 5H_2O(l)$
$I^-(aq) + 3H_2O(l) \rightarrow IO_3^-(aq) + 6H^+(aq) + 6e^-$
b $6H_3AsO_4(aq) + 2I^-(aq) \rightarrow 3As_2O_3(s) + 2IO_3^-(aq) + 9H_2O(l)$

22 Ag, Cu, Sn, Ni, Mg, Li

23 **a** $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
b no reaction
c no reaction
d $Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s)$
e no reaction
f no reaction
g no reaction
h $Pb(s) + 2Ag^{2+}(aq) \rightarrow Pb^{2+}(aq) + 2Ag(s)$

24 **a** no
b yes. $Zn(s) + 2AgNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + 2Ag(s)$
c yes. $Zn(s) + SnCl_2(aq) \rightarrow ZnCl_2(aq) + Sn(s)$
d yes. $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

25 Place 10 mL of each solution into a clean test-tube. Add a small piece of magnesium ribbon to each solution. The magnesium should be coated by displaced metal in the silver nitrate and lead nitrate solutions, but not in the sodium nitrate. The lead coating will be black. Over time, the silver coating will change from black to silver as more metal is deposited. To confirm the identity of the silver nitrate solution, take a fresh sample and add a small piece of copper. Copper will displace silver from the solution, giving silver deposit and a blue solution. Copper will not displace lead from the solution.

26 zinc

27 Coatings of metals other than iron would be expected on the nails placed in 1 M solutions of $CuSO_4$ and $Pb(NO_3)_2$. These solutions contain oxidants that are strong enough to react with iron metal. The iron, in turn, reduces the metal ions in the solution, forming a coating on the nail.

28 Individual students' responses required.

29 **a** **i** +3
ii +2
iii +4
b $S_2O_4^{2-}(aq) + 2H_2O(l) \rightarrow 2HSO_3^-(aq) + 2H^+(aq) + 2e^-$
$S_2O_4^{2-}(aq) + 2H^+(aq) + 2e^- \rightarrow S_2O_3^{2-}(aq) + H_2O(l)$

30 **a** Oxidation number of nitrogen in $(NH_4)_2Cr_2O_7$ is –3 and in N_2 it is 0.
Oxidation number of chromium in $(NH_4)_2Cr_2O_7$ is +6 and in Cr_2O_3 it is +3.
Nitrogen has been oxidised and chromium has been reduced.
b **i** $2NH_4^+(s) \rightarrow N_2(g) + 8H^+(aq) + 6e^-$
ii $Cr_2O_7^{2-}(s) + 8H^+(aq) + 6e^- \rightarrow Cr_2O_3(s) + 4H_2O(g)$
c Reaction i is oxidation, reaction ii is reduction
d $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + Cr_2O_3(s) + 4H_2O(g)$
e $NH_4^+(s)/N_2(g)$ and $Cr_2O_7^{2-}(aq)/Cr_2O_3(s)$

31 **a** $Fe_2O_3(s) + 6e^- \rightarrow 2Fe(l) + 3O^{2-}(s)$
b reduction
c $Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(l) + Al_2O_3(s)$
d 5.29 g (3 significant figures)

32 **a** $Ag^+(aq)$; $Mg^{2+}(aq)$
b Mg(s); Ag(s)
c A coating of silver will form on the lead when it is placed in silver nitrate solution because Ag^+ ions are stronger oxidants than Pb^{2+} ions.
d zinc and magnesium

33 S < R < T

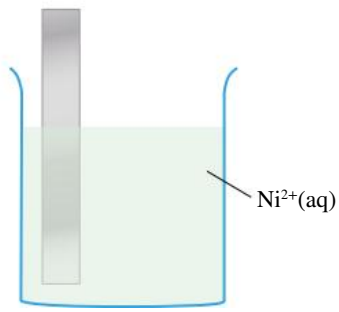
Chapter 9 Galvanic cells

Section 9.1 Galvanic cells

9.1 Key questions

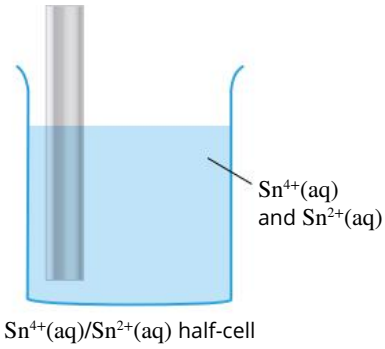
1 D

2 **a**

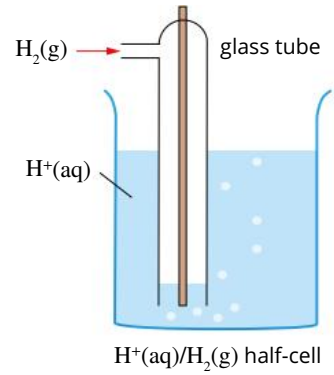


$Ni^{2+}(aq)/Ni(s)$ half-cell

b

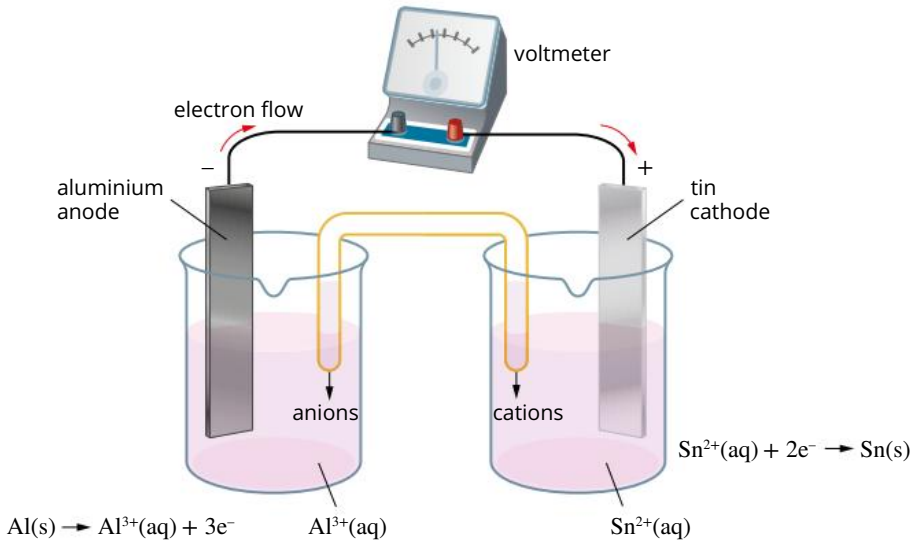


c



3 **a** $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$
b $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

4



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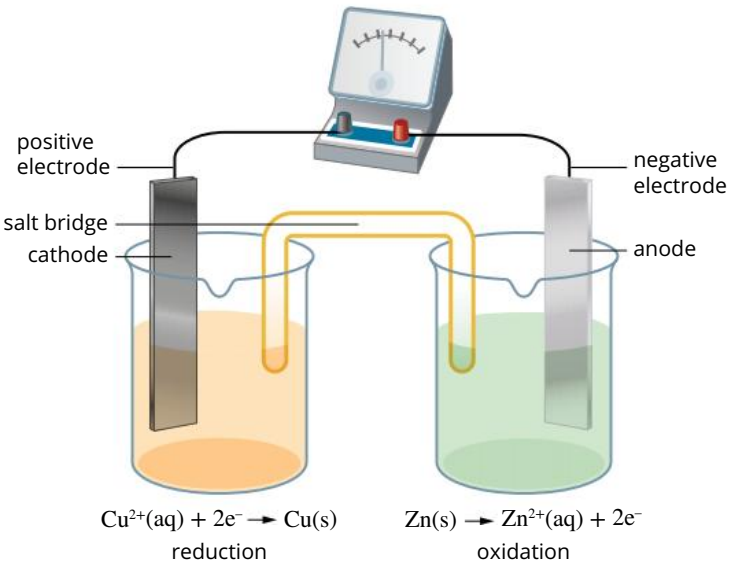
5 $Al(s) \mid Al^{3+}(aq) \parallel Sn^{2+}(aq) \mid Sn(s)$

6

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



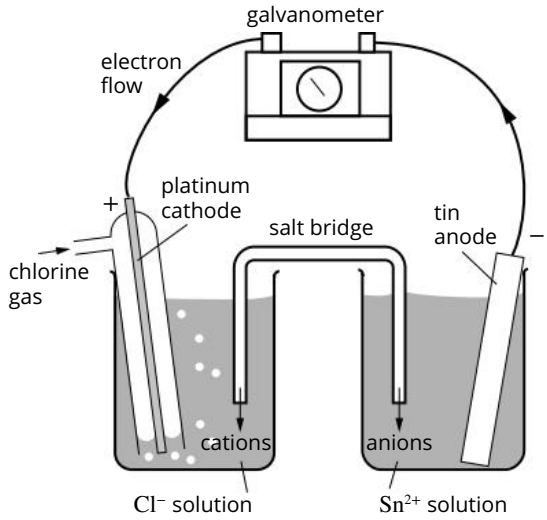
Section 9.2 The electrochemical series

WE 9.2.1 The nickel electrode will be the anode and the tin electrode will be the cathode.
Electrons flow from the negative electrode (anode) to the positive electrode (cathode).

9.2 Key questions

1 **a** Reduction: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$
Oxidation: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$
b $3Pb^{2+}(aq) + 2Al(s) \rightarrow 3Pb(s) + 2Al^{3+}(aq)$
c The lead electrode will be the cathode and the aluminium electrode will be the anode.

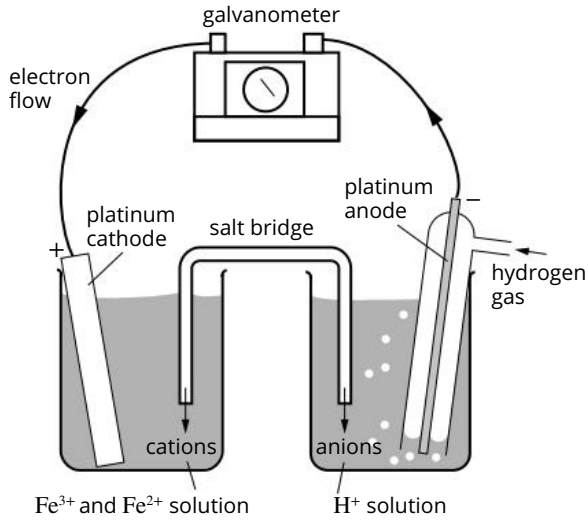
2



$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$

Overall reaction: $Cl_2(g) + Sn(s) \rightarrow 2Cl^-(aq) + Sn^{2+}(aq)$

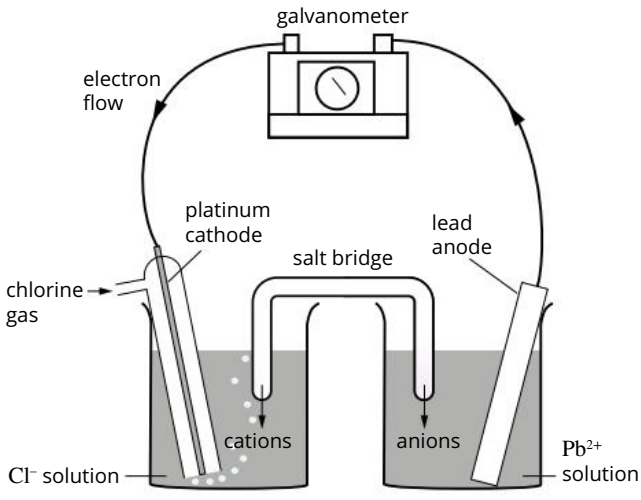
3 a



$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

Overall reaction: $2Fe^{3+}(aq) + H_2(g) \rightarrow 2Fe^{2+}(aq) + 2H^+(aq)$

b



$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$

Overall reaction: $Cl_2(g) + Pb(s) \rightarrow Pb^{2+}(aq) + 2Cl^-(aq)$

4 Question 1 cell: 1.55 V
Question 2 cell: 1.50 V
Question 3a cell: 0.77 V
Question 3b cell: 1.49 V

Section 9.3 Predicting direct redox reactions

WE 9.3.1

a No reaction occurs because both I_2 and Pb^{2+} are oxidising agents.

b No reaction 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.

9.3 Key questions

1 B **2** C

3 a A reaction occurs
$Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(l)$

b A reaction occurs.
$Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(s)$

c No reaction occurs.

d A reaction occurs.
$Br_2(l) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(s)$

4 a $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$

b Chemical energy is transformed into heat energy.

5 $CuSO_4$: A reaction occurs.
$MgCl_2$: No reaction occurs.
$Pb(NO_3)_2$: A reaction occurs.
$ZnCl_2$: No reaction occurs.

Section 9.4 Everyday sources of power

9.4 Key questions

1 Secondary cells can be recharged, whereas primary cells cannot.

2 A **3** B, C, G **4** A

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

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

Section 9.5 Corrosion

9.5 Key questions

1 $2Fe(s) + O_2(aq) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq)$
$4Fe(OH)_2(s) + O_2(aq) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$
In the first equation the oxidation number of iron increases from 0 to +2; in the second equation the oxidation number of iron increases from +2 to +3.

2 Moisture in the air contains a higher amount of dissolved salts (e.g. NaCl(aq)). Salts are good electrolytes and accelerate the rusting process because they increase the conductivity of moisture on the surface of the iron.

3 a magnesium and zinc

b Only metals more reactive (i.e. more easily oxidised) than iron will act as sacrificial anodes. These more reactive metals will be oxidised in preference to the iron. The iron will become the cathode (the site of reduction) and no oxidation of the iron will take place.

4 Reduction of oxygen occurs when there is plenty of moisture and the oxygen concentration is high; that is, at or just above the surface of the water. A cathodic region forms here. So, the anodic region is close to the cathode and where the oxygen concentration is less; that is, just below the surface. Oxidation, or corrosion, therefore occurs more rapidly below the surface.

5 As zinc is more reactive than steel, it will be the anode and steel will be the cathode. Oxidation, and so corrosion, of the nails will thus be prevented.

Chapter 9 Review

1 D **2** A

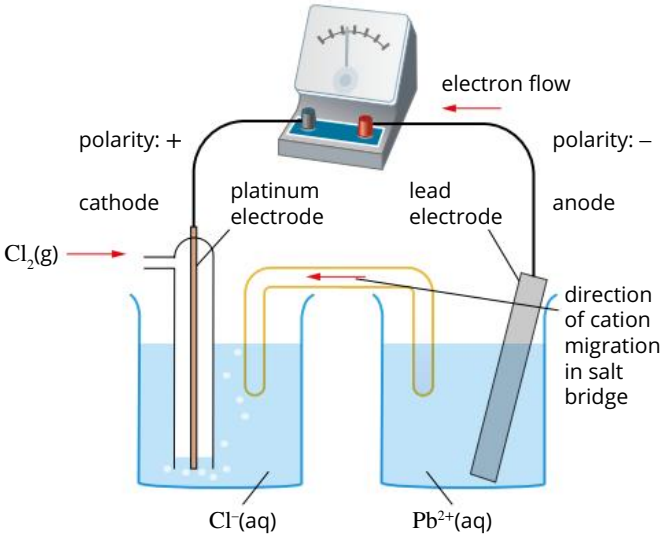
3 **a** Oxidant: a substance that causes another substance to be oxidised and is reduced in the process. Reductant: a substance that causes another substance to be reduced and is oxidised in the process.

b Anode: electrode at which oxidation occurs. Cathode: electrode at which reduction occurs.

c Conjugate redox pair: an oxidant and its corresponding reduced form, e.g. Cu^{2+}/Cu. The reduced form has gained electrons. Conjugate acid–base pair: A conjugate acid contains one more hydrogen ion or proton than the base.

d External circuit: section of a circuit where the electrons flow, e.g. through wires. Internal circuit: part of cell where the current is due to the movement of ions, e.g. in the salt bridge.

4 **a**

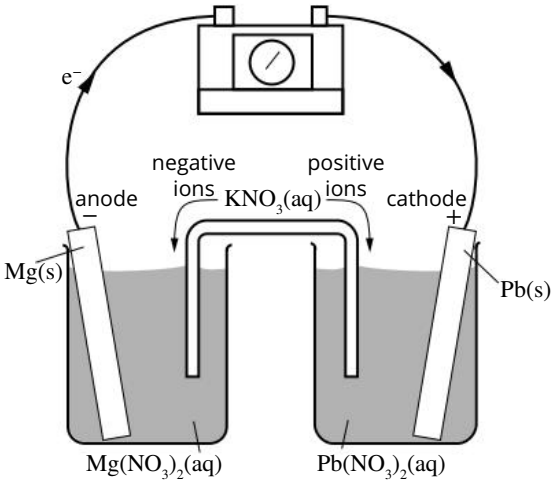


half-equation: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

half-equation: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e$

b $Pb(s) \mid Pb^{2+}(aq) \parallel Cl^-(aq) \mid Cl_2(g) \mid Pt$

5 **a**



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

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

Overall: $Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s)$

c Lead electrode is the cathode; magnesium electrode is the anode

d Anions will migrate to the $Mg^{2+}(aq)/Mg(s)$ half-cell, cations to the $Pb^{2+}(aq)/Pb(s)$ half-cell.

6 cell potential difference = higher half-cell $E°$ – lower half-cell $E°$

$= E°\ (Cu^{2+}(aq)/Cu(s)) - E°\ (Zn^{2+}(aq)/Zn(s))$

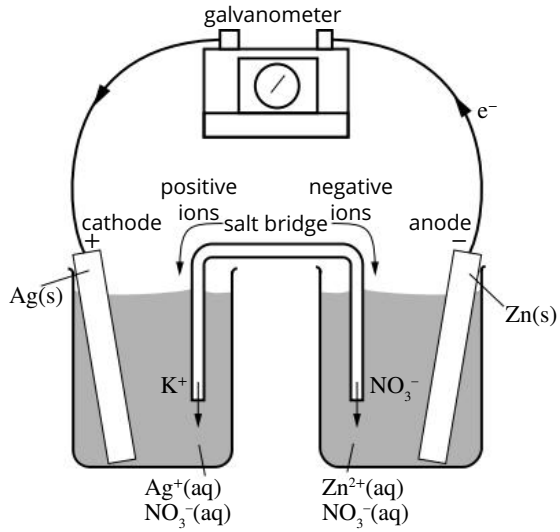
$= 0.34 - (-0.76)$

$= 1.10\,V$

7 $Sn^{2+} > Fe^{2+} > Br^-$.

8
- $Ni^{2+}(aq)/Ni(s)$ and $Br_2(l)/Br^-(aq)$
- $Fe^{2+}(aq)/Fe(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$
- $Ni^{2+}(aq)/Ni(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$
- $Ni^{2+}(aq)/Ni(s)$ and $Fe^{2+}(aq)/Fe(s)$

9 **a**

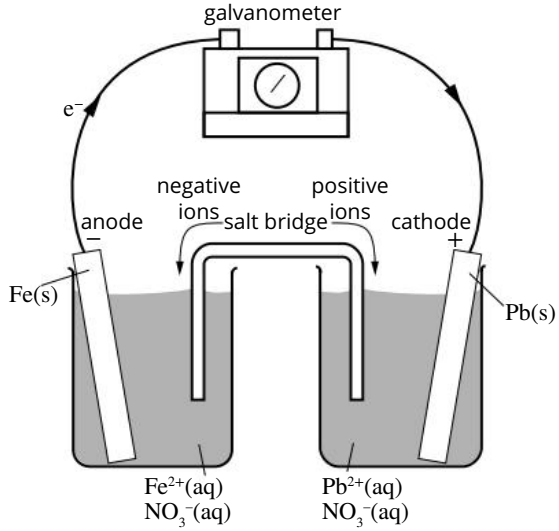


Cathode (+): $Ag^+(aq) + e^- \rightarrow Ag(s)$

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

Overall: $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$

b

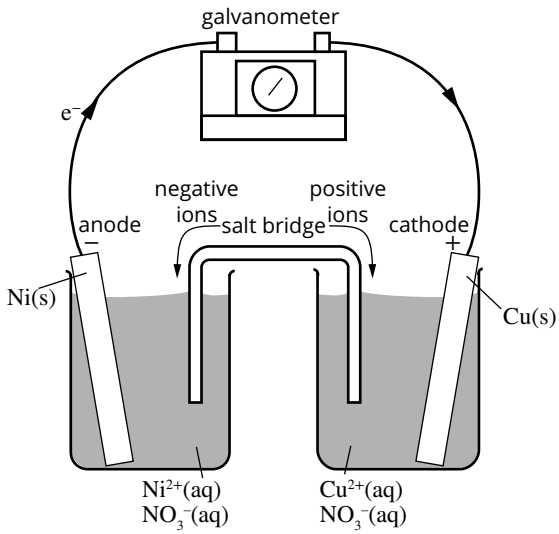


Cathode (+): $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

Anode (–): $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

Overall: $Fe(s) + Pb^{2+}(aq) \rightarrow Fe^{2+}(aq) + Pb(s)$

c



Cathode (+): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Anode (–): $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$

Overall: $Ni(s) + Cu^{2+}(aq) \rightarrow Ni^{2+}(aq) + Cu(s)$

10 $B^{2+} > A^{2+} > C^{2+} > D^{2+}$

11 **a** **i** A reaction occurs.
ii $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (oxidation); $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ (reduction)
iii $Zn(s) + Cl_2(g) \rightarrow Zn^{2+}(aq) + 2Cl^-(aq)$
b **i** No reaction occurs.
c **i** A reaction occurs.
ii $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (oxidation); $Ag^+(aq) + e^- \rightarrow Ag(s)$ (reduction)
iii $2Ag^+(aq) + Zn(s) \rightarrow 2Ag(s) + Zn^{2+}(aq)$
d **i** No reaction occurs.

12 **a** $3Cu^{2+}(aq) + 2Al(s) \rightarrow 3Cu(s) + 2Al^{3+}(aq)$
b No reaction occurs.
c $2Ag^+(aq) + Zn(s) \rightarrow 2Ag(s) + Zn^{2+}(aq)$
d $2H^+(aq) + Fe(s) \rightarrow H_2(g) + Fe^{2+}(aq)$
e No reaction occurs.

13 **a** $Ag^+(aq)$; $Mg^{2+}(aq)$
b Mg(s); Ag(s)
c A coating of silver will form on the lead when it is placed in silver nitrate solution because Ag^+ ions are stronger oxidants than Pb^{2+} ions.
d zinc and magnesium

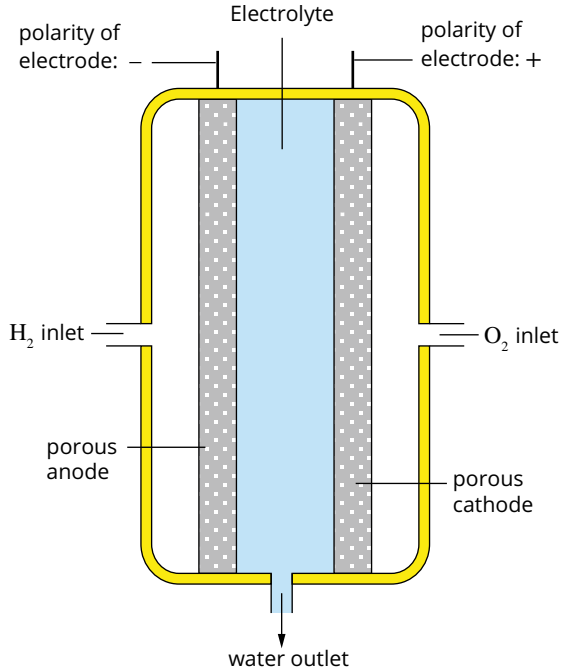
14 **a** oxidising agent
b strong reducing agent
c true
d false
e true

15 **a** $Fe^{2+}(aq)$ and $H^+(aq)$ are formed
b $2Fe^{3+}(aq) + H_2(g) \rightarrow 2Fe^{2+}(aq) + 2H^+(aq)$
c If significant reaction had occurred, the yellow solution containing Fe^{3+} ions would have become pale green as Fe^{2+} ions formed. Because no reaction was observed, the rate of the reaction may have been slow. Alternatively, it must be remembered that the electrochemical series is only valid for certain conditions. It is possible that under the conditions in which the experiment was performed, little reaction would occur.

16 Galvanic cell: device that converts chemical energy into electrical energy
Primary cell: a non-rechargeable galvanic cell
Secondary cell: a rechargeable galvanic cell
Fuel cell: a cell in which reactants are supplied continuously

17 **a** Electrons flow away from the negative electrode (anode), through the external circuit, to the positive electrode (cathode). Therefore, oxidation occurs at the anode and reduction occurs at the cathode.
b A battery consists of a number of cells connected together in series.
c When a cell discharges, chemical energy is converted to electrical energy. When it is recharged, electrical energy is converted to chemical energy.

18



19 A

20 **a** all types of cells
b all types of cells
c all types of cells
d secondary cells only
e all types of cells
f primary and secondary cells only
g fuel cells only

21 Convenience and flexibility of the portable equipment powered by these cells. Furthermore, the price of individual cells is regarded as relatively low.

22 D

23 $Fe^{2+}(aq) + OH^-(aq)$
$Fe(OH)_2(s)$
$Fe(OH)_3(s)$
$Fe_2O_3 \cdot xH_2O(s)$

24 Copper is not a very reactive metal and so is not easily oxidised.

25 Near the seaside, moisture in the air contains a higher amount of dissolved salts (e.g. NaCl(aq)). Salts are good electrolytes and accelerate the rusting process. They do this because they increase the conductivity of moisture on the surface of the steel, (which is composed mainly of iron).

26 half-cells, anode, cathode, negative, positive, cannot, can

27 By referring to the electrochemical series, you will see that the position of the Mn^{2+}/Mn pair in the series must be determined in relation to the Zn^{2+}/Zn pair and the H_2O/H_2, OH^- pair. The student could construct an electrochemical cell from an Mn^{2+}/Mn half-cell and a Zn^{2+}/Zn half-cell. If the manganese electrode was found to be the positive electrode, then Mn^{2+} would be a stronger oxidising agent than Zn^{2+} and the Mn^{2+}/Mn pair should be placed between the Zn^{2+}/Zn pair and the Fe^{2+}/Fe pair in the series.
If the manganese electrode were negative, then Mn^{2+} would be a weaker oxidising agent than Zn^{2+} and the Mn^{2+}/Mn pair should be placed below the Zn^{2+}/Zn pair. In this case, the student could

determine whether to place the manganese pair above or below the H_2O/H_2, OH^- pair by constructing a cell from an Mn^{2+}/Mn half-cell and an H_2O/H_2, OH^- half-cell and finding the polarity of the manganese electrode.

28 **a** Bromine is a stronger oxidising agent than iodine, so it reacts with iodide ions. Because bromine is a weaker oxidising agent than chlorine, bromine does not react with chloride ions.

b Hydrogen peroxide acts as both a strong oxidising agent and as a weak reducing agent. (It appears in the electrochemical series on the left side of one half-reaction and the right side of another.) Hydrogen peroxide therefore reacts with itself. The reaction is very slow unless a catalyst such as manganese dioxide is added.

c Sn^{2+} ions can be oxidised to Sn^{4+} ions by a suitable oxidising agent. Tin metal can reduce Sn^{4+} ions so that they re-form Sn^{2+} ions.

d Zinc is a stronger reducing agent than iron and, if the two metals are in contact, the zinc is oxidised preferentially. For this reason, the presence of a zinc block on the iron hull of a ship protects the hull from corrosion.

29 A reducing agent stronger than I^- ions would react with iodine. By referring to the electrochemical series, you can see that a solution containing Sn^{2+} ions might react and cause the stain to be removed.

30 The electrochemical series is based on reactions occurring under standard conditions of 25°C (298 K), 1 bar (100 kPa) pressure and 1 mol L^{-1} concentration and can only be used to predict the possibility of reaction occurring under these conditions. The series gives no information about the rate of reactions so even if a reaction is predicted it may be so slow that no reaction is apparent.

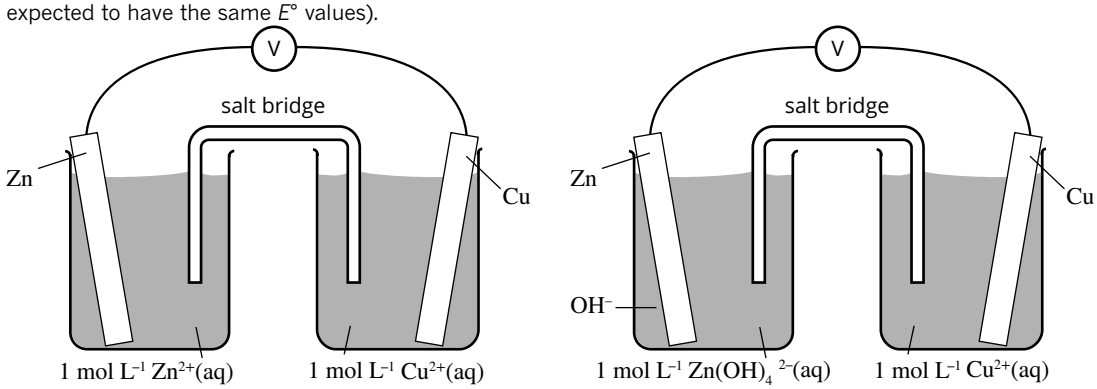
---

31 **a** $Zn(s) + 4OH^-(aq) + Cu^{2+}(aq) \rightarrow Zn(OH)_4^{2-}(aq) + 2Cu(s)$

b The student should make two electrochemical cells consisting of the:

- Cu^{2+}/Cu half-cell and the 'alkaline zinc half-cell'
- Cu^{2+}/Cu half-cell and the Zn^{2+}/Zn half-cell as shown in the diagrams.

The cell voltages should be measured and if they are identical then the two half-cells have the same $E°$ values (they would not be expected to have the same $E°$ values).



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32 **a**

- Both cells are designed to convert chemical energy into electrical energy at relatively high efficiencies.
- Oxidation and reduction reactions take place in different places within the cells.
- Both have an anode, which is negative, at which an oxidation half-reaction occurs.
- Both have a cathode, which is positive, at which a reduction half-reaction occurs.
- Both have an electrolyte, which provides ions to balance charges formed at the electrodes; cations flow towards the cathode and anions flow towards the anode.

b

- A fuel cell produces electrical energy continuously when reactants are provided; primary cells can produce power for only a limited time until their reactants are depleted.
- A fuel cell uses a combustible fuel and air or oxygen; primary cells can be made from different combinations of two conjugate redox pairs.
- The reactants in fuel cells are usually gaseous; a range of solids, liquids and gases can be used as the reactants in primary cells.
- Electrodes in fuel cells must be porous to allow contact between reactant gases and the electrolyte; electrodes in primary cells need not be porous.
- Catalysts are used in fuel cells to increase cell efficiency; catalysts are not required in primary cells.

33 Advantages:

- Much more efficient than power stations and fossil-fuel-driven vehicles
- Almost the only product apart from electricity is water, so fewer carbon emissions
- Generate power continuously as they are supplied with gaseous fuel, which is ideal for commercial power generation
- Operate more quietly than internal combustion engines
- Hydrogen can be generated using renewable energy or from biogas
- Heat produced as a by-product can be used for other purposes, including electricity generation.

Disadvantages:

- Costly to produce
- Rate of the cell reaction is slow, so expensive catalytic material is needed
- Most hydrogen is produced from fossil fuels, in a process that creates greenhouse gases and consumes energy
- Lack of a hydrogen distribution network and the costs associated with the construction of pipelines, filling stations etc.
- Storage issues caused by hydrogen's low energy content per unit volume
- Safety issues due to the explosive nature of hydrogen

Chapter 10 Electrolysis

Section 10.1 Electrolytic cells

10.1 Key questions

1 A **2** B

3 non-spontaneous, electrical energy, chemical energy, positive, negative, oxidation, reduction

4 Anode half-equation: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
Cathode half-equation: $Zn^{2+}(l) + 2e^- \rightarrow Zn(l)$
Overall reaction: $Zn^{2+}(l) + 2Cl^-(l) \rightarrow Cl_2(g) + Zn(l)$

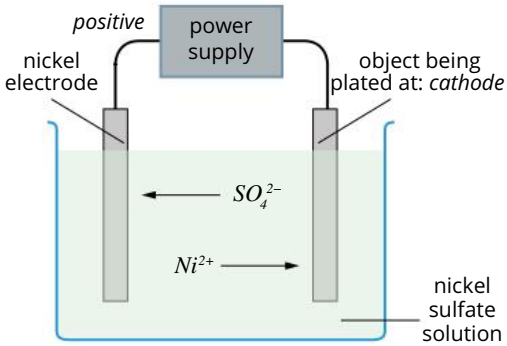
5 **a** Nickel will be formed at the negatively charged nickel rod.
b At the cathode: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
At the anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
c $2Ni^{2+}(aq) + 2H_2O(l) \rightarrow 2Ni(s) + O_2(g) + 4H^+(aq)$

Section 10.2 Industrial applications of electrolysis

10.2 Key questions

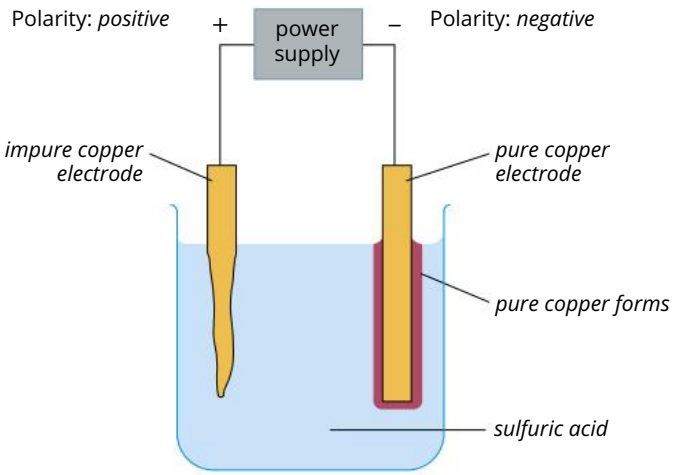
1 D

2 **a**
electrode polarity:



b $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$
c $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
d SO_4^{2-} ions will be attracted to the positive anode and Ni^{2+} ions will be attracted to the negative cathode. The SO_4^{2-} ions do not react at the electrode.

3 **a**



b $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
c $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

4 Cu^{2+} ions are produced at the anode at the same rate as they are consumed at the cathode. The concentration of the ions therefore remains constant.

Chapter 10 review

1 **a** In galvanic cells, the anode is negative and the cathode is positive; in electrolytic cells the anode is positive and the cathode is negative.
b In galvanic cells, the direction of electron flow is determined by the cell reaction; in electrolytic cells the direction of electron flow is determined by the external power supply. Direction of electron flow is always from anode to cathode through the external circuit.
c In galvanic cells, chemical energy is converted into electrical energy; in electrolytic cells electrical energy is converted into chemical energy.
d Galvanic cell reactions occur spontaneously; electrolytic cell reactions are non-spontaneous.

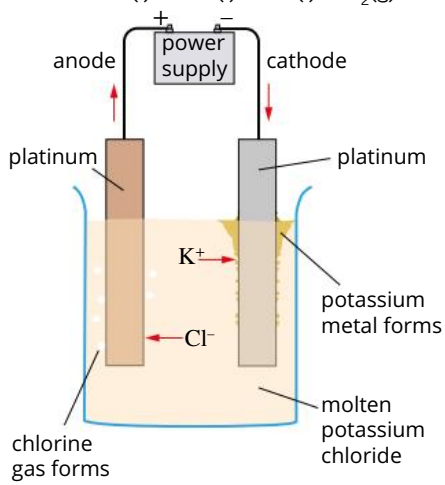
2 (clockwise from top left): chemical energy, non-spontaneous reactions, electrolyte, anode, cathode

3 D

4 **a** galvanic cells
b electrolytic cells
c both
d galvanic cells
e both

5 Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
Cathode: $Zn^{2+}(l) + 2e^- \rightarrow Zn(l)$
Overall: $Zn^{2+}(l) + 2Cl^-(l) \rightarrow Zn(l) + Cl_2(g)$

6



7 **a** **i** $2I^-(aq) \rightarrow I_2(aq) + 2e^-$
ii $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
b $2I^-(aq) + 2H_2O(l) \rightarrow I_2(aq) + H_2(g) + 2OH^-(aq)$

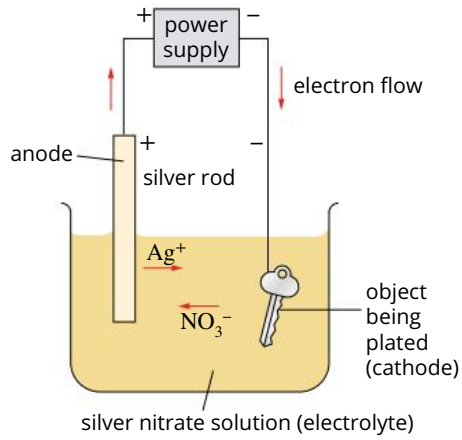
8 cathode, reduction, positive, oxidation

9 B

10 Iron is likely to rust in the wet environment of a bathroom. Nickel and chromium layers are deposited on bathroom taps by an electroplating process in order to prevent contact between the iron and water and oxygen. The surface of the taps also gains a lustrous, attractive appearance. (Nickel is used in combination with chromium to improve corrosion resistance.)

11 C

12 **a**



b The reactions at the electrodes would be reversed. The silver plating would dissolve from the key and be redeposited on the silver electrode.

13 A. In an electrorefining cell for copper, impure copper is placed at the anode and a thin sheet of pure copper is placed at the cathode. The anode is positive and the cathode is negative. Copper ions in the electrolyte solution are reduced to copper metal at the cathode, so this electrode increases in mass.

14 anode, oxidation, negative, reduction, cathode, anode, cathode.

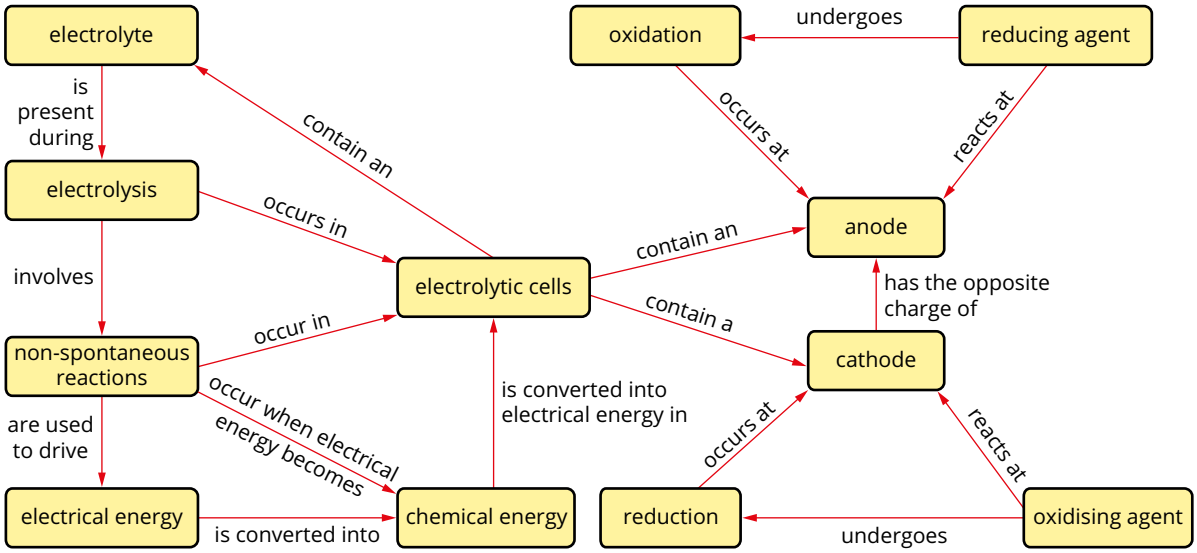
15 **a** A spontaneous reaction occurs naturally, either in electrochemical cells or when chemicals are mixed directly. The reaction does not need to be driven by an external source of energy. Non-spontaneous reactions are the reverse of spontaneous reactions; they are reactions that would not normally occur without the application of electrical energy.

b The anode is an electrode where oxidation occurs; the cathode is an electrode where reduction occurs.

c An electrochemical cell is a device that converts chemical energy into electrical energy, or vice versa. Both galvanic and electrolytic cells are electrochemical cells. An electrolytic cell only converts electrical energy into chemical energy.

d Electrorefining is a process of purification of a metal by electrolysis. Electroplating is a process that uses electrolysis to deposit a layer of metal on the surface of another material.

16



17 By definition, oxidation always occurs at the anode. The process of oxidation involves loss of electrons. In a galvanic cell, since negatively charged electrons are produced at the anode, this electrode is described as negative.
However, in an electrolytic cell, the positive terminal of the power supply is connected to the positive electrode of the cell. The power supply draws electrons away from the electrode, causing an oxidation reaction to occur. The positive electrode is therefore the anode.

18 The reaction in a galvanic cell is spontaneous and if the reactants in the cell were in the one container and in contact with each other, the reaction between them could occur directly, releasing energy as heat rather than as electricity.
In electrolysis cells the reaction is non-spontaneous, so that both the electrode reactions can occur within the same container. However, the products of the electrolysis reaction should not be allowed to come into contact with each other, or a reaction may occur.

Unit 3 Review

Section 1: Multiple choice

1	A	**2**	D	**3**	D	**4**	C
5	B	**6**	B	**7**	C	**8**	B
9	C	**10**	D	**11**	A	**12**	D

Section 2: Short answer

1 **a** **i** The concentration of sodium thiosulfate is higher, so there will be more frequent collisions between reactant particles. While the probability of any particular collision being successful is unchanged, the higher frequency of collisions overall will increase the frequency of successful collisions and hence the rate of reaction.

ii The higher temperature means the particles in the mixture will be moving faster and hence colliding more frequently. Also, and more significantly, having faster-moving particles means there will be a higher proportion of collisions that are successful, because there is a greater chance of a collision having energy greater than the activation energy. These two factors combine to give a higher frequency of successful collisions and hence a higher rate of reaction.

b **i** The rates of the forward and reverse reactions are equal up until time T.

ii The addition of reactant W increases the frequency of collisions between reactants and so the rate of the forward reaction increases initially. Because the forward reaction is now the faster, there will be a net forward reaction. This increases the concentration of the products, so the reverse reaction speeds up. When the two rates become equal again, equilibrium has been re-established and no further change in the rates occurs.

iii Because the forward reaction is faster (the reverse reaction has slowed to a greater extent), there will be a net forward reaction and the equilibrium shifts to the right.

iv Exothermic. Lowering the temperature will always induce a shift in the position of equilibrium in the direction of the exothermic reaction, which in this case must be the forward reaction since that is the direction of the shift.

v Both rates increase equally. This is the characteristic effect of a catalyst.

2 **a** A is NO_2. B is N_2O_4.

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

c Final concentration will be unchanged, but reached in less time.

d **i** increase

ii decrease

iii no change

3 **a** **i** $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

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

iii Water (H_2O) is a stronger oxidising agent than Li^+ and would be preferentially reduced at the cathode, producing hydrogen gas rather than lithium metal.

iv A mixed electrolyte will have a lower melting temperature, making the process safer and less expensive. Potassium chloride is appropriate because K^+ will not be reduced in preference to Li^+.

b Graphite is a good electrical conductor, relatively inexpensive, relatively inert and it has a high melting temperature.

c Metallic cathodes are always inert because the electrolytic process ensures only reduction can occur at their surface. However, the iron in a steel anode would likely be a better reducing agent than the target species, so that the outcome would be the oxidation of the electrode itself rather than the desired electrode reaction.

4 a A pair of electrodes (anode and cathode) and an electrolyte.

b In a galvanic cell, reactants undergo spontaneous reaction to generate electricity. The energy transformation is: chemical energy → electrical energy.
In an electrolytic cell, electricity is used to drive non-spontaneous reactions to produce useful chemical products (often very reactive ones). The energy transformation is: electrical energy → chemical energy.

c Electrons always flow from the site of oxidation (the anode) to the site of reduction (the cathode). In a galvanic cell, the electrons flow spontaneously from the oxidation reaction at the anode, which is therefore designated negative. In an electrolytic cell, the electrons are driven through the cell from the negative terminal of an external power source to its positive terminal. Thus, the electrode designated negative in the electrolytic cell receives electrons from the power source and is the site of reduction, making it the cathode.

d A galvanic cell employs a spontaneous redox reaction (favourable oxidising–reducing agents combination) to produce an electron flow. If the reactants come into direct contact, electrons flow directly between them and no current is produced. In an electrolytic cell, there are no favourable combinations and instead non-spontaneous reactions occur by forcing a current through the cell, forming reactive products that would react spontaneously if allowed to come into contact.

5 a i $H_2S(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + H_3O^+(aq)$

ii $K = \frac{[H_3O^+][HS^-]}{[H_2S]}$

b 1.0 mol L^{-1}

c i A solution that resists changes in pH over a small range of values.

ii This buffer system contains the weak acid hydrogen sulfide and its conjugate weak base the hydrogen sulfide ion. The equilibrium can be written as:
$H_2S(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + H_3O^+(aq)$
If a small amount of the strong acid HCl is added, the extra H_3O^+ will move the position of equilibrium to the left so as to partly compensate for the increase in concentration of product according to Le Châtelier's principle. The concentration of H_3O^+ will fall and so the pH will rise to near (but still below) its original value.

d $2Ag^+(aq) + H_2S(aq) \rightarrow 2Ag(s) + S(s) + 2H^+(aq)$

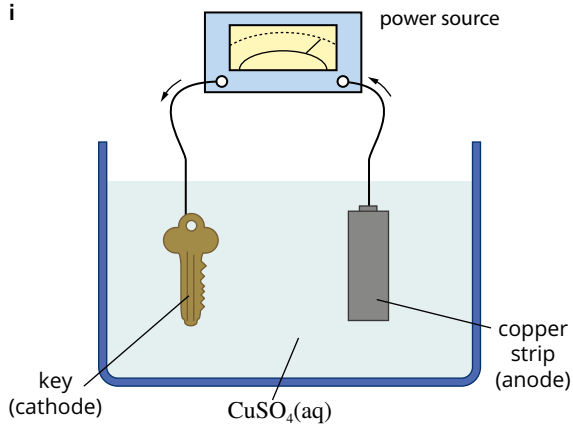
6 a i $Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$

ii The Fe atoms have lost electrons to form Fe^{2+} ions, while the H^+ ions have gained electrons to form H_2 molecules. Redox reactions involve this type of electron transfer. Or the oxidation number of Fe increases from 0 to +2 and the oxidation number of H reduces from +1 to 0.

iii $Fe_2O_3(s) + 3H_2SO_4(aq) \rightarrow Fe_2(SO_4)_3(aq) + 3H_2O(l)$

iv O^{2-} ions have gained H^+ ions to form H_2O, while H_2SO_4 molecules have lost H^+ ions to form SO_4^{2-} ions. Acid–base reactions involves this type of proton (H^+) transfer.

b i



ii The key needs to be connected to the negative electrode.

iii cathode

iv The concentration of Cu^{2+} ions in the electrolyte does not change because the copper ions are continually supplied by the oxidation of the copper anode as copper ions are consumed at the cathode.

v Reaction at the anode would be: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$. As H^+ ions are produced, the pH would decrease.

Section 3: Extended answer

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

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

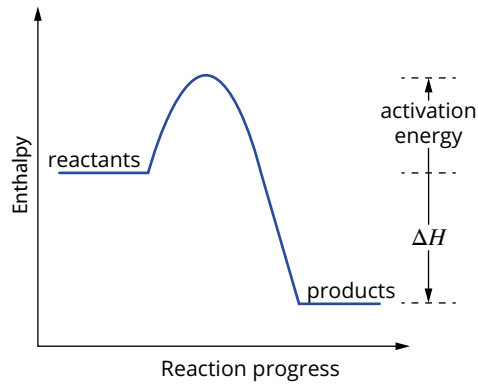
b i Catalysts

ii The yield would be poorer. Because the reaction is exothermic, increasing the temperature would favour the reactants/shift the position of equilibrium to the left/lower the equilibrium constant.

iii High pressure will increase the reaction rate, so products form faster. Also, because the number of product particles (1 on the right-hand side) is smaller than the number of reactant particles (3 on the left-hand side), high pressure will favour the forward reaction and increase yield.

c Exposure to CO will drive the first reaction to the right. This lowers the concentration of free haemoglobin (Hb_4), which drives the second reaction to the left, removing $Hb_4.O_2$.

d



e i $2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

ii $CH_3OH(g) + H_2O(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$

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

iv In a fuel cell chemical energy is converted to electrical energy, with some loss of heat energy. In direct combustion, chemical energy is converted to thermal energy.

v For example: They are similar in that both have electrodes and an electrolyte. They are different in that fuel cell electrodes have a catalytic function, while those in galvanic cells do not.

f i $PbO_2(s) + Pb(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
ii 1.69 – (–0.36) = 2.05 V
iii E° values are determined at standard conditions (1.0 mol L^{-1} solutions). Concentrations in the lead-acid cell are not 1.0 mol L^{-1}, and so electrode potential values may differ.
iv Discharging is operating as a galvanic cell. Oxidation occurs at the negative anode.
v Positive to positive. Negative to negative.

2 a i An acid that only partially ionises in water.
ii $K = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$

b i To show that the reaction is complete.
ii $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$
iii 2.31 mol L^{-1}
iv NaOH completely dissociates in water.
$[OH^-] = 0.10$
$[H_3O^+] \times [OH^-] = 10^{-14}$
$\therefore 0.10 \times [H_3O^+] = 10^{-14}$
$\therefore [H_3O^+] = 10^{-13}$ mol L^{-1}
$\therefore pH = -\log_{10}[H_3O^+] = -\log_{10}10^{-13} = 13$

c i 25.0 mL
ii 0.10 mol L^{-1} HCl has a pH of 1.0
iii 7.0
iv Greater than 7.0. At the equivalence point the titration flask will contain the products of the reaction, including the conjugate base of ethanoic acid (CH_3COO^-). This basic species gives the solution a pH of greater than 7 at the equivalence point.

d i $H_2O_2(aq) + H_2O(l) \rightleftharpoons HO_2^-(aq) + H_3O^+(aq)$
ii The rate of the decomposition reaction is slow, especially without the catalytic action of light (storage in dark bottles). Cooling the solution further slows the rate at which the H_2O_2 reacts with itself.

e i The self-ionisation reaction of water produces ions which allow the liquid to conduct. However, the concentration of ions is extremely low, accounting for the very poor conductivity.
$2H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(aq)$
ii 7.4
iii 1.45×10^{-7} mol L^{-1}
iv oxidising agent

Chapter 11 Key products from the chemical industry

Section 11.1 Yield and the chemical industry

WE 11.1.1 76.5%
WE 11.1.2 43.2%

11.1 Key questions

1 246.34 g
2 82.5%
3 a 31.5%
b The overall yield would be reduced by a factor of 5 (because the yield of step B → C is reduced by a factor of 5).
4 6.350×10^2 g

Section 11.2 Calculations involving limiting reagents

WE 11.2.1 a $Pb(NO_3)_2$
b 0.837 g

11.2 Key questions

1 II, IV, I, V, III
2

Nitrogen molecules available	Hydrogen molecules available	Ammonia molecules produced	Nitrogen molecules in excess	Hydrogen molecules in excess
2	10	4	0	4
879	477	318	720	0
9 mol	6 mol	4 mol	7 mol	0 mol

3 a $2Na(s) + Cl_2 \rightarrow 2NaCl(s)$
b 63.8 g
4 a $Pb(NO_3)_2$ is in excess by 0.50 mol.
b $Pb(NO_3)_2$ is in excess by 1.75 mol.
c KI is in excess.
$m(PbI_2) = 1.39$ g
d $Pb(NO_3)_2$ is in excess.
$m(PbI_2) = 8.64$ g

Section 11.3 Some key products

11.3 Key questions

1 A and D
2 a

	Increase	Decrease	No change
Reaction rate	Addition of a catalyst Increasing pressure	Reducing temperature	
Equilibrium yield	Reducing temperature Increasing pressure		Addition of a catalyst

b Increasing the partial pressure of nitrogen will increase the frequency of collisions between nitrogen and hydrogen molecules and so increase the rate of the forward reaction. The yield of ammonia at the new equilibrium will also increase as the rate of forward reaction will be higher at the new equilibrium than it was at the original equilibrium.

3 A = $N_2(g)$
B = $H_2(g)$
C = $N_2(g)$, $H_2(g)$ and $NH_3(g)$
D = $NH_3(l)$
E = $N_2(g)$ and $H_2(g)$
4 D
5

Burner	Converter	Absorption tower
$O_2(g)$, S(l)	$O_2(g)$, $SO_2(g)$	$SO_3(g)$, $H_2SO_4(l)$

6 Sulfur dioxide dissolves in rain, making rain acidic due to formation of sulfurous acid. Also, sulfur dioxide corrodes metal and is harmful to plants and aquatic animals.

Chapter 11 review

1 a 3.26 g
b 72.1%
2 a 68.4%
b 3.70×10^6 g
c 2.53×10^6 g
3 9.96×10^5 g
4 The reaction of sulfur dioxide and oxygen is reversible, and the yield of this reaction will be affected by the reaction conditions. The other two reactions in the process are not reversible.

5

Carbon atoms available	Oxygen molecules available	Carbon dioxide molecules produced	Carbon atoms in excess	Oxygen molecules in excess
8	20	8	0	12
1000	3000	1000	0	2000
9 mol	6 mol	6 mol	3 mol	0 mol

6 **a** oxygen
b 1.5 mol
7 **a** 22.6 g
b 4.93 g
8 2.43×10^6 g
9 **a** Rock phosphate is insoluble in water and plants can only absorb nutrients through their roots when dissolved in water.
b 1492 kg

10 Ammonia has a lower boiling point than both nitrogen and hydrogen. This is because there are only dispersion forces of attraction between neighbouring nitrogen molecules and neighbouring hydrogen molecules, while there are dispersion and hydrogen bonding forces between neighbouring ammonia molecules. This means more energy is needed to overcome the force of attraction between neighbouring ammonia molecules.
11 **a** $NH_3 + HNO_3 \rightarrow NH_4NO_3$
b $2NH_3 + CO_2 \rightarrow CO(NH_2)_2 + H_2O$
c urea

12 The steam reforming process used to recover the hydrogen from methane releases the greenhouse gas CO_2 to the atmosphere. As methane is the main component of natural gas, a fossil fuel, the carbon released in the CO_2 has not been a part of the carbon cycle for millions of years, which leads to an increase in CO_2 in the atmosphere and so contributes to global warming.
13 **a** A = molten sulfur; B = sulfur dioxide; C = sulfur trioxide; D = unreacted sulfur dioxide; E = oleum diluted to form sulfuric acid
b If moisture is present in the air, it may react with sulfur dioxide to form sulfurous acid as shown in the reaction: $H_2O + SO_2 \rightarrow H_2SO_3$
14 converter, V_2O_5, moderate, beds, cooled, SO_2, absorption tower, converter, SO_2
15 C **16** D
17 **a** Yield of H_2 will be maximised under conditions of high temperature and low pressure. Le Châtelier's principle predicts that increasing the temperature of a reaction favours the endothermic direction, so in this case the forward reaction will be favoured, thus increasing yield of H_2. Le Châtelier's principle predicts that decreasing the pressure of a reaction favours the side with most gas molecules, so in this case the forward reaction will be favoured, thus increasing yield of H_2.
b The high temperature will increase the rate of reaction because a higher proportion of collisions will have energy above the activation energy. The low pressure will reduce the rate of reaction because this will reduce the frequency of collisions between reactant molecules.
18 **a** 75–100 atm
b Both the forward and reverse reaction rates will be smaller at the new equilibrium because at the lower temperature the proportion of molecules colliding with energy above the activation energy will be smaller (as well, the frequency of collisions between molecules will be less). Le Châtelier's principle predicts that lowing the temperature of a reaction favours the exothermic direction, so in this case the forward reaction will be favoured, thus increasing yield of NH_3.
c Both the forward and reverse reaction rates will be less at the new equilibrium because at the lower pressure the frequency of collisions between molecules will be less. Le Châtelier's principle predicts that reducing the pressure in a gaseous reaction will favour the side with more gas molecules, so in this case the reverse reaction will be favoured, thus decreasing yield of NH_3. The combination of increased yield from the lower temperature and decreased yield from the lower pressure mean the yield remains at about 20%.
19 **a** 9.59×10^5 L
b 5.19×10^6 g
20 **a** $2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$
b Release of ammonium ions from the ammonium sulfate allows them to undergo hydrolysis to produce hydronium ions, which increases the soil acidity.
$NH_4^+(aq) + H_2O(l) \rightarrow NH_3(aq) + H_3O^+(aq)$

Chapter 12 Resources and the environment

Section 12.1 Green chemistry

WE 12.1.1 55.2%

12.1 Key questions

1 A philosophy of designing resource-efficient, environmentally friendly and low-hazard chemical products and processes.
2 The focus of green chemistry is to eliminate waste and pollution through technological and engineering means before they are generated, whereas environmental chemistry studies chemical processes that occur in the natural environment and how they are affected by human activities such as mining and pollution.
3 Prevent waste, design safe chemicals and products, design less hazardous chemical syntheses, use renewable raw materials, use catalysts, avoid using excess reactants, avoid chemical derivatives, maximise atom economy, use safer solvents and reaction conditions, increase energy efficiency, design for degradation, analyse in real time to prevent pollution and minimise the potential for accidents.
4 Using renewable materials ensures that there is a constant, environmentally friendly source of raw material as opposed to using non-renewable materials that will eventually run out.
5 The new ibuprofen synthesis has a much higher atom economy, which means less costly raw material ends up as waste products. Also, because there are fewer steps in the newer synthesis, it is likely that it is much faster-acting than the old one.
6 Water is a highly polar molecule, whereas hydrophobic substances such as oil and grease are non-polar. A non-polar solvent is required to form dispersion forces with the non-polar oil and grease.
7 Glycine is environmentally benign, cheaper, recyclable and non-toxic and can be used for *in situ* leaching.
8 Introduce an additional source of fresh, oxygenated water to the Peel–Harvey Estuary. Reduce the use of phosphate-containing fertilisers in the Peel–Harvey region.

Chapter 12 review

1 D **2** C **3** false
4 A **5** false
6 Use fewer reagents, generate less waste, use renewable materials and be more energy efficient.
7 Storing, treating and disposing of waste costs significant amounts of money. Reducing the amount of waste produced would reduce running costs, thereby increasing profit margins. Also, using renewable materials means that production would not have to cease once a finite starting resource has been exhausted.
8 Catalysts allow reactions to use less energy and to proceed at a rate that does not necessitate high concentrations, thereby using fewer resources.
9 Using nearby resources reduces the requirement to transport large quantities of materials over large distances, which consumes a large amount of energy.

10 This would have caused air pollution as a result of incinerating waste, resulting in photochemical smog (due to the release of volatile organic compounds and oxides of nitrogen) and acid rain (due to the release of oxides of sulfur and nitrogen).
11 By using smaller quantities of reagents and disposing of chemicals correctly according to the teacher's instructions.
12 Carbon dioxide: asphyxiant in high concentrations and liquid may cause cold burns. Perchloroethylene: eye and skin irritation, toxic if swallowed, irregular heartbeat and possible carcinogen.

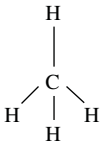
Chapter 13 Structure of organic molecules

Section 13.1 Diversity of carbon compounds

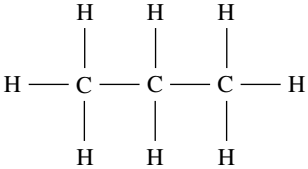
WE 13.1.1 *cis*-5-methylhept-2-ene

13.1 Key questions

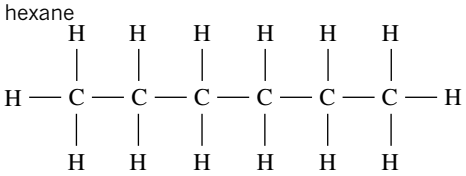
1 A, D
2 **a** CH_4
b It is a compound of carbon and hydrogen.
c Carbon has the electronic configuration of 2,4. Each carbon atom needs four electrons to complete its outer shell. Hydrogen has an electronic configuration of 1. Each hydrogen atom needs one electron to complete its outer shell. Because 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.
d This tetrahedral arrangement gives minimum electrostatic repulsion between the four pairs of bonding electrons. The hydrogen atoms are arranged around the central carbon atom in a tetrahedral configuration.



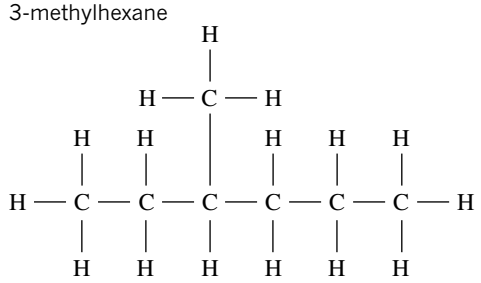
3 **a** Propane. This hydrocarbon contains three carbon atoms, so the stem name is prop-. Its formula fits the general formula of an alkane, C_nH_{2n+2} ($n = 3$ so $2 \times 3 + 2 = 8$). Hence the name of the hydrocarbon is propane.
b $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$
c



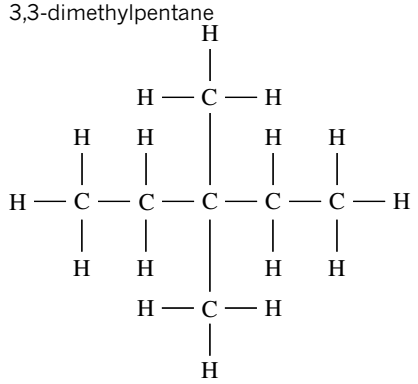
d $CH_3CH_2CH_3$
4 **a** butane
b heptane
c 2-methylpentane
d 2-methylbutane
e 2,4-dimethylpentane
5 **a** butane
b methylpropane
c 2,4-dimethylpentane
d 3-methylhexane
6 **a** hexane



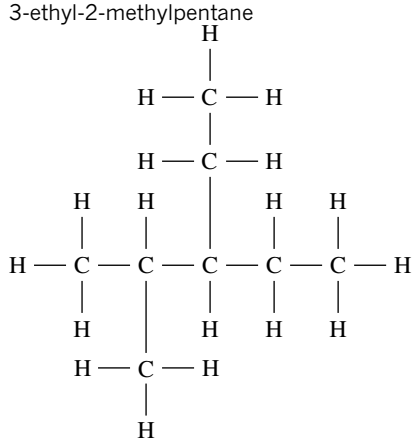
b 3-methylhexane



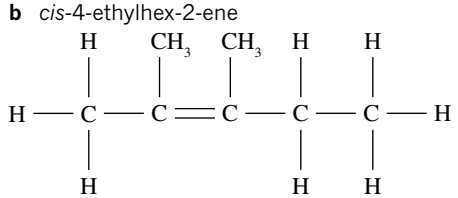
c 3,3-dimethylpentane



d 3-ethyl-2-methylpentane



7 **a** methylbut-2-ene
b *cis*-4-ethylhex-2-ene
8

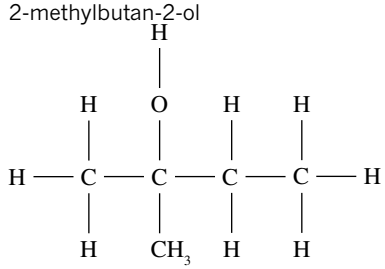


Section 13.2 Functional groups

WE 13.2.1 propan-2-ol
WE 13.2.2 2,4-dimethylpentan-3-ol
WE 13.2.3 5-methylhexanoic acid
WE 13.2.4 methyl butanoate

13.2 Key questions

1 2-methylbutan-2-ol

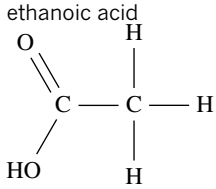


2 **a** pentan-1-ol
b octan-4-amine

3 **a** ketones
b aldehydes
c amides
d esters

4 **a** methyl methanoate
b methanoic acid
c propyl butanoate
d methyl ethanoate
e ethyl hexanoate

5 ethanoic acid



Section 13.3 Properties of organic compounds

13.3 Key questions

1 alkane, weak dispersion forces, increase, insoluble, weaker, hydrogen bonding

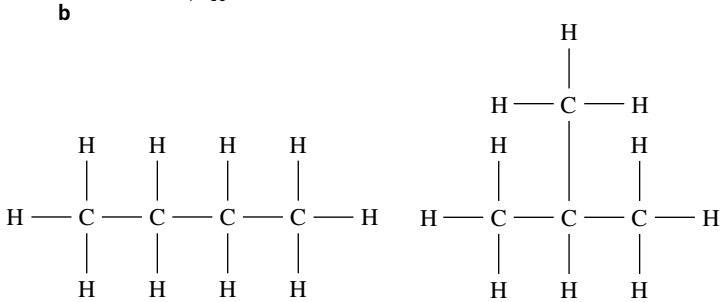
2 $CH_3CH(CH_3)CH_3$, $CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_3$, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Boiling point will increase with molecular size. The presence of branching within the molecule will produce a lower boiling point compared to a molecule of similar size with a straight chain structure.

3 CHCH, CH_3CHCH_2, $CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2OH$, $CH_3CH_2CH_2COOH$

Section 13.4 Isomers overview

13.4 Key questions

1 **a** butane (C_4H_{10})
b



2 The carbon atoms in hydrocarbons have four bonds to other atoms. According to the valence shell electron repulsion theory, the angle around between each bond is 109.5° and the geometry around each carbon is tetrahedral. This means that carbon–carbon bonds are much less than 180° and so the chain is zig-zag shaped.

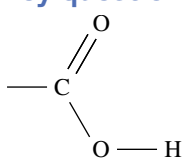
3 **a** alkenes i, iii, iv and v
b alkenes i and iii
c alkene ii

Section 13.5 IUPAC nomenclature overview

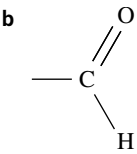
WE 13.5.1 6-chlorohexan-1-amine

13.5 Key questions

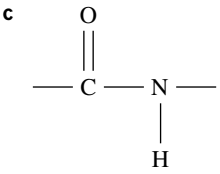
1 **a**



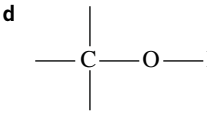
b



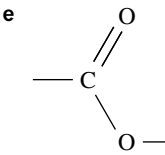
c



d

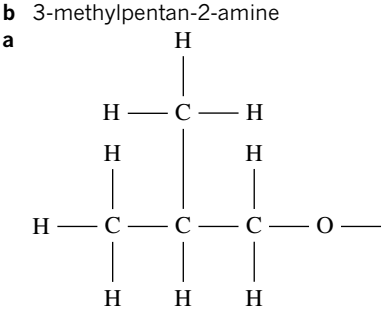


e

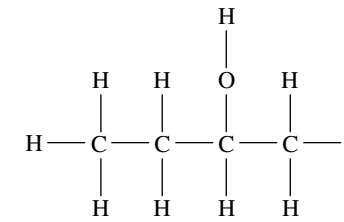


2 **a** 3-hydroxybutanoic acid
b 3-methylpentan-2-amine

3 **a**



b



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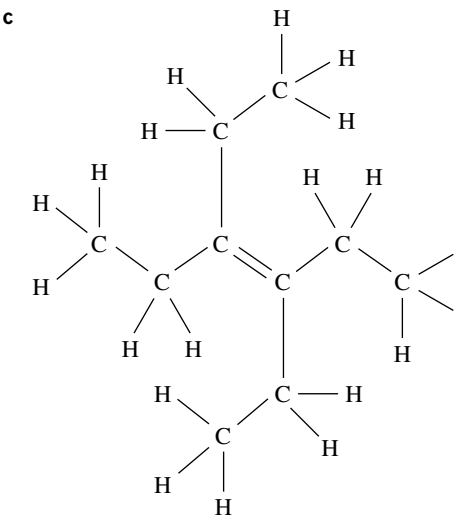


4 **a** **i** $NH_2CH_2CH_2CH_3$
ii $CH_3CH(OH)CH(CH_2CH_3)CH_3$
b The name of an amine is given by the suffix amine, so the name of structure a(i) should be propanamine.

The name of an alcohol is given the suffix -ol, so the first correction is naming this butan-2-ol to represent the position of the hydroxyl group on the second carbon. The second correction is naming the branched alkyl, which in this case is ethyl. This part of the name is not incorrect, so the correct name is 3-ethylbutan-2-ol.

Section 13.6 Determining formulae of organic compounds

WE 13.6.1 % carbon = 64.9%
% hydrogen = 13.5%
% oxygen = 21.6%
WE 13.6.2 CH_2O
WE 13.6.3 CH_3
WE 13.6.4 C_6H_6

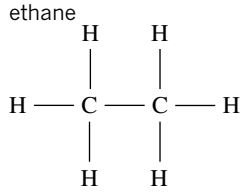
13.6 Key questions

1 D.
2 % of carbon 76.6%, % of hydrogen 6.4%, % of oxygen 17%
3 **a** Carbon = 60.0 g; oxygen = 26.7 g; hydrogen = 13.3 g
b n(C) = 5.00 mol, n(O) = 1.67 mol, n(H) = 13.3 mol
c C = 2.99, O = 1, H = 7.96
d C : O : H = 3 : 1 : 8
e C_3H_8O
4 $C_6H_{14}O_6$
5 C_2H_6O

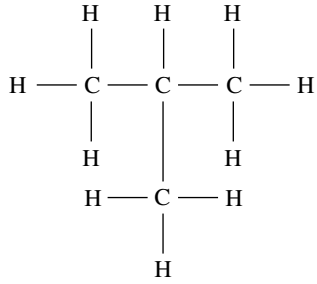
Chapter 13 review

1 Carbon atoms can use two electrons each to bond to form very long chains. This leaves the other two valence electrons able to bond other non-metal atoms onto the chain. In addition, there can be double and triple bonds between carbon atoms, as well as ring structures. All these possible variations mean that an enormous number of different compounds containing carbon can be formed.
2 A
3 **a** alkanes
b $C_{17}H_{36}$
c $C_{15}H_{32}$
d 234 g

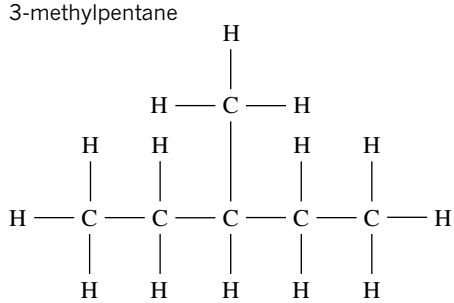
4 **a** ethane



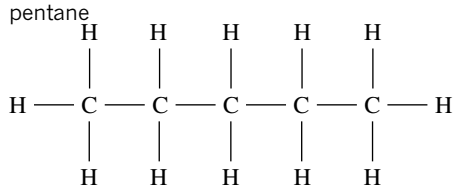
b methylpropane



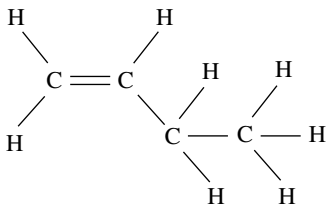
c 3-methylpentane



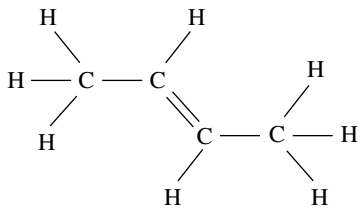
d pentane



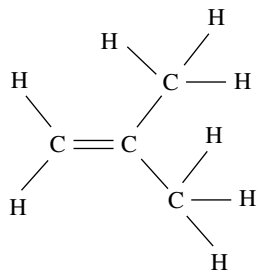
5 but-1-ene



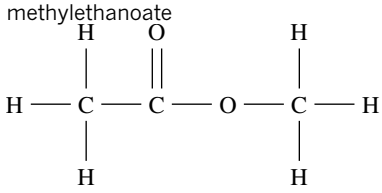
but-2-ene



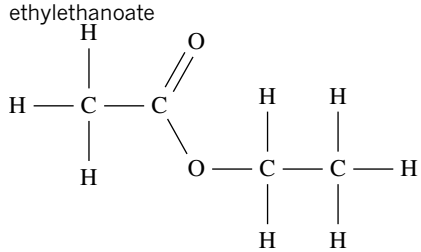
methylpropene



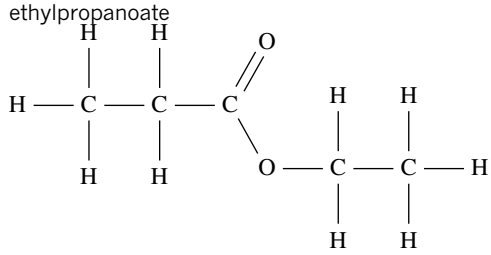
6 hydroxyl; polar; hydrogen; intermolecular; small
7 **a** True
b True
c False
8 D
9 A
10 **a** pentanoic acid
b 3-methylbutanoic acid
c 4-methylhexanoic acid
d 3-ethylpentanoic acid
11 **a** methylethanoate



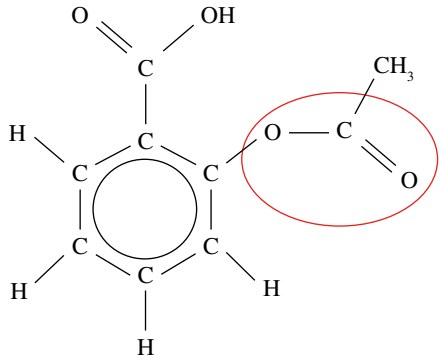
b ethylethanoate



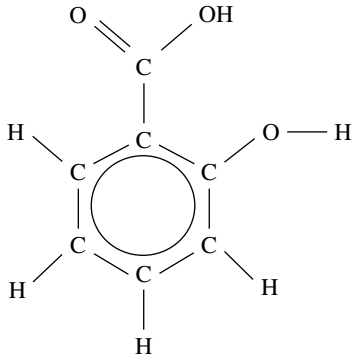
c ethylpropanoate



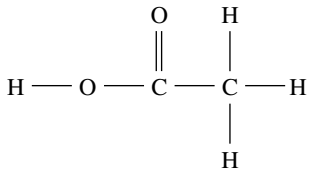
12 **a** ester functional group is circled in red.



b the alcohol



the carboxylic acid



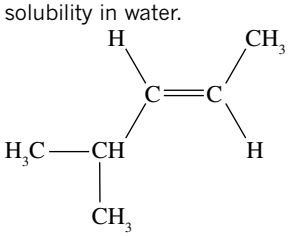
13 Aldehydes contain a carbonyl group at the end of a carbon chain, ketones contain a carbonyl group within the chain, a carboxylic acid has a carbonyl group with a hydroxyl group attached to the carbon, an amide has a carbonyl group with an amino group attached to the carbon.

14 Alcohols contain a hydroxyl group so hydrogen bonds can form between alcohol molecules. Hydrogen bonds are stronger than the dispersion forces between alkane molecules. This results in alcohols having a higher boiling point than their corresponding alkane.

15 Hydrogen bonds and dispersion forces are the intermolecular forces in both methanol and butan-1-ol, but butan-1-ol has a higher boiling point because it is a larger molecule, so the dispersion forces between its molecules are stronger.

16 As the length of the carbon chain increases, the proportion of the carboxylic acid molecule that is non-polar increases, decreasing its solubility in water.

17



18 *cis*-5-methylhept-2-ene

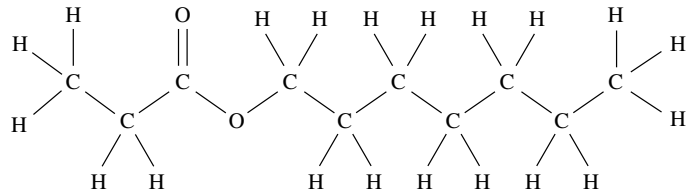
19 **a** butyl ethanoate

b *trans*-2-methylhex-3-ene

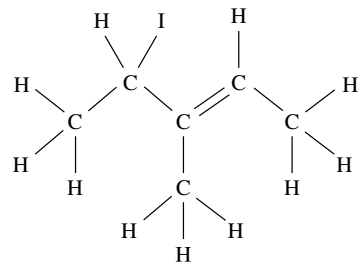
c *cis*-1-bromobut-2-ene

20

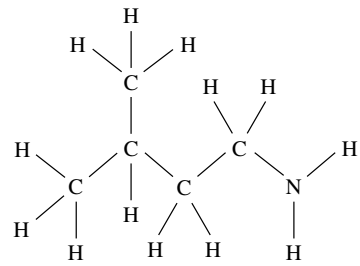
a



b



c



21 0.10 g

22

Empirical formula	Relative molecular mass	Molecular formula
CH	78.0	C_6H_6
CH_3	30.0	C_2H_6
CH_2O	90.0	$C_3H_6O_3$
C_3H_6O	116.0	$C_6H_{12}O_2$
CH_2	98.0	C_7H_{14}

23 **a** The molecular formula is always a whole-number multiple of the empirical formula. The empirical formula provides the simplest whole-number ratio of atoms in a compound. The amount of each atom is found by using $n = \frac{m}{M}$, where m is the mass in grams and M is the molar mass in $g\,mol^{-1}$.

	C	H
Mass	85.7 g	14.3 g
Molar mass	$12\,g\,mol^{-1}$	$1\,g\,mol^{-1}$
Amount using $n = \frac{m}{M}$	$n = \frac{85.7}{12.0} = 7.14\,mol$	$n = \frac{14.3}{1.0} = 14.3\,mol$
Divide all by the smallest amount	$\frac{7.14}{7.14} = 1$	$\frac{14.3}{7.14} = 2$

CH_2

b C_3H_6

c alkene

24 **a** CH_2O

b $C_2H_4O_2$

25 CH_3

26 **a** single covalent bond
b hydroxyl group
c methyl group
d carboxyl group

27 student poster

28 **a** An alkene contains one double carbon–carbon bond, which requires two carbon atoms. The first alkene is therefore ethene.
b The carbon atom has four electrons in the outer shell, which are available for sharing with other atoms to produce four covalent bonds.

29 **a** Polyunsaturated: contains many double bonds; mono-unsaturated: contains one carbon–carbon double bond; saturated: contains only single bonds between carbon atoms.
b Individual student response required.

30 **a** The double bond cannot be in the '4' position as it must be between two carbon atoms. If the 4-carbon is involved in a double bond it should have priority in the name and so be called but-1-ene.
b The longest chain in this arrangement is 5 carbons long, so the stem should be pent- and the branch should be methyl. The correct name is 2-chloro-3-methylpentane.
c The double bond has higher priority than the methyl groups so the name should be 4,4-dimethylpent-2-ene.
d The longest chain in this arrangement is 7 carbons long, so the stem should be hept- and there are no branches. The correct name is 4-bromoheptane.

31 **a** **i** primary alcohol
ii heptan-1-ol
b **i** chloroalkane
ii 4-chloroheptane
c **i** secondary alcohol
ii hexan-2-ol
d **i** carboxylic acid
ii pentanoic acid
e **i** amine
ii butan-2-amine
f **i** alkane
ii 2-methyloctane
g **i** alkene
ii 2-methylpropene

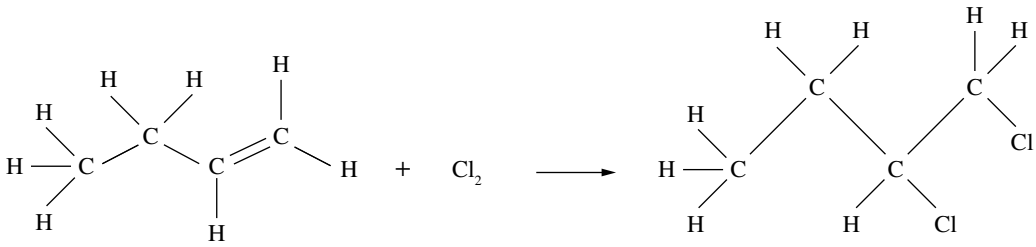
Chapter 14 Reactions of organic molecules

Section 14.1 Chemical properties of alkenes

14.1 Key questions

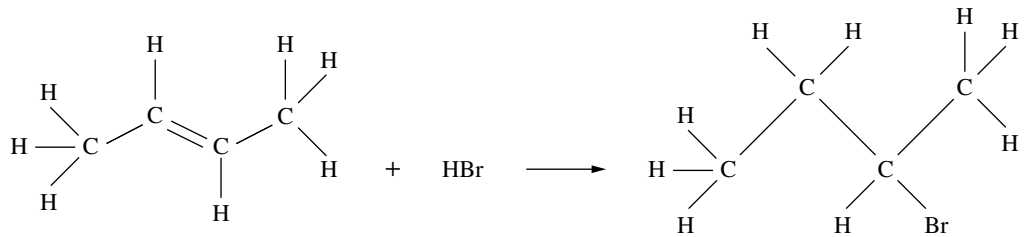
1 **a** chloroethane
b 1,2-dichloroethane
c ethanol
d ethane

2 **a**



but-1-ene 1,2-dichlorobutane

b

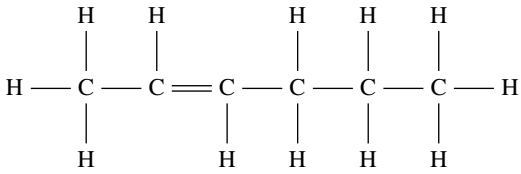


but-2-ene 2-bromobutane

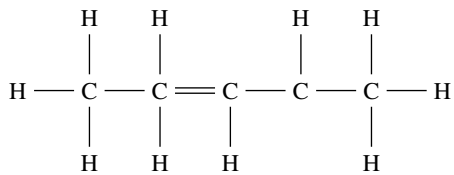
3 **a** ethanol
b 3-chlorohexane or 4-chlorohexane

4 **a** $CH_2CHCH_3 + H_2 \rightarrow CH_3CH_2CH_3$
b $CH_3CHCHCH_3 + I_2 \rightarrow CH_3CHICHICH_3$
c $CH_3CHCHCH_2CH_3 + H_2O \rightarrow CH_3CH_2CHOHCH_2CH_3$

5 **a**



b



Section 14.2 Chemical properties of alcohols

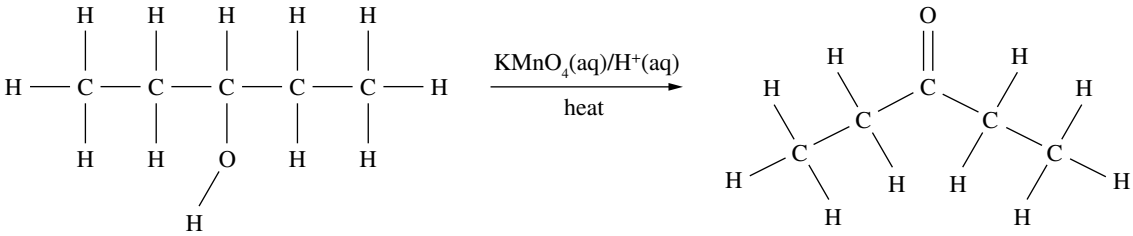
WE 14.2.1 $C_4H_9OH(aq) \rightarrow C_4H_8O(aq) + 2H^+(aq) + 2e^-$
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
$3C_4H_9OH(aq) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3C_4H_8O(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

14.2 Key questions

1 **a** $2C_5H_{12}O(g) + 15O_2(g) \rightarrow 10CO_2(g) + 12H_2O(g)$

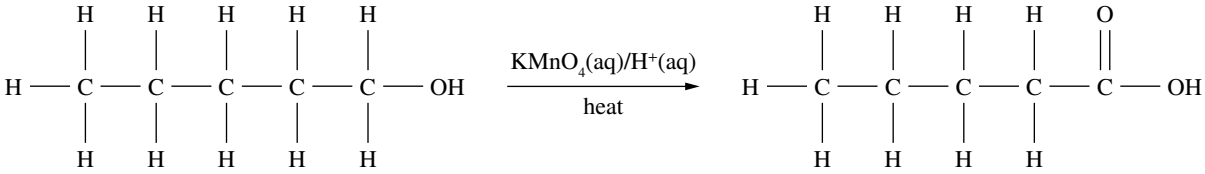
b pentan-3-ol, secondary; 2-methylbutan-2-ol, tertiary; pentan-1-ol, primary

c Pentan-3-ol will oxidise to pentan-3-one. The solution will change from deep purple to colourless.

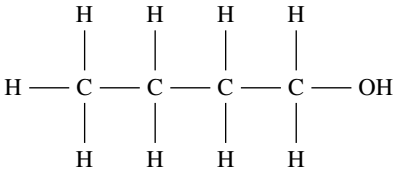


2-Methylbutan-2-ol is a tertiary alcohol so will not react under the conditions described. No colour change will be observed; the solution will remain deep purple.

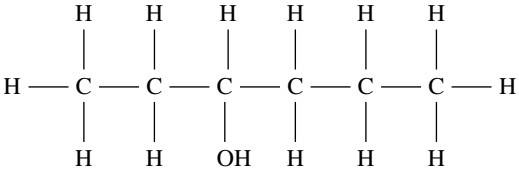
Pentan-1-ol will oxidise to the carboxylic acid. The solution will change from deep purple to colourless as the reaction proceeds.



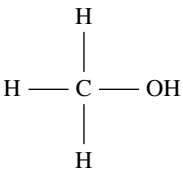
2 **a** butan-1-ol



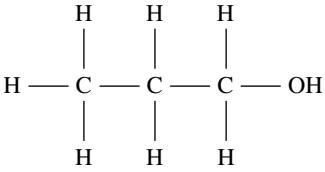
b hexan-3-ol



c methanol



d propan-1-ol



3 **a** Oxidation half-equation:
$CH_3CHOHCH_3 \rightarrow CH_3COCH_3 + 2H^+ + 2e^-$
Reduction half-equation:
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
Redox equation:
$5CH_3CHOHCH_3 + 2MnO_4^- + 6H^+ \rightarrow 5CH_3COCH_3 + 2Mn^{2+} + 8H_2O$

b Oxidation half-equation:
$CH_3CH_2CH_2CH_2OH + H_2O \rightarrow CH_3CH_2CH_2COOH + 4H^+ + 4e^-$
Reduction half-equation:
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
Redox equation:
$3CH_3CH_2CH_2CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3CH_2CH_2COOH + 4Cr^{3+} + 11H_2O$

Section 14.3 Chemical properties of carboxylic acids

14.3 Key questions

1 **a** $CH_3CH_2CH_2COOH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2CH_2COO^-(aq) + H_3O^+(aq)$

b $H_2O > CH_3CH_2CH_2COOH > CH_3CH_2CH_2COO^- = H_3O^+$
Butanoic acid, like other carboxylic acids, is a weak acid and will ionise only to a small extent. That is, the acid ionisation constant is much less than one and thus when butanoic acid is mixed with water only a small percentage of butanoic acid molecules will ionise to form hydronium ions and butanoate ions.

2 $CH_3CH_2COO^-$; propanoate ion

3 **a** $CH_3COOH(aq) + HCO_3^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l) + CO_2(g)$

b $2Na(s) + 2CH_3CH_2COOH(aq) \rightarrow 2CH_3CH_2COO^-(aq) + 2Na^+(aq) + H_2(g)$

4 A

5 $HCOOH + CH_3CH_2CH_2OH \rightleftharpoons HCOOCH_2CH_2CH_3 + H_2O$
Name of organic product: propyl methanoate

6 **a** pentan-1-ol and ethanoic acid

b ethanol and octanoic acid

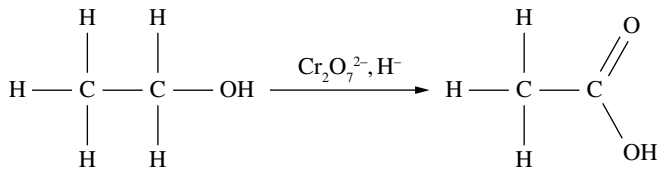
c hexan-1-ol and propanoic acid

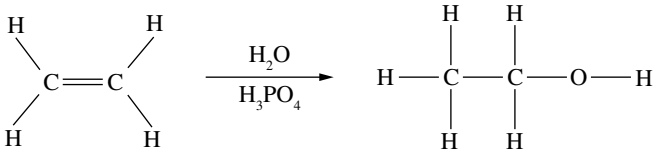
d propan-1-ol and butanoic acid

Section 14.4 creating molecules: an introduction to organic synthesis

WE 14.4.1

$CH_3COOH + CH_3OH \xrightarrow{H_2SO_4} CH_3COOCH_3$





14.4 Key questions

1 **a** Butan-1-ol $\xrightarrow{Cr_2O_7^{2-}, H^+}$ butanoic acid

b Pent-1-ene $\xrightarrow{H_2O, H_3PO_4}$ pentan-2-ol $\xrightarrow{Cr_2O_7^{2-}, H^+}$ pentan-2-one

2 **a** Ethene $\xrightarrow{H_2O, H_3PO_4}$ ethanol

b 1 methanol $\xrightarrow{K_2Cr_2O_7, H^+}$ methanoic acid

2 Propan-1-ol + methanoic acid $\xrightarrow{H^+}$ 1-propyl methanoate

3 1 ethene $\xrightarrow{H_2O, H_3PO_4}$ ethanol

2 ethanol $\xrightarrow{K_2Cr_2O_7, H^+}$ ethanoic acid

3 ethanoic acid + ethanol $\xrightarrow{H^+}$ ethyl ethanoate + water

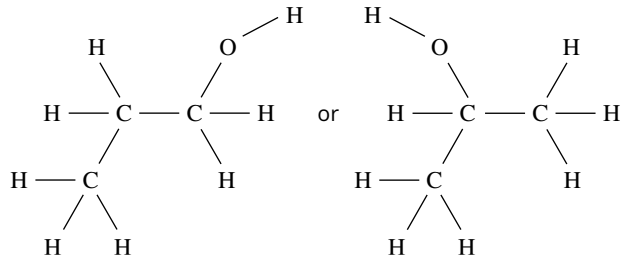
4 Continual addition of ethene and steam keeps the reactant concentrations high and the system never reaches an equilibrium. This means the forward reaction rate is always greater than the reverse so favouring production of ethanol.

Chapter 14 review

1

Reactants	Type of reaction	Product(s)
Alkene and hydrogen	Addition (hydrogenation)	Alkane
Alkene and hydrogen bromide	Addition	Bromoalkane
Alkene and water (with a catalyst and heat)	Addition (hydration)	Alcohol
Alkene and bromine	Addition	Dibromoalkane
Alkene in the presence of a catalyst	Addition polymerisation	Saturated hydrocarbon polymer

2 **a**



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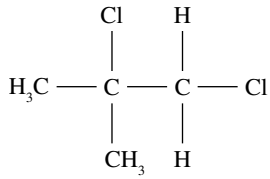


3 **a** hydrogen bromide

b hydrogen chloride

c chlorine gas

d hydrogen gas and nickel catalyst (or other suitable metal—usually a transition metal such as platinum or palladium).

4 **a** C_3H_8; propane; alkane

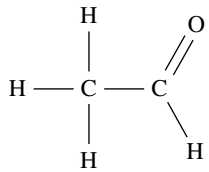
b C_2H_6O; ethanol; alcohol

5 **a** aldehyde, carboxylic acid

b ketone

c no reaction will occur.

6 **a**



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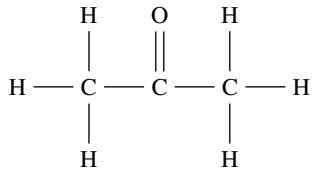
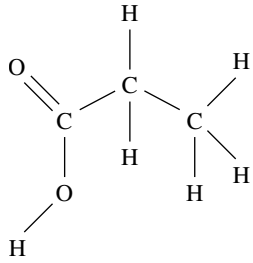


7 **a**



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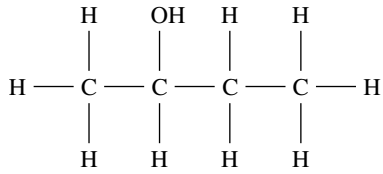

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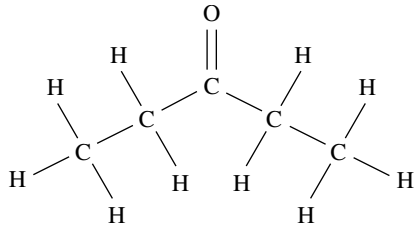

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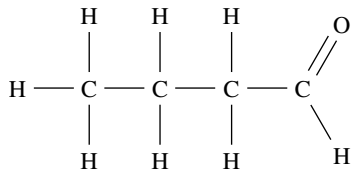


8 Oxidation half-equation: $CH_3CH_2CH_2OH + H_2O \rightarrow CH_3CH_2COOH + 4H^+ + 4e^-$

Reduction half-equation: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Redox equation: $5CH_3CH_2CH_2OH + 4MnO_4^- + 12H^+ \rightarrow 5CH_3CH_2COOH + 4Mn^{2+} + 11H_2O$

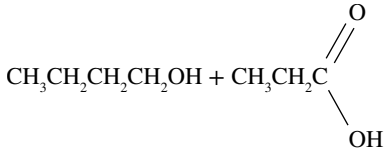
9 In this test, the determination of whether an unknown alcohol is primary, secondary or tertiary depends on observing if any colour change in the permanganate solution from purple to colourless occurs. If the permanganate is added rapidly and in excess, any colour change will be masked by the excess permanganate; the solution will be purple despite any possible reaction occurring.

10 $CH_3CH_2COOH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COO^-(aq) + H_3O^+(aq)$
acid base conjugate base conjugate acid
Propanoic acid, like all carboxylic acids, is a weak acid so concentrations of the propanoate and hydronium ions will be much less than those of the propanoic acid and water molecules.

11 **a** zinc ethanoate, carbon dioxide and water
b zinc ethanoate and water
c zinc ethanoate and hydrogen gas
d zinc ethanoate and water

12 **a** $2HCOOH + Na_2CO_3 \rightarrow 2HCOONa + H_2O + CO_2$
b $2CH_3CH_2COOH + Mg(OH)_2 \rightarrow (CH_3CH_2COO)_2Mg + 2H_2O$

13 **a** $CH_3CH_2COOCH_3(l)$
b $CH_3COO(CH_2)_4CH_3(l)$
c $HCOOCH(CH_3)_2(l)$
d



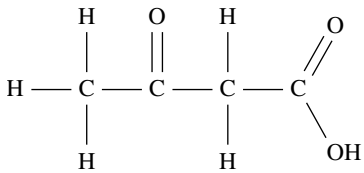
14 **a** CH_2CH_2
b H_3PO_4
c H^+
d CH_3COOH
e H_2SO_4
f $CH_3COOCH_2CH_3$

15 Step 1: hydration (addition). Step 2: oxidation. Step 3: condensation

16 Step 1: hydration of ethene: $CH_2CH_2 + H_2O \rightarrow CH_3CH_2OH$
Step 2: production of propanoic acid: $CH_2CH_2 + H_2O + CO \rightarrow CH_3CH_2CO_2H$
Step 3: condensation: $CH_3CH_2OH + CH_3CH_2CO_2H \rightarrow CH_3CH_2CO_2CH_2CH_3 + H_2O$

17 In the redox reaction of alcohols with permanganate and dichromate, hydrogen ions are needed as a reactant. The sulfuric acid added to the permanganate and dichromate solutions is the source of hydrogen ions. In the condensation reaction of an alcohol with a carboxylic acid, the sulfuric acid acts as a catalyst increasing the rate of reaction.

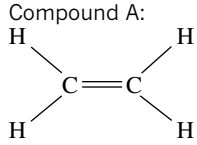
18 **a**



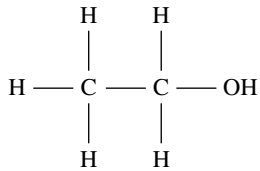
The functional group produced is a ketone.
b During the oxidation of alcohols by dichromate, there is an increase in the number of C–O bonds and a simultaneous decrease (at the same carbon atom) in the number of C–H bonds. Like the tertiary C atom in tertiary alcohols, the carboxylic acid C atom has no C–H bonds so cannot be oxidised by dichromate.

19 **a** Theoretically, yield will be improved by a low temperature. The reaction is exothermic, so a low temperature will favour the exothermic reaction, which is the forward reaction. (Note: in practice to achieve a reasonable rate of reaction, a compromise temperature of about 300°C is used.)
A high pressure will favour a high yield because there is one molecule of gas on the product side of the reaction versus two molecules of gas on the reactant side. Thus, a high pressure will favour the forward reaction. (A high pressure will also favour the rate of reaction, but in practice a pressure of 60–70 atm is used, which in industrial terms is not especially high. If too high a pressure is used, ethene will polymerise. Also, it is expensive to build the pipes and reaction vessels needed to withstand very high pressures.)
b Cooling condenses only the ethanol because it has a lower boiling point than ethene. Ethanol has hydrogen bonding and dispersion forces as its intermolecular forces, while non-polar ethene has only dispersion forces as its intermolecular force.

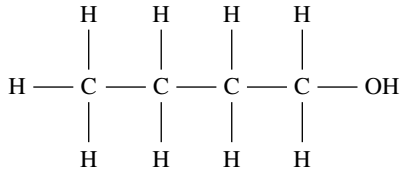
20 **a** Compound A:



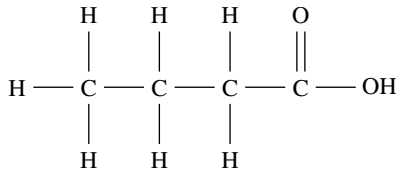
Compound B:



Compound C:



Compound D:



b Compound B. Both compounds display hydrogen bonding, so will hydrogen bond with water molecules, but compound C has stronger dispersion forces. For one substance to dissolve in another, the solute–solute attractions need to be overcome by solute–solvent attractions. Because compound C has stronger dispersion forces, the attractive forces between neighbouring C molecules will be greater than those between neighbouring B molecules, and so C will have lower water solubility.

Chapter 15 From monomers to polymers

Section 15.1 Polymers: a diverse class of materials

15.1 Key questions

1 **a** Polymers are covalent molecular substances composed of many small molecules joined together to form a long chain.
b Monomers are small molecules that react together to form long polymer chains.
c Repeating units are identical small segments that are repeated along a polymer chain.

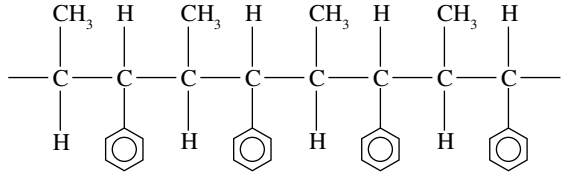
2 Thermosetting and thermoplastic polymers differ in their behaviour upon heating. Thermosetting polymers have extensive covalent cross-linking between polymer chains and burn or decompose upon heating. Thermoplastic polymers do not have cross-linking and melt when heated, allowing them to be reshaped.

3 Polymer A would have stronger intermolecular forces between polymer chains because the reduced branching allows polymer chains to pack together more closely. Branching increases the distance between polymer chains and hence reduces the strength of the dispersion forces.

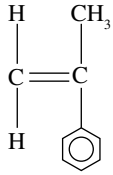
4 Natural rubber exhibits properties typical of elastomers. Therefore, it would be expected to have occasional cross-linking, but not to be extensively cross-linked. The polymer chains need to be able to move past each other when stretched, but also to have sufficient cross-linking to pull the chains back to their original position when the stretching force is removed.

Section 15.2 Addition polymerisation

WE 15.2.1



WE 15.2.2

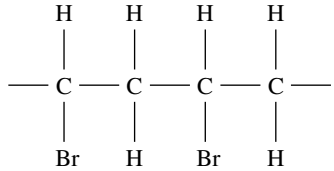


15.2 Key questions

1 D

2 4

3 **a**



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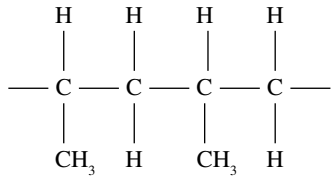

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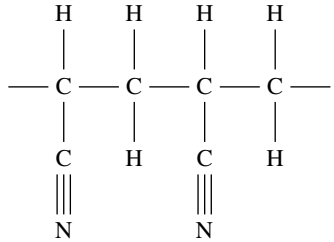


4 **a** CHCl=CHCl

b CH_3-CH=CHCl

c $CHF=CH_2$

5 **a** High-density polyethene (HDPE) is made of relatively unbranched chains of polyethene, which can pack more closely together than the chains of low-density polyethene (LDPE) can. LDPE contains branched chains of polyethene that cannot pack together as closely. Therefore, HDPE is stronger and slightly less flexible than LDPE. Both HDPE and LDPE are chemically unreactive, waterproof non-conductors and only slightly permeable to gases.

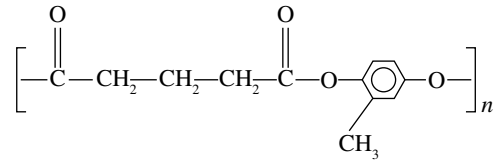
b **i** LDPE

ii HDPE

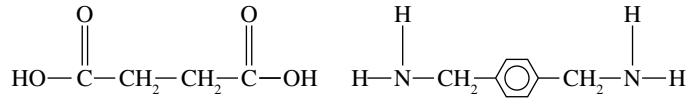
iii LDPE

Section 15.3 Condensation polymerisation

WE 15.3.1



WE 15.3.2



15.3 Key questions

1 C

2 Water

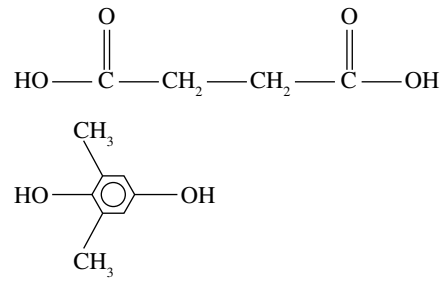
3 **a** polyamide

b polyamide

c polyester

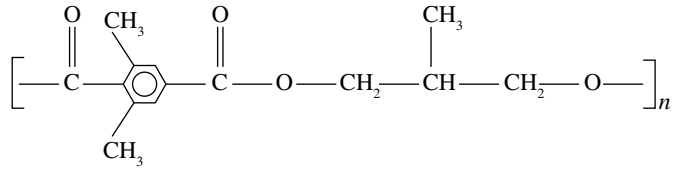
d polyester

4 **a**



b $HOOC(CH_2)_4COOH$ and $H_2N(CH_2)_6NH_2$

5 **a**



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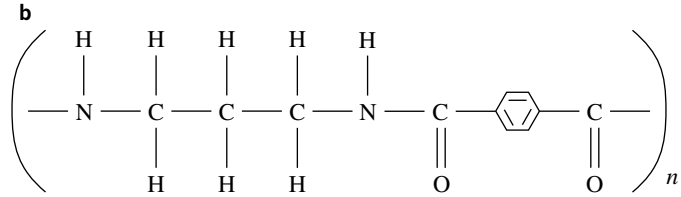

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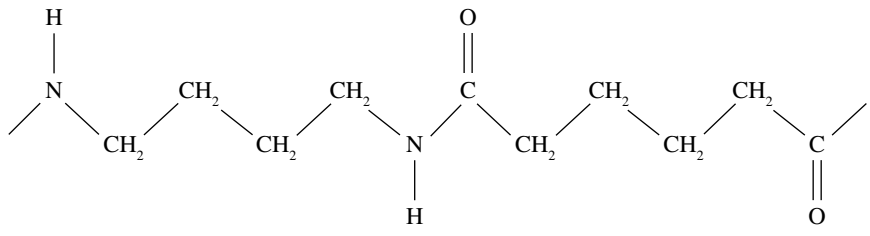


Section 15.4 Designing polymers for a purpose

15.4 Key questions

1 **a** weak dispersion forces
b dipole–dipole attractions
c weak dispersion forces
d weak dispersion forces
e dipole–dipole attractions

2 The monomers are ethene and tetrafluoroethene.

3 –H (in polyethene)
–F (in Teflon)
–Cl (in polyvinyl chloride)
$-C_6H_5$ (in polystyrene)
$-NC_{12}H_8$ (in polyvinyl carbazole)

4 **a** increase the crystallinity
b increase the crystallinity
c decrease the crystallinity

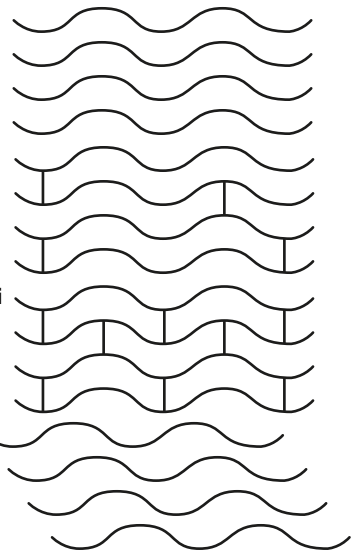
5 **a** increase flexibility
b improved heat insulating properties or mechanical properties
c increased crystallinity, resulting in a harder, more brittle polymer

Chapter 15 Review

1 **a** A monomer is a small molecule that can react to form long chains of repeating units, called polymers. Monomers often contain a carbon–carbon double bond.
b Thermoplastic materials soften when heated because the bonds between molecules break and the molecules become free to move.
c Thermosetting materials do not melt when heated, but at high temperatures covalent bonds are broken and the material decomposes or burns. They cannot be moulded into a different shape.
d A cross-link is one or more covalent bonds that connect neighbouring polymer chains.
e A plasticiser is a chemical added to plastics to make them more flexible.

2 **a** false
b false
c false
d true

3 **a** **i**

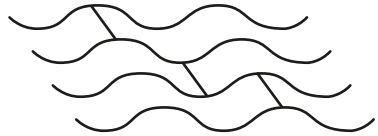


ii

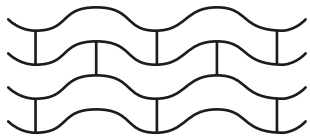
iii

b

polymer easily stretched



Some stretching, but polymer tends to return to its original shape.



no stretching possible

4 An elastomer has occasional cross-linking that prevents the chains from slipping past each other too far and pulls the chains back to their original positions when the force is removed. See Figure 15.1.15.

5 Thermosetting polymers have much stronger inter-chain bonds than thermoplastic polymers.

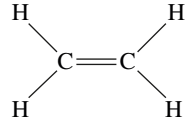
6 The inter-chain bonds in thermosetting polymers are about the same strength as the covalent bonds within chains. When heated to a high temperature both the inter-chain and covalent bonds break.

7 Distinguishing between thermoplastic and thermosetting polymers is important. The former get soft when heated, whereas the latter remain rigid and will burn if heating continues.
a thermosetting
b thermoplastic
c thermosetting
d thermoplastic
e thermoplastic

8 **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.

9 A, C, and D

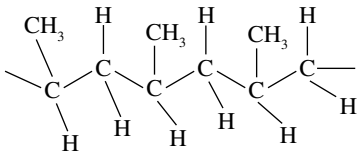
10 **a** It has a carbon–carbon double bond.
b

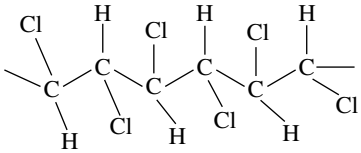


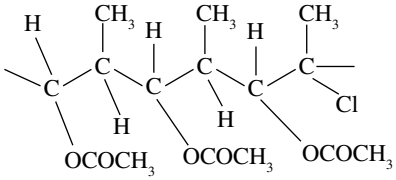
c No, because it is a saturated compound.

11 **a** Several thousand ethene monomers react to make one molecule of polyethene.
b Ethene (CH_2=CH_2) is unsaturated because it contains a double bond. Polyethene is saturated because it contains only single bonds between carbon atoms.
c The empirical formula is the simplest whole-number ratio of elements in a compound. The empirical formula of ethene (CH_2=CH_2) is CH_2.

12







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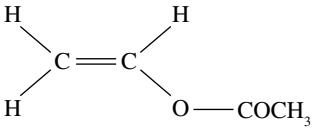
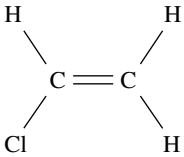


14 **a**



b 6

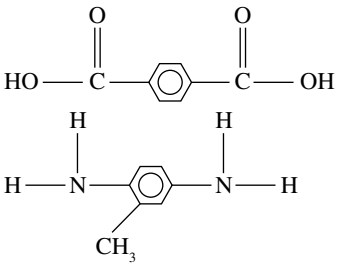
c dipole–dipole bonds

15 **a** PVC is flexible, non-conducting and strong, has a high melting point and low flammability.

b PVC has no free charged particles to conduct electricity. It has strong inter-chain bonding due to dipoles, which increase its strength and raise its melting point. PVC contains strong bonds that does not burn easily and it produces chemicals that extinguish flames when burned. PVC is plasticised to make it flexible.

16 It has stronger dispersion forces between polymer chains. Both polymers are non-polar, but the Teflon monomers have a higher molar mass compared to ethene. This means a greater number of electrons are present in the polymer and hence the dispersion forces are greater.

17



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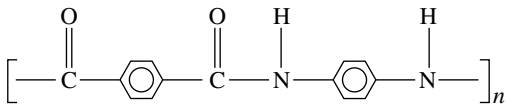
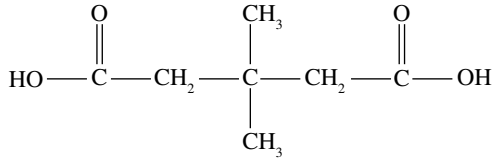
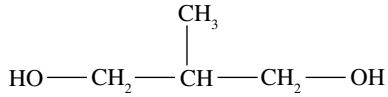


19 c and d

20





21 A single monomer that can be used to produce a polyester must contain both a carboxylic acid and an alcohol in the same molecule. Similarly, to produce a polyamide using a single monomer, the monomer must contain both an amine and a carboxylic acid functional group. So your structure should include one of these combinations of two functional groups.

22 As the polymer chains are held further apart by the plasticisers, it makes it easier for the polymer chains to slide over each other. As a result, these materials have a lower softening temperature, and are more malleable and soft.

23 Polymers without extensive branching and regular chain structures are most likely to form crystalline regions.

24 Left: C_8H_8; middle: C_3H_3N; right: C_4H_6

25 **a** thermoplastic with high melting temperature

b lower density/more transparent polymer

26 thermoplastic

27 The monomers used to create addition polymers must be unsaturated. For condensation polymerisation, the monomers may be saturated or unsaturated, but they must each contain two functional groups that react together. For addition polymerisation, no side-products are produced during the polymerisation reaction. For condensation polymerisation, small molecules (usually water) are released during the reaction.

28 The relative molecular mass would have increased. The melting point of the polymer would have increased.
The overall strength of inter-chain forces would have increased.
The electrical conductivity of the polymer would have remained the same.

Chapter 16 From fats and oils to soaps and biodiesel

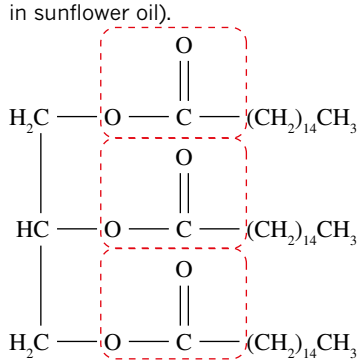
Section 16.1 Fats and oils

16.1 Key questions

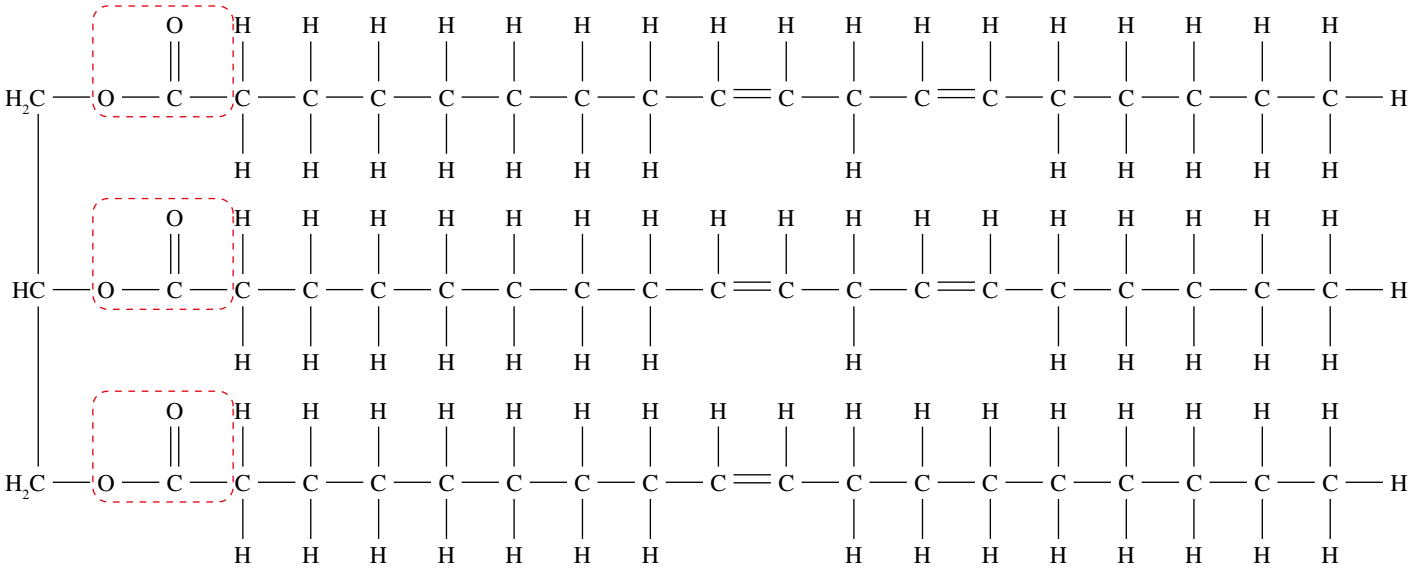
1 **a** Animal because it is a saturated fat (stearin).

b Plant because it is an unsaturated fat (predominant triglyceride in sunflower oil).

2 **a**



b



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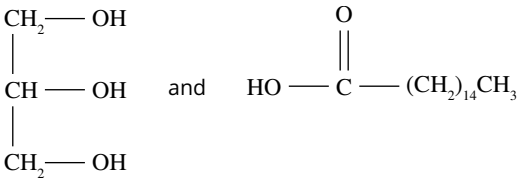
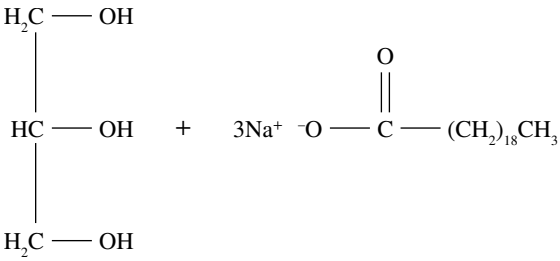


Section 16.2 Production of soaps

WE 16.2.1



16.2 Key questions

1 C

2 acidic, basic, saponification, salts, glycerol

3 Water that contains significant concentrations (>120 ppm) of metal ions, such as calcium and magnesium.

4 Soap forms an insoluble scum. Scum is the insoluble salts of calcium and magnesium. They are off-white in colour. Because these salts are insoluble, this reduces the concentration of soap in the water, meaning more soap must be added in hard water areas to achieve the same result. The insoluble scum can deposit on laundry, leaving it stiff and discoloured.

5 Similarities: both contain both ionic and covalent bonds, have a cleaning action; both have a long hydrocarbon chain section in their molecules
Differences: starting materials are obtained from different sources, detergents from petrochemicals and soaps from natural fats and oils. Detergents are unaffected by the presence of calcium and magnesium ions and do not form scum as soaps do.

Section 16.3 The cleaning action of soaps and detergents

16.3 Key questions

1 A, non-polar tail; B, hydrophobic; C, hydrophilic; D, charged end

2 micelles, hydrophobic/non-polar, polar/hydrophilic

3 **a** Broken: the ionic bonds between the metal cation and the organic anion, dispersion forces between molecules of soap
Formed: ion–dipole forces between the anions and cations from the dissociated soap molecule, dispersion forces between non-polar portion of anion and water

b Broken: dispersion forces between non-polar portion of anion and water
Formed: dispersion forces between non-polar portions of anions

c Broken: dispersion forces between the grease and the fabric
Formed: dispersion forces between the grease and micelles

Section 16.4 Production of biodiesel

16.4 Key questions

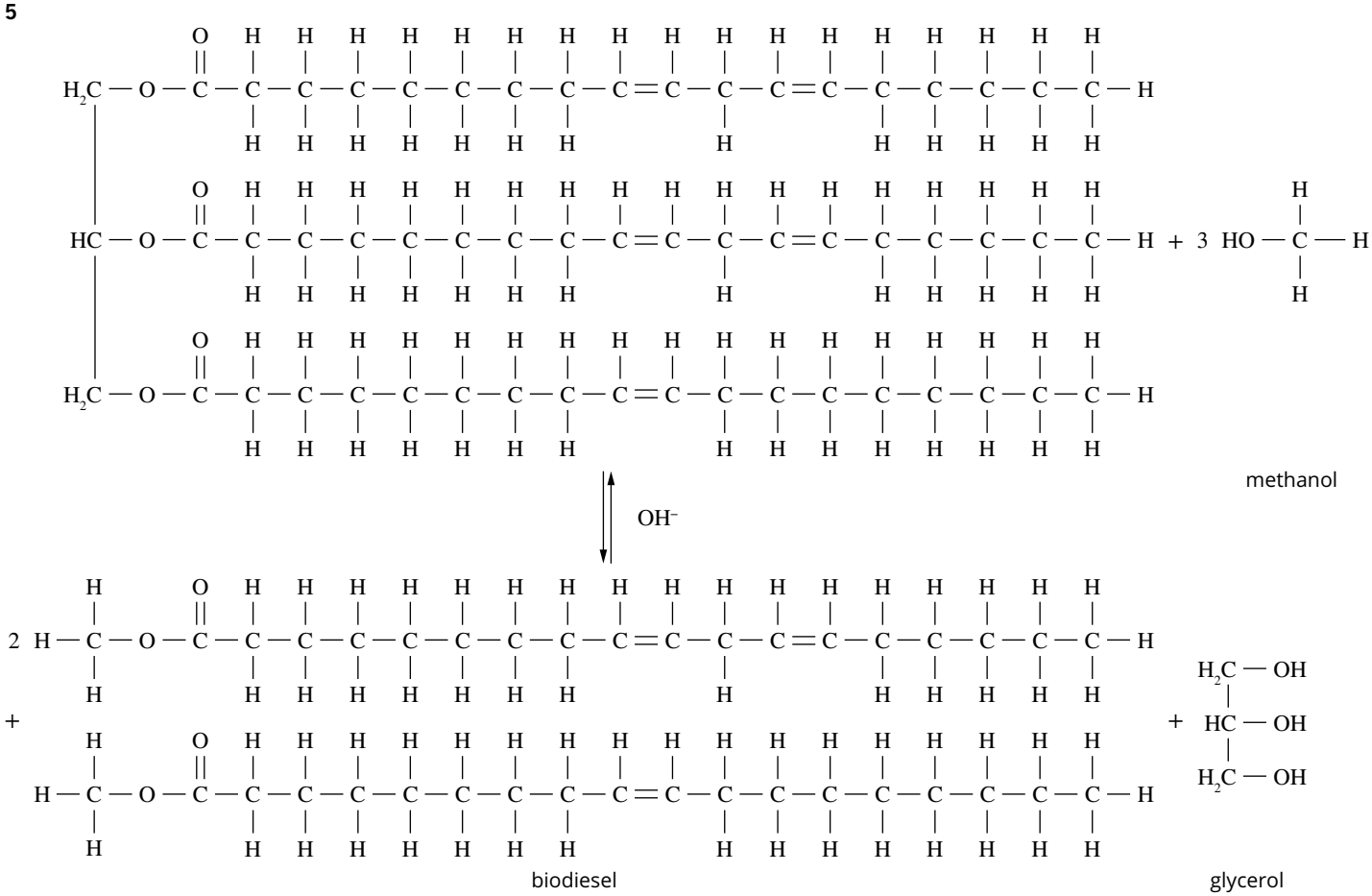
1 transesterification

2 **a** true
b true
c false
d true
e false
f true

3 CO_2 is absorbed from the atmosphere during the growth of plants used as raw materials in the production of biodiesel.

4 Advantages: lipase catalyst may be used more than once; requires lower temperature, meaning less energy is used in the process; can be carried out at a lower pressure
Disadvantages: longer time for reaction to complete; yield is typically much lower

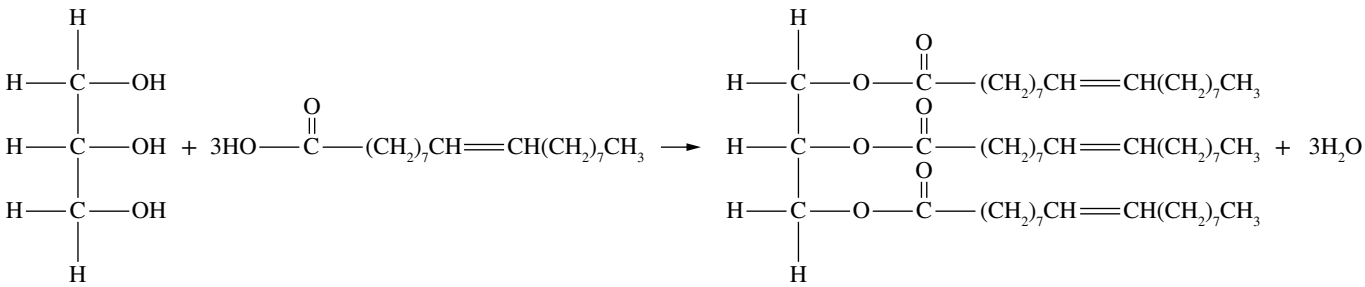
5



Chapter 16 Review

1 hydroxyl and carboxyl

2 **a**



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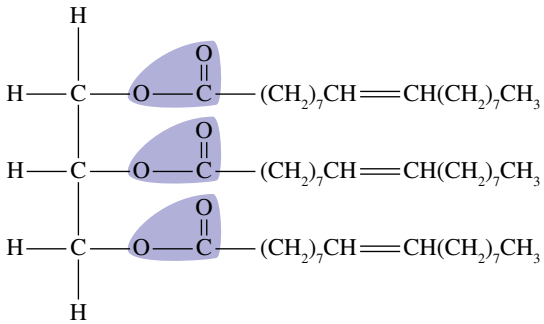
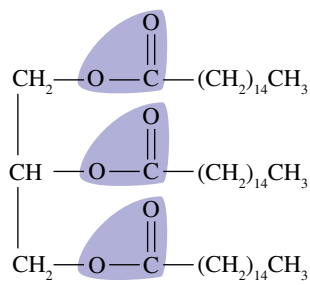


3 **a**



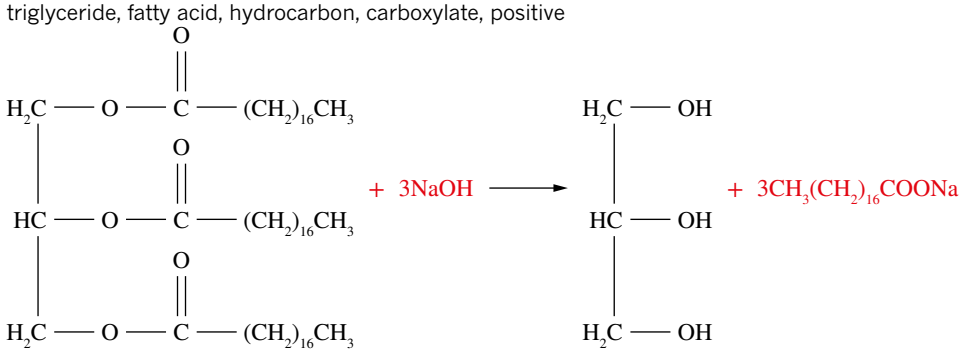
b Saturated because the alkyl groups in the molecules ($CH_3(CH_2)_{14}$) contain only single carbon–carbon bonds. Alkyl groups with the general formula C_nH_{2n+1} are saturated.

4 B

5 **a** 0.6 mol
b 0.2 mol

6 triglyceride, fatty acid, hydrocarbon, carboxylate, positive

7



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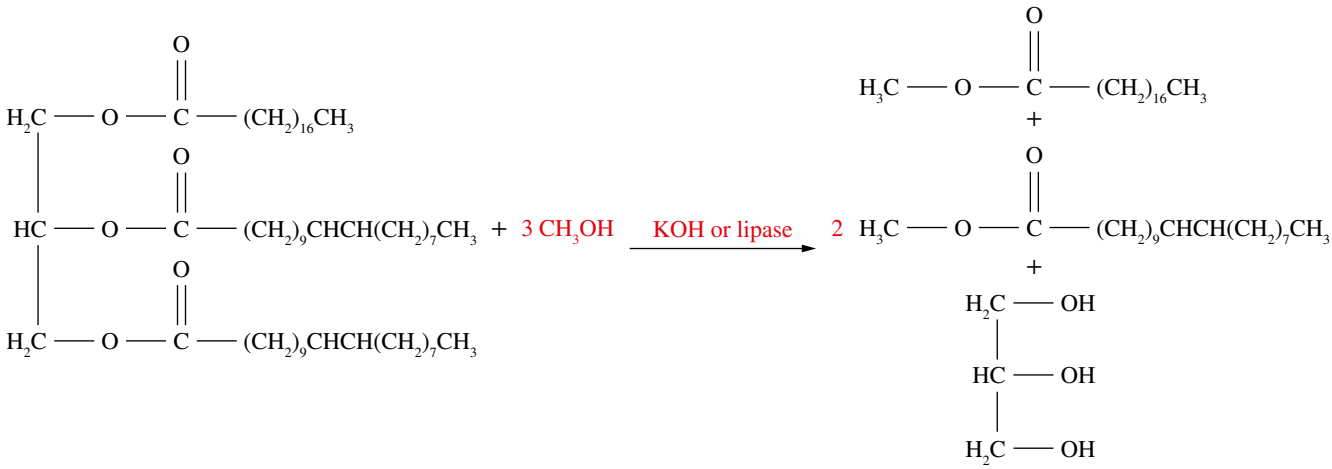
8 **a** glycerol
b a fat
c a fatty acid
d a detergent
e a soap

9 In unsaturated soap molecules, the double bonds present mean that the hydrocarbon chain of the soap occupies more space than a similar, but saturated, hydrocarbon chain.
The effectiveness of the soap micelles relies on the formation of dispersion forces between the hydrocarbon ends of the soap. As the unsaturated chains cannot get as close to one another, the dispersion forces will be weaker and this results in the soap micelle not being as stable.
The C=C double bond is more reactive than the single bonds in the hydrocarbon chain from the saturated fat. The soap will more likely be oxidised to form products that have an unpleasant odour. As the unsaturated soap molecules occupy more space, molecules cannot get as close to one another and hence the dispersion forces would be anticipated to be weaker in these soaps. The soap will be soft, or may even be a liquid soap.

10 Petrodiesel comes from crude oil, which is a non-renewable resource. Biodiesel is made from oil that comes from plants that capture atmospheric carbon dioxide as they grow. This serves to offset the carbon dioxide produced from burning biodiesel.

11



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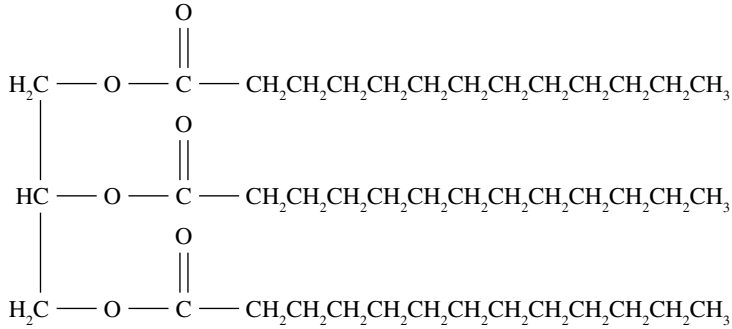
12 The main reactant or reactants used in a chemical process come from sources that can be regenerated in a relatively short time period.

13 A substance that provides an alternative reaction pathway with a lower activation energy. This increases the rate of reaction because more molecules collide with energy greater than or equal to the activation energy for this different pathway.

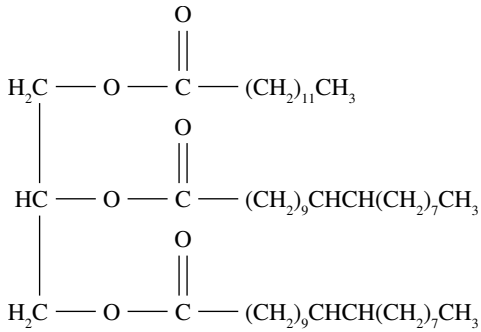
14 **a** methanol
b glycerol

15 By increasing the concentration of the methanol, the rate of the forward reaction will increase, pushing the equilibrium position to the right (towards the products). This has the effect of maximising the yield for the reaction.

16 **a**



b At least one 'fatty acid' in the triglyceride must be unsaturated.



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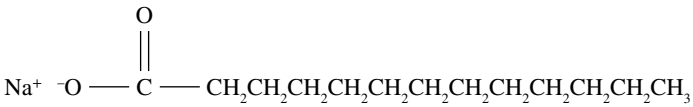

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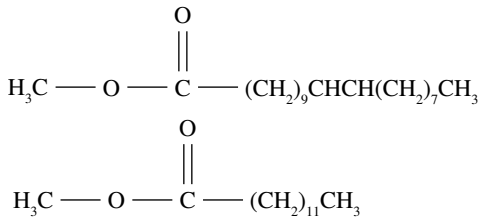


and

Biodiesel is a mixture of the constituent fatty acids of the triglyceride used. As there are both saturated and unsaturated constituent fatty acids, some of each must be present in the biodiesel.

17 At a ratio approaching 3:1, a competing saponification reaction can occur. This produces soap molecules. The purification of biodiesel relies on two steps. The first of these is separation, where the differences in the polarity of the glycerol, which is polar, and the biodiesel, which is relatively non-polar, ensure that the two substances do not dissolve in one another. The intermolecular forces capable of forming between the glycerol and the biodiesel do not release a sufficient amount of energy to compensate for the energy required to break apart the intermolecular forces between molecules of the same type. This results in two separate layers being formed. When soap molecules are present in the reaction mixture, this allows for micelles to stabilise each substance in the other and, as a result, the two liquids will mix and form an emulsion. This would significantly increase the amount of time necessary for the mixture to be distilled and would certainly affect yield adversely.

18 Both saponification and transesterification can rely on the use of a base to break the ester bonds present in the triglyceride.
In saponification, the resulting hydrolysis introduces three hydrogen atoms to form glycerol and water while the carboxylate ions will produce a metal fatty acid salt, once glycerol and sufficient water are removed. In transesterification, the ester bond is broken, splitting the alcohol and fatty acid, but these then form methyl esters (as well as and glycerol).
Overall, saponification starts with an ester (the triglyceride) and ends with three fatty acids and an alcohol (glycerol). Transesterification starts with one ester (the triglyceride) and three alcohols (three methanol molecules) and ends with three esters (from each of the fatty acids) and one alcohol (glycerol).

Chapter 17 From amino acids to proteins

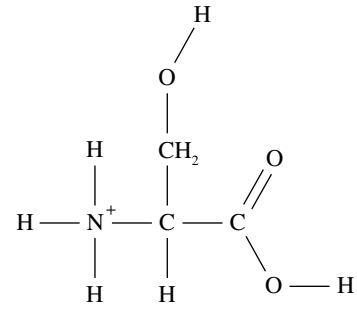
Section 17.1 Amino acids

17.1 Key questions

1 A

2 Nine out the 20 amino acids required by the body cannot be manufactured in the body. They must be provided by the food we eat.

3 **a**



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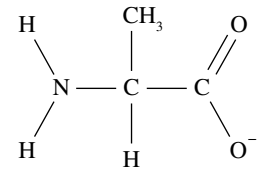

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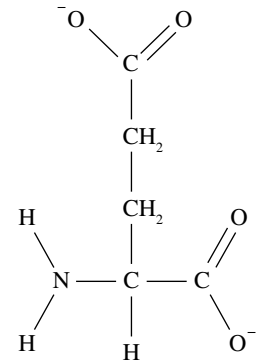


4

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

Section 17.2 The formation of proteins

17.2 Key questions

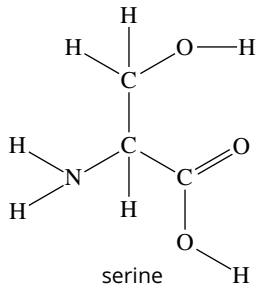
1

Tripeptide	Three amino acids joined by peptide links in a polypeptide chain
Side chain	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

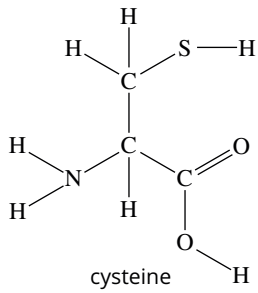
2 **a** a: amino group, B: amide group, C; side chain, D: carboxyl group
b alanine, serine, leucine

3 B

4 **a**



serine



cysteine

b $H_2NCH(CH_2OH)COOH + H_2NCH(CH_2SH)COOH \rightarrow H_2NCH(CH_2OH)CONHCH(CH_2SH)COOH + H_2O$

c $H_2NCH(CH_2SH)CONHCH(CH_2OH)COOH$

d Condensation

Section 17.3 Primary and secondary structures of proteins

17.3 Key questions

1 **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 attraction between the partial positive charge on the H of a –N–H bond in a peptide link with the partial negative charge on the O of a –C=O bond of a peptide link, four amino acid units along the chain.

2 The sequence of amino acids gives proteins their unique shape based on interactions of functional groups in different regions of the sequence. As protein shape is related to function, determining this sequence allows scientists to understand more about the role of specific proteins.

3 nine, peptide/amide, condensation polymerisation, alanine, lysine, glycine, valine, methionine

4 α-Helices result from 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. This results in this section of the protein coiling into an α-helix. 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. The resulting structure is similar to a pleat.

Section 17.4 Tertiary structure of proteins

17.4 Key questions

1 B and C

2

Bond type	Required components in R group	Amino acid examples
Hydrogen bond	Contains –O–H, –N–H and –C=O	Serine, threonine, histidine
Dipole–dipole interaction	Any polar group such as those containing –S–H, –O–H or –N–H	Cysteine, asparagine
Ionic interaction	Contains $–NH_3^+$ and another group that contains $–COO^-$	Aspartic acid, glutamic acid, lysine, arginine
Covalent cross-link	Cysteine side groups react to form a disulfide bridge (–S–S–)	Cysteine
Dispersion force	Any non-polar group	Alanine, leucine, phenylalanine

3 **a** Dispersion forces

b Ionic bonding

c Hydrogen bonding

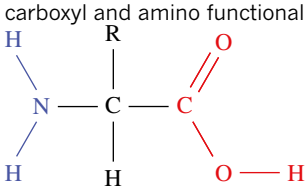
d Covalent bonding

Chapter 17 Review

1 C

2 carboxyl and amino functional groups

3

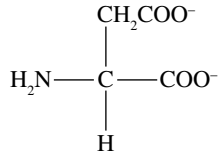


4 **a** **i** carboxyl

ii amino

b A molecule that contains positive and negative charges, but has no charge overall.

c **i**



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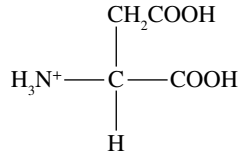

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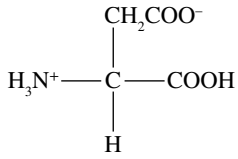


5 The carboxyl and amino groups react to form amide links between amino acids

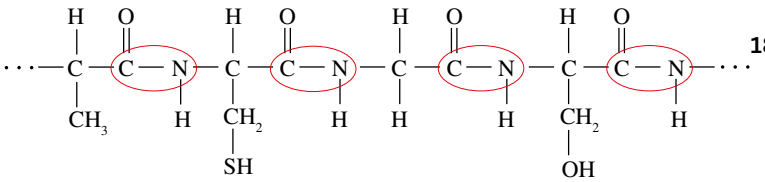
6 B

7 **a** $H_2NCHCH_3CONHCH_2COOH$, $H_2NCH_2CONHCHCH_3COOH$

b 6 (using each amino acid once in each peptide)

c very large numbers

d



e alanine, cysteine, glycine, serine

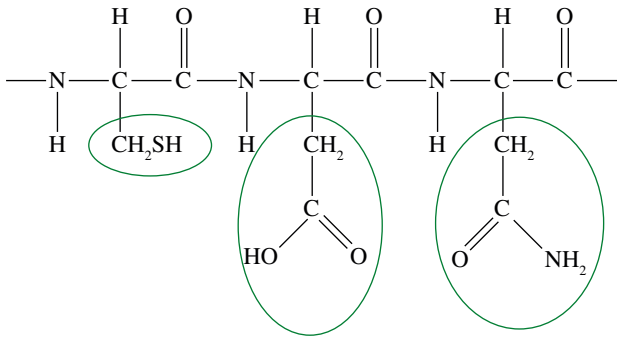
8 **a** covalent bond/peptide bond/amide bond

b hydrogen bond

c α-helix

9 β-Pleated sheets are formed when two adjacent strands of peptide lie in a plane and form hydrogen bonds between their respective backbones.

10



11 The activity of an enzyme, which is a type of protein, depends on its three-dimensional shape. The tertiary structure results from a combination of hydrogen bonding, electrostatic attraction between polar groups and disulfide linkages. If the wrong amino acid is introduced into the chain, these bonds may not form and the tertiary structure may be distorted. In some instances, the enzyme becomes inactive, depending upon how the tertiary structure is altered.

12 Primary structure refers to the sequence of amino acids in a protein.
Secondary structure refers to the folding of a section due to, for example, hydrogen bonding between peptide links.
Tertiary structure refers to the overall three-dimensional shape of a protein.

13 **a** ionic interactions

b dipole–dipole interactions

c dispersion forces

14 Nearby cysteine residues are capable of forming covalent bonds with each other between the sulfur atoms. These covalent bonds are strong and help to stabilise the tertiary structure (three-dimensional shape) of the keratin protein.

15 Replacing leucine with serine would have a greater effect on the tertiary structure than replacing with isoleucine. This is because isoleucine and leucine both have non-polar amino acid side chains and would therefore form similar strength interactions with nearby amino acid side chains. Serine is a polar amino acid with a side chain capable of forming hydrogen bonds with other amino acid side chains. This may result in the protein changing its three-dimensional shape.

16 C, low
D
A

17 **a** inside

b surface

c inside

d surface

18 The primary structure of a protein is the sequence of amino acids. These amino acids are joined together by amide groups, formed from the condensation reaction between the carboxyl and amino groups on two amino acids. The amide groups are therefore integral to the primary structure of the protein in that they link the sequence of amino acids together. The secondary structure of the protein also depends on these amide groups. Hydrogen bonds form between the oxygen in the C=O of one amide group and the hydrogen in the N–H of another amide group. These hydrogen bonds help to stabilise the α-helices and β-sheets that make up the secondary structure of the protein.

Chapter 18 Uses of proteins

Section 18.1 Investigating proteins

18.1 Key questions

1 Scientists can search the PDB for proteins with similar primary structures. Depending on the level of similarity, the function of these similar proteins may provide a good estimate of the function of the protein of interest. This is because proteins with similar primary structures usually have similar three-dimensional shapes, and therefore similar biological functions.

2 The PDB is an invaluable resource to scientists. It provides them with the means to share information about protein structure, function and known interactions between them. It is important that it remain freely available so that all scientists are able to benefit equally from the information.

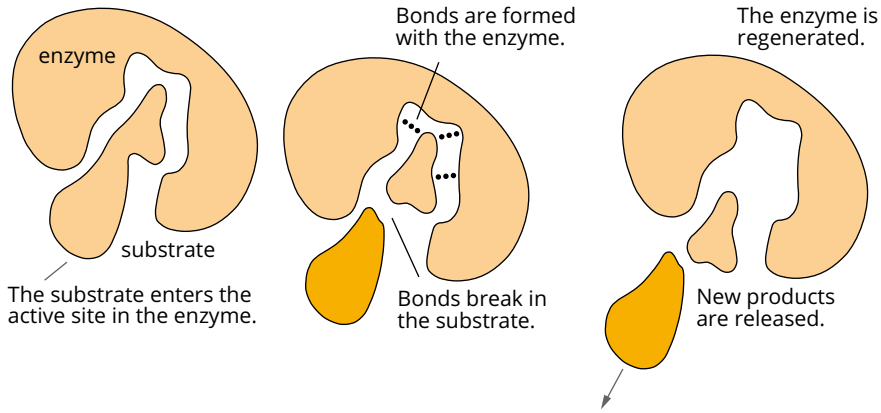
3 A polypeptide consists of amino acid units that are joined by peptide bonds, –CONH–. B is a peptide bond. All of the bonds between atoms in the polypeptide chain are covalent bonds, such as A. The sequence of amino acids in the polypeptide chain is known as its primary structure.
Each amino acid unit has a side chain (or R group) that distinguishes it from other amino acids. For example, the group labelled D is the side chain of tyrosine.
Interactions between the side chains are responsible for producing the tertiary structure of the polypeptide and its overall three-dimensional shape. A covalent bond, known as a disulfide bridge, can form when the side chains of two cysteine units interact, labelled C in the model.

Section 18.2 Enzymes

18.2 Key questions

1 D

2 **a**



b Hydrogen bonds, ion–dipole interaction, dipole–dipole interactions, ionic interactions

3 **a** true
b true
c false
d true

Section 18.3 Enzymes: dependence on pH and temperature

18.3 Key questions

1 During hydrolysis, covalent bonds between carbon atoms and nitrogen atoms are broken. This breaks the protein into its component amino acids. Denaturation is a result of the disruption of interactions between the side chains of the amino acids and the amide links that form the peptide chain. These interactions are responsible for the three-dimensional shape of the enzyme. When the shape is altered, the enzyme ceases to function but the primary structure remains intact.

2

Structure of side chain	Is the side chain acidic or basic or neither?	Is the side chain positively charged, negatively charged or neutral?	
		In a solution of pH 2	In a solution of pH 11
$-CH_2COOH$	Acidic	Neutral	Negative
$-CH_2CH(CH_3)_2$	Neither	Neutral	Neutral
$-CH_2OH$	Neither	Neutral	Neutral
$-(CH_2)_4NH_2$	Basic	Positive	Neutral

3 **a** Denaturation occurs when there is a change to the structure and shape of an enzyme that prevents it from functioning. The enzyme is said to be 'denatured'.
b Denaturation usually involves disruption of the bonds that hold the enzyme's protein chain in a particular shape, followed by unfolding of the chain. The unfolded chains will often clump together, in a process called coagulation.
c no
d The overall three-dimensional shape of an enzyme is known as its tertiary structure. Since enzyme action depends upon the existence of a suitable hollow or cavity within the molecule, the tertiary structure is crucial to the enzyme's operations.

4 **a** Changes to the pH of the solution can change the charge of acidic or basic side groups on the amino acids of the protein. These changes can cause the protein to denature, disrupting the three-dimensional shape of the active site and reducing enzyme activity.
b A decrease in temperature reduces the frequency and energy of the collisions between reactants. This reduces the rate of reaction observed as a reduction in enzyme activity. It can also reduce the flexibility of the enzyme structure, reducing its effectiveness as a catalyst according to the induced fit model.

Section 18.4 Enzymes in industry

18.4 Key questions

1 91.3%

2 A high temperature would produce a high reaction rate, but would also result in a lower yield because the forward reaction is exothermic. A moderate temperature is used as a compromise between rate and yield.

3 A high pressure favours both the production of ethanol and a high rate of reaction. As there are 2 moles of gaseous reactants and 1 mole of gaseous products, a high pressure favours the forward reaction (formation of ethanol), in that the system responds to try and partially counteract the imposed change.

Chapter 18 Review

1 **a** true
b true
c False; a mutation will not necessarily cause a loss in protein function. If the mutation is far away from the active site of the protein, then its activity may not be affected at all. Similarly, if the mutation results in exchanging an amino acid with similar characteristics, then it may not have a large effect on the protein's secondary and tertiary structure. For example, exchanging aspartic acid for glutamic acid may not have a large impact on the protein.

2 When a protein is being synthesised, secondary structures such as α-helices and β-pleated sheets form as a result of hydrogen bonds between the amide groups on adjacent regions of the polypeptide chain. The protein chain then folds further and interactions such as hydrogen bonds, dipole–dipole interactions, dispersion forces and disulfide bridges can form between amino acid side chains. This can result in amino acid units that are far apart in the protein's primary structure ending up adjacent to one other in the protein's three-dimensional shape.

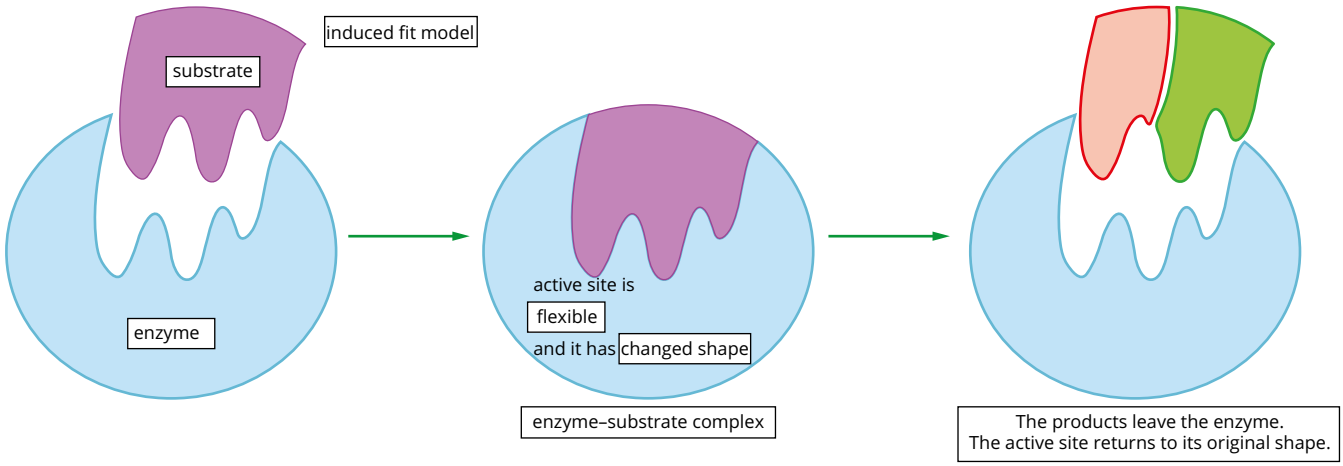
3 **a** Almost all the chemical reactions occurring in living organisms are controlled by enzymes. Enzymes speed up the reactions that are essential for life processes by as much as 10^{10} times; reactions that do not contribute to the functioning of a creature are not catalysed and occur at much slower rates.

b The shape and functional groups in the active site of the enzyme allow it to bind only with certain substrates, so that only a specific reaction is catalysed. In a similar way, a lock will only open using a key of a certain shape.

4 **a** true
b true
c false
d false
e true
f true
g true

5 If the substituted amino acid lies within the active site of the protein, it may not have a significant effect on the overall three-dimensional shape of the protein, yet have a large impact on the strength of the interactions that hold the enzyme–substrate complex together. For example, if a serine amino acid unit is substituted for an alanine within the active site of the protein, the alanine side chain will only be able to form dispersion forces with the substrate, rather than hydrogen bonds. This alteration to the strength of the enzyme–substrate interactions may alter the activity of the enzyme.

6

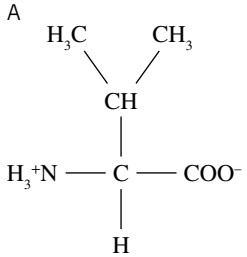


7 Insulin is a protein that is released into the bloodstream in response to rising blood sugar levels. As a result, it has an optimal pH of ~7, the pH of blood. If it were ingested and entered the acidic environment of the stomach, it would be exposed to low pH conditions and may become irreversibly denatured and lose its function. Side chains, such as aspartic acid and glutamic acid, which would be negatively charged at pH 7, would become neutral at lower pH levels. This would affect the types of interactions they are able to have with other side chains, altering the three-dimensional shape of insulin and ultimately its function.

8 The catalytic property of the enzyme can be destroyed by changing its shape—in a process called denaturation. This can be done by heating the pineapple. Alternatively, canned pineapple can be used to make this dessert because the fruit is heated during the canning process.

9 A

10



11 A, optimum temperature, fastest reaction rate. B, less frequent collisions, lower energy reactants. C, enzyme denatures, tertiary structure changes, three-dimensional shape of active site alters and enzyme activity drops.

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

13 Fermentation: uses conditions of low temperatures and normal pressures. Grain or other plant materials are used as a starting material. The ethanol requires many distillation steps to purify it. Hydration of ethene: uses conditions of moderate temperatures and high pressures. Crude oil is used as a starting material. The ethanol produced does not require as many distillation steps to purify it.

14 **a** Increasing pressure would increase both the yield and the rate of reaction.

b Decreasing the temperature would increase the yield of ethanol, but would decrease the rate of reaction.

15 Advantages: enzymes are highly specific and reactions can be conducted at atmospheric temperature and pressure. They are also biodegradable.
Disadvantages: enzymes are highly sensitive to changes in temperature and pH. They can also be more expensive to produce.

16 Distillation can separate liquids in a mixture based on differences in their boiling points. When an ethanol–water mixture is heated, the ethanol will boil first and enter the gaseous phase, separating it from the water. The ethanol vapour is then cooled down (condensed) and collected as a liquid.

17 A biological washing powder has the advantage of being biodegradable. It also does not require high temperatures, so clothes can be washed in colder water, resulting in lower energy costs. The disadvantages are that the enzymes are very sensitive to changes in temperature or pH, meaning that if the water temperature is too hot, the enzymes will not function as well. Some individuals are also sensitive to the enzymes in biological detergents and they can cause skin irritation.

18 Ethanol is a solvent that is capable of forming hydrogen bonds (as well as dispersion forces) with the amino acid side chains and amide groups in the protein backbone. As the ethanol concentration increases, it will form a greater number of these interactions with the protein. These interactions may interfere with the existing dipole-dipole interactions, dispersion forces, hydrogen bonds and disulfide bonds that are maintaining the three-dimensional shape of the enzymes and cause the protein to denature. If the shape of the enzyme is lost, its ability to catalyse the fermentation process will also be lost.

Chapter 19 Science inquiry skills in chemistry

Section 1.1 Questioning

WE 19.1.1

Independent variable: concentration of the silver ions in the silver nitrate solution

Dependent variable: voltage of the galvanic cell

Controlled variables: concentration of Fe^{2+} ions in the anode half-cell, same silver cathode, temperature

Hypothesis: the voltage of the galvanic cell is directly proportional to the concentration of the silver ions.

19.1 Key questions

1 **a** A statement that can be tested. This involves making a prediction based on previous observations.
b A theory is a hypothesis that is supported by a great deal of evidence from a wide variety of sources. A principle is a theory that is so strongly supported by evidence that it is unlikely to be shown to be untrue in the future.

2 **a** amount of sodium hypochlorite
b time
c temperature
d pH

3 qualitative

4 C

5 **a** valid
b reliable
c accurate

Section 19.2 Planning investigations

19.2 Key questions

1 B

2 **a** In a control experiment, two groups of subjects are tested; the groups, or the tests performed on them, are identical except for a single factor (the variable), which is not changed in the control experiment.
b The dependent variable is the variable that is measured to determine the effect of changes in the independent variable. The independent (experimental) variable is the variable that is changed in an experiment. For example, in an experiment testing the effect of soil pH on flower colour, the independent variable would be soil pH and the dependent variable would be flower colour.

3 **a** source/location of water
b pH
c temperature of solutions

4 **a** Litmus paper and universal indicator give qualitative information about pH through colour.
b A calibrated pH meter will give quantitative information and is more accurate than using litmus paper or universal indicator

Section 19.3 Reducing uncertainty in data

19.3 Key questions

1 **a** systematic errors
b random errors

2 **a** systematic
b random
c mistake

3 The experimental design may be poor because of a:
- lack of objectivity
- lack of clear and simple instructions
- lack of appropriate equipment
- failure to control variables.

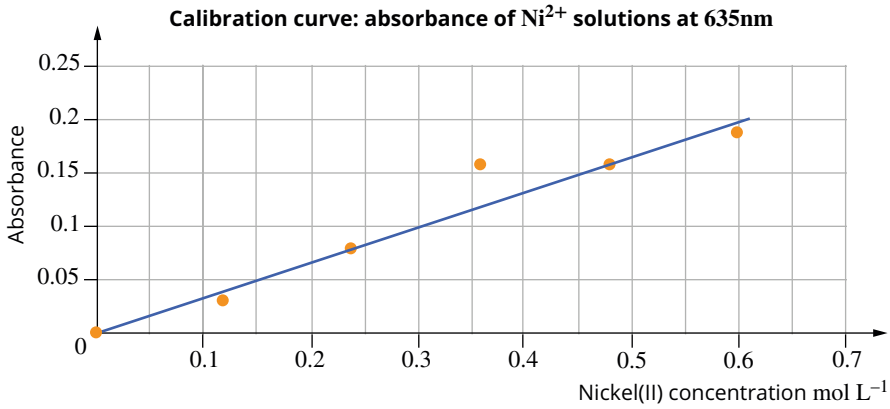
Other problems not specifically related to the experiment could be:
- a poor hypothesis that could not be tested objectively
- conclusions that do not agree with the results
- interpretations that are subjective.

Section 19.4 Processing data and information

19.4 Key questions

1 Add a trend line or line of best fit.

2 **a**



b Data point 4 (0.36, 0.159) is an outlier.
c A point in the data that does not fit the trend.

Section 19.5 Analysing data and information

19.5 Key questions

1 The proportional relationship between two variables.

2 An inversely proportional relationship

3 Directly proportional

4 Time restraints and limited resources

Section 19.6 Conclusions

19.6 Key questions

1 B

2 The statement 'Many repeats of the procedure were conducted' is unquantified. 'Thirty repeats of the procedure were conducted' is better because the number of trials is quantified.

Section 19.7 Communicating

19.7 Key questions

1 **a** g mol^{-1}
b mol L^{-1}

2 **a** Divide the value in mL by 1000.
b To make the numbers easier to comprehend; to use the units that match the units on the measuring device (e.g. volumes on pipettes are given in mL).

Chapter 19 Review

1 **a** dependent variable
b controlled variable
c independent variable

2 **a** Reflect
b Create
c Analyse
d Investigate
e Apply
f Identify
g Describe

3 Independent variable, source of the water; dependent variable, calcium ion concentration; controlled variables, temperature, time of testing, method of testing

4 **a** It can dissolve or eat away at substances, including tissues such as your skin or lungs.
b It Is toxic (poisonous) if inhaled.
c It is a highly combustible liquid that could catch fire.

5 Accuracy refers to the ability of the method to obtain the correct measurement close to a true or accepted value.
Validity refers to whether an experiment or investigation is, in fact, testing the set hypothesis and aims.

6 **a** Mistake
b Random error
c Systematic error

7 A linear (or directly proportional) relationship

8 Evaluate the method; identify issues that could affect validity, accuracy, precision and reliability of data; state systematic sources of error and uncertainty; and recommend improvements to the investigation if it is to be repeated

9 A trend is a pattern or relationship that can be seen between the dependent and independent variables. It may be linear, in which the variables change in direct proportion to each other to produce a straight trend line. The relationship may be in proportion but non-linear, giving a curved trend line. The relationship may also be inverse, in which one variable decreases in response to the other variable increasing. This could be linear or non-linear.

10 Any issues that could have affected the validity, accuracy, precision or reliability of the data plus any sources of error or uncertainty

11 To avoid plagiarism and ensure creators and sources are properly credited for their work.

12 A

13 0.0230 L or 2.30×10^{-2} L (ensure that you keep the same number of significant figures)

14 **a** Independent variable—concentration of the electrolyte
Dependent variable—cell voltage
Controlled variables—type of electrolyte, distance between the electrodes, temperature, supply of oxygen and hydrogen
b Cell potential, measured in volts, it would be quantitative.
c Voltmeter that reads to two decimal places; accurate volumetric glassware, such as burettes and pipettes, to measure out the concentrations of the solutions, which measure to the nearest 0.1 of a millilitre.
d Raw data is data collected in the field and recorded as measurements are taken. Processed data tabulates this into a form in which the reader can clearly see the concentration of the electrolyte and the measured voltage generated by the cell. This can also then be processed and graphed with the independent variable on the *x*-axis (concentration) and dependent variable on the *y*-axis (voltage).
If the hypothesis is correct, the graph would show an increase in voltage as the concentration increases, i.e. a line with a positive gradient. If this line was a straight line, it would indicate a linear (directly proportional) relationship between the voltage and the concentration.

Unit 4 Review

Section 1: Multiple choice

1	B	**2**	B	**3**	A	**4**	C
5	C	**6**	D	**7**	C	**8**	C
9	B	**10**	C	**11**	B	**12**	C

Section 2: Short answer

1 **a** $C_6H_{12}O_6(aq) \rightarrow 2C_2H_6O(aq) + 2CO_2(g)$

b **i** $CH_2CH_2(g) + H_2O(g) \xrightarrow{H_3PO_4} CH_3CH_2OH(g)$
ii addition
iii The forward reaction reduces pressure in the system because there are fewer moles of gaseous products than reactants. Use of a high pressure will move the equilibrium to the right to lower the pressure, according to Le Chatelier's principle. Use of high pressure increases reaction rate because the frequency of collisions between particles is increased.

c Use of the enzyme catalyst allows the reaction to take place at a much lower, more economical temperature and pressure. Glucose, obtained from plants, is a renewable raw material, while ethene, obtained from fossil fuels, is not renewable. For long-term production viability, a renewable source is preferred.

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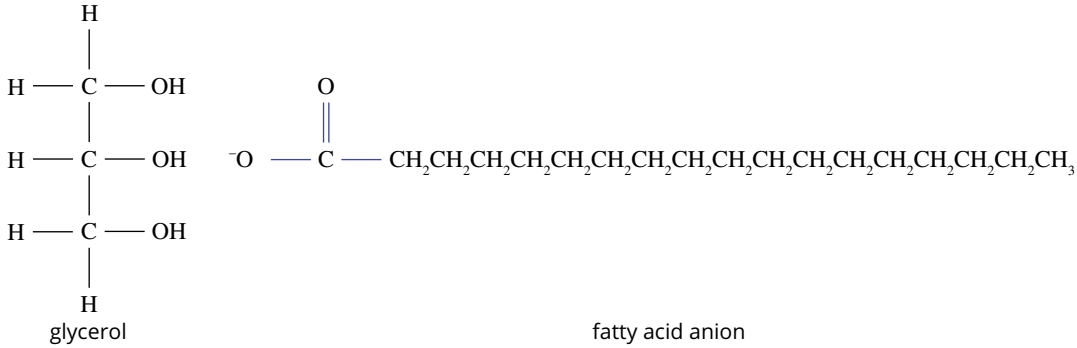
2 **a** **i**



glycerol fatty acid anion

ii Carboxylate

b i Anionic ($-SO_3^-$)

ii Ion–dipole

iii Dispersion forces

c i Detergents lather in hard water where soaps do not.

ii Many detergents are produced from a non-renewable resource (petroleum) or many detergents are non-biodegradable.

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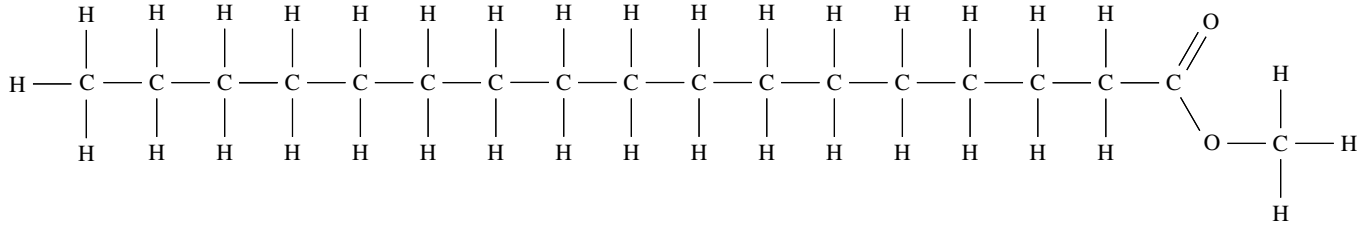
d i



ii dipole–dipole bonds and dispersion forces

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3 a i $(CH_3)_2CHCH_2CHCHCH_2CH_3$

ii $CH_3CH_2CH(CH_3)CH_2CHO$

iii $CH_3COCH_2CONH_2$

b i *trans*-pent-2-ene

ii 3-ethylhexan-3-amine

iii methyl butanoate

c i Acidified dichromate ($Cr_2O_7^{2-}/H^+$) or acidified permanganate (MnO_4^-/H^+)

ii H_2 and Ni catalyst (other metals sometimes used)

d i $CH_3CH_2COOH + CH_3CH_2OH \rightarrow CH_3CH_2COOCH_2CH_3 + H_2O$

ii $CH_3CH_2COOH + CH_3CH_2NH_2 \rightarrow CH_3CH_2COO^- + CH_3CH_2NH_3^+$

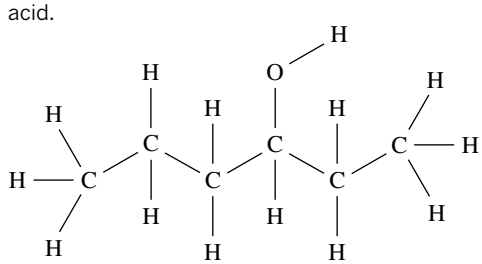
4 a i –1

ii $CH_3CH_2OH((l) \rightarrow CH_3CHO(l) + 2H^+(aq) + 2e^-$

b i $\frac{2.42}{2.869} = 84.3\%$

ii Ethanol and ethanal may evaporate from the reaction vessel, or the reaction is a reversible reaction and so does not go to completion, or some ethanal is lost in the collection process, or some ethanal was oxidised further to produce ethanoic acid.

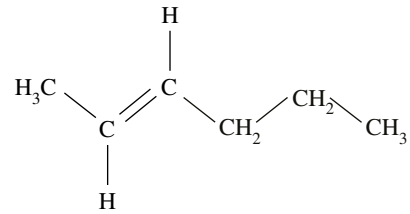
5 a i



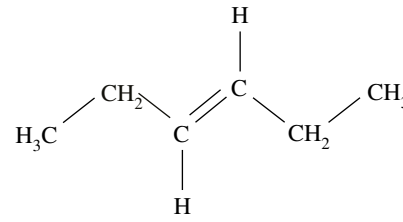
ii secondary

iii Both ethanol and hexan-3-ol can hydrogen bond with water to allow some solubility. In the alcohol homologous series, water solubility decreases from ethanol to hexanol because each additional CH_2 group reduces the polarity of the molecules, increasing the effect of the non-polar, hydrocarbon part that cannot form hydrogen bonds to water molecules. Thus the larger hexan-3-ol molecule is almost insoluble.

b



hex-2-ene



hex-3-ene

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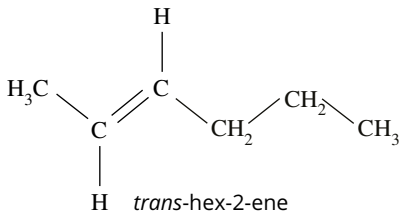
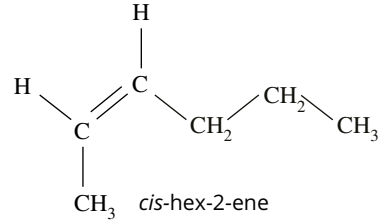
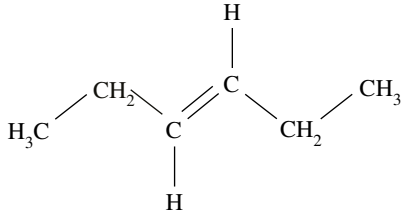
c



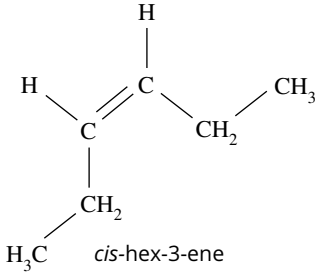
trans-hex-2-ene



cis-hex-2-ene



trans-hex-3-ene



cis-hex-3-ene

6 **a** **i** O
ii L or N
iii N

b **i** Lowered. Lowering the temperature will favour the forward exothermic reaction.
ii Lowering the temperature will decrease the rate of the reaction.
iii High pressure equipment is expensive, and the use of high pressures for harmful gases such as sulfur dioxide is potentially dangerous. With the use of a catalyst, satisfactory yields are achieved at the safer, cost-effective lower pressure.

c **i** Not change
ii Not change
iii Increase

Section 3: Extended answer

1 **a** m(C in the sample) = m(C in the CO_2) = $\frac{12.01}{44.01} \times 11.60 = 3.166\,g$

m(H in the sample) = m(H in the H_2O) = $\frac{2.016}{18.016} \times 4.74 = 0.530\,g$

m(O in sample) = 6.500 – 3.166 – 0.530 = 2.804 g

C:H:O = $\frac{3.166}{12.01} : \frac{0.530}{1.008} : \frac{2.804}{16.00}$ = 0.264:0.526:0.175 = 1.5:3.0:1.0 = 3:6:2

Empirical formula is $C_3H_6O_2$

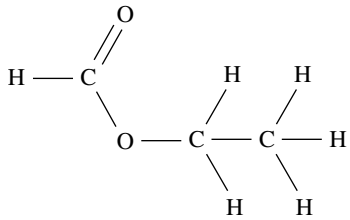
$pV = nRT = \frac{mRT}{M}$

$M = \frac{mRT}{pV} = \frac{5.01 \times 8.314 \times 473}{120 \times 2.22} = 74.0\,g\,mol^{-1}$

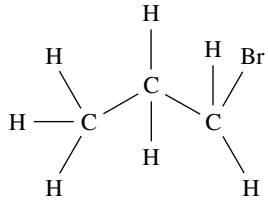
This is the same value as the empirical formula mass

∴ Molecular formula is $C_3H_6O_2$.

b **i** methyl ethanoate
ii Add sodium carbonate to samples of the two isomers. Isomer I (an ester) will show no reaction. Isomer II (a carboxylic acid) will react to evolve carbon dioxide (colourless, odourless gas produced).
iii Ethyl methanoate



c **i**



ii Dispersion forces will be similar in both molecules as they are very similar in molar mass. Compound C, propan-1-ol, contains a hydroxyl group which can form hydrogen bonds between the molecules. This bonding is stronger than the dipole–dipole bonding between propanone molecules. The stronger bonding leads to the higher boiling point.
iii The purple permanganate solution, when mixed with the colourless propanol, will decolorise. The products, including the manganese(II) ion and propanoic acid (isomer II), are colourless.

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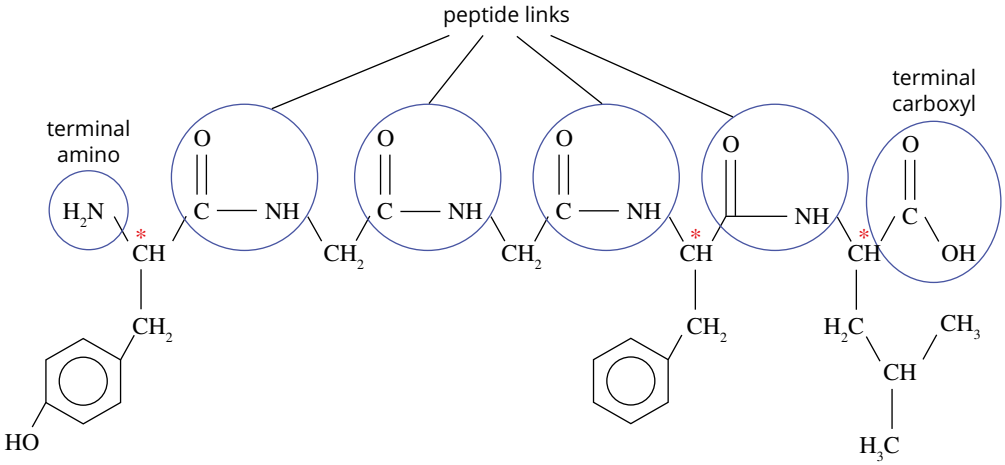
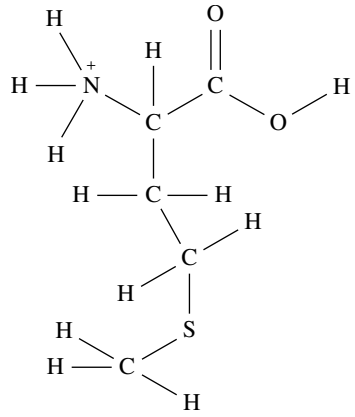
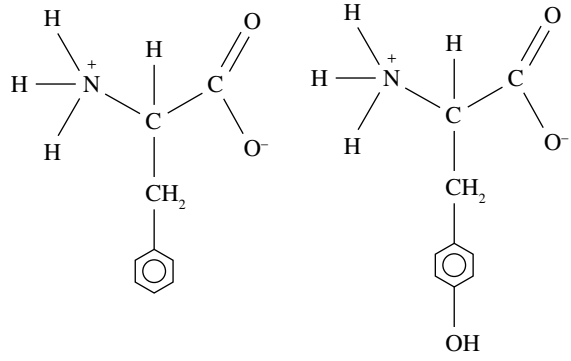
2 **a** **i** glycine, tyrosine, phenylalanine
ii and **iii**

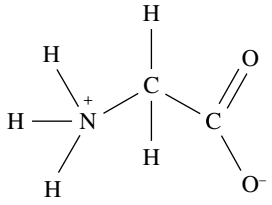


iv



v





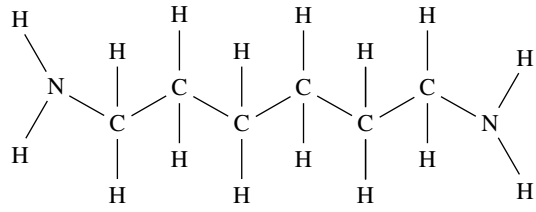
b i The primary structure of a protein relates to the formation of peptide linkages between the amino acids because they are linked together in a specific sequence; because this is a condensation reaction between carboxyl and amino functional groups, water is produced as a by-product. Secondary and tertiary structures do not involve condensation reactions.

ii These are features of the secondary structure of proteins, maintained by hydrogen bonding between the regularly spaced peptide linkages along the backbone of all protein chains.

iii Even before the disruption to bonding becomes sufficient to permanently denature an enzyme, changes in pH that affect the functional groups at the active site can significantly interfere with the substrate interactions and reduce activity.

iv The bonding that maintains the tertiary structure of a protein includes types of widely varying strength, including some strong covalent bonding in the form of disulfide bridges. Proteins with higher proportions of the stronger bonding types involved in their tertiary structures will tend to be more stable to heat.

c i



ii $H_2N(CH_2)_6NH_2 + 2HCl \rightarrow {}^+H_3N(CH_2)_6NH_3^+ + 2Cl^-$

iii Both have amide links between the monomer residues.

iv Nylon is a copolymer with only two alternating monomers. Proteins have 20 different monomers with a wide range of combinations and sequences.

Glossary

A

accumulator A secondary, or rechargeable, electrochemical cell.

accuracy The ability to obtain the actual ('correct') value when taking a measurement.

accurate 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 described as accurate.

acid A substance capable of donating a hydrogen ion (proton) (Brønsted-Lowry theory).

acid–base reaction A reaction in which one substance, an acid, donates a hydrogen ion (proton) to another substance, a base.

acid rain Rainwater that has reacted with acidic emissions from industry and vehicles and has a pH less than 5.5.

acidic salt A salt that dissociates in aqueous solution and one of its ions donates a proton to water, producing hydronium ions.

acidic proton A proton 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, the pH of an acidic solution is less than 7.

acidification The decrease in pH that is occurring due to the absorption of carbon dioxide from the atmosphere.

acidity The concentration of H_3O^+ ions in an aqueous solution. Acidity is measured using the pH scale.

acidity constant The equilibrium constant (K_a) for the ionisation/dissociation of an acid in aqueous solution. Also know as the acid dissociation constant.

acidosis When the pH of the blood drops to potentially lethal levels.

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 location on an enzyme's structure at which a reaction is catalysed. It is usually a hollow or a cavity in the protein structure, where the enzyme binds and interacts with the substrate.

actual yield The mass of product actually obtained during a chemical reaction. This will be less than or equal to the theoretical 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.

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 form a single product.

alcohol A homologous series of organic molecules that contains the hydroxyl (–OH) functional group.

aldehyde A homologous series of organic molecules which contains the carbonyl functional group, C=O, 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.

aliquot A fixed volume of liquid measured by a pipette.

alkali A substance capable of accepting a hydrogen ion (proton) (Brønsted-Lowry theory).

alkaline cell A commercial electrochemical cell with an alkaline electrolyte that is a moist paste rather than a solution.

alkane A saturated hydrocarbon that contains only single bonds; alkanes have a general formula of C_nH_{2n+2}.

alkene An unsaturated hydrocarbon containing one or more carbon–carbon double bonds. Alkenes with one double bond 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 can be present as branches in organic compounds.

alloy A substance formed when other materials (e.g. carbon, other metals) are mixed with a metal.

α-amino acid A type of organic molecule that contains an amino group and a carboxylic acid group where the amino group is bonded to the carbon atom (the α-carbon atom) that is attached to the carboxyl group.

α-helix One type of secondary structure found in proteins. It has a spiral shape and it is maintained by hydrogen bonding between amino acid units in the chain

amide A compound containing the $-CONH_2$ functional group.

amide functional group A functional group found in the homologous series of amides consisting of an amine group attached to a carbonyl group $-CONH_2$.

amine A homologous series of organic molecules that contains the amino ($-NH_2$) functional group.

amino acid The monomer molecule used to make proteins. Amino acids contains an amino ($-NH_2$) group and a carboxyl (–COOH) functional group.

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).

anhydrous Containing no water.

anion A negatively charged ion, e.g. a chloride ion, Cl^-.

anioinic detergent A synthetic detergent where the active component is a negatively charged ion.

anode An electrode at which an oxidation reaction occurs.

atom economy A method of tracking the atoms in a reaction equation to calculate the mass of the atoms of reactants actually used to form products as a percentage of the total mass of the reactants. Atom economy can be calculated from the formula:

$$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all products}} \times 100$$

average titre The average of concordant titres.

B

back titration A technique used when a sample containing an acid or base is unable to be analysed by direct titration. A known amount of base or acid is added in excess to the original sample. The amount of the original sample is calculated by using a titration to determine how much of the added chemical remains unreacted.

base A substance capable of accepting a hydrogen ion (proton).

base hydrolysis A hydroloysis reaction catalysed by a strong base, e.g. sodium hydroxide.

basic salt A salt that dissociates in aqueous solution and one of its ions accepts a proton to water-producing hydroxide ions.

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.

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.

biodegradable Capable of being decomposed by bacteria or other living organisms.

biodiesel A fuel derived from vegetable oil or animal fat, consisting of long-chain alkyl esters. Biodiesel is typically made by reacting triglycerides with an alcohol.

bioethanol A fuel that can be produced from crops or other organic material. Examples of biofuels are ethanol from the fermentation of sugars, methane from animals, and biogas produced from plant and animal waste materials.

biofuel A fuel that can be produced from crops or other organic material. Examples of biofuels are ethanol from fermentation of sugars, methane from animals, and biogas produced from plant and animal waste materials.

biogas A mixture of gases produced by the breakdown of organic matter in the absence of oxygen.

bromothymol blue A widely used indicator. The indicator is yellow in acidic solutions and blue in basic solutions. In a neutral solution of pH 7, the colour of the indicator is green, midway between yellow and blue.

Brønsted–Lowry theory A theory that defines an acid as a proton (hydrogen ion) donor and a base as a proton acceptor. In the reaction $HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$, HCl is the proton donor and is classified as an acid. H_2O is a proton acceptor and is classified as a base.

buffer capacity A measure of the effectiveness of a buffer solution to resist a change in pH when either a strong acid or strong base is added.

buffer solution A solution that resists change to pH when small quantities of an acid or a base are added. Buffers are composed of a weak acid and its conjugate weak base, or a weak base and its conjugate weak acid.

burette Glassware used for volumetric analysis to transfer a variable volume of solution accurately.

C

C-terminal The end of a protein or polypeptide with a free carboxyl group (–COOH).

calcification The precipitation of dissolved ions as calcium carbonate in the form of shells, corals and structures in marine organisms. Once they are formed, such structures are vulnerable to dissolution if concentrations of ions in the water change. High acidity levels limit the formation of corals and shells.

carbon cycle The series of processes by which carbon compounds are interconverted in the environment, chiefly involving the incorporation of carbon dioxide into living tissue by photosynthesis and its return to the atmosphere through respiration, the decay of dead organisms, and the burning of fossil fuels.

carbon neutral A process that absorbs the same amount of carbon as it generates. The carbon dioxide absorbed from the atmosphere by a carbon neutral process compensates for the carbon dioxide produced by the process.

carbonyl functional group A functional group that consists of a carbon atom double bonded to an oxygen atom, –CO–. This group is present in aldehydes, ketones, carboxylic acids, amides and esters.

carboxyl functional group A functional group that consists of a hydroxyl group attached to the carbon of a carbonyl group, –COOH. This group is present in carboxylic acids.

carboxylate A salt of a carboxylic acid. Carboxylates contain the charged group $–COO^–$.

carboxylic acid A homologous series of organic molecules that contain the carboxyl functional group (–COOH).

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.

cation A positively charged ion.

chain isomer An isomer of an organic molecule caused by branching of the hydrocarbon chain.

chemical (HAZCHEM) code A warning symbol on the label of a chemical.

chlorophyll Pigment in green plants.

***cis* isomer** An isomer in which the highest priority groups attached to the carbons of a double bond are on the same side of the double bond plane.

***cis–trans* isomers** Isomers that occur when two different groups are attached to each carbon in a carbon-carbon double bond. They occur because there is restricted rotation around the carbon–carbon double bond.

climate change A change in global or regional climate patterns, in particular a change apparent from the mid- to late 20th century onwards and attributed largely to the increased levels of atmospheric carbon dioxide produced by the use of fossil fuels.

closed system A system in which matter does not enter from or escape into the surroundings.

collision theory A theoretical model that accounts for the rates of chemical reactions in terms of collisions between particles occurring during a chemical reaction.

combustion A rapid reaction with oxygen accompanied by the release of large amounts of energy.

competing equilibria Two or more equilibrium systems (reversible reactions) that involve common reactants that can occur in the same space.

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 specified volume of solution.

concentration fraction The ratio of concentrations of products to reactants in a reversible reaction, as expressed in the equilibrium law. It can also be called the reaction quotient.

concordant titres A set of titres that vary within a narrow range, ideally within 0.10 mL from highest to lowest of one another.

condensation polymer A polymer formed by a condensation reaction, involving the elimination of a small molecule (often water) when monomers bond together. For this to occur the monomers have functional groups at both ends of the molecule.

condensation polymerisation Formation of a polymer by condensation reactions.

condensation reaction A reaction in which two molecules link together by eliminating a small molecule, such as water.

condensed formula A simple representation of the structural formula of an organic molecule. A condensed structural formula shows the atoms connected to each carbon atom, but not all the bonds, e.g. $CH_3CH_2CH_3$.

confidence interval A range of values that has a stated chance, expressed as a percentage, of including the actual value of a specific measurement.

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 and the product that is formed when the oxidising agent gains electrons. e.g. Cu^{2+}/Cu are a conjugate redox pair. Alternatively, it may be considered as a reducing agent and the product that is formed when the reducing agent loses electrons. e.g. $Cl^–/Cl_2$ are a conjugate redox pair.

contact process The process used for the industrial production of sulfuric acid.

control experiment An identical experiment carried out at the same time, but the independent variable is not changed.

controlled variable A variable that must be kept constant during a investigation.

copolymer A polymer that is made from two or more monomers.

credible Reliable and can be backed up with evidence; a credible source provides information that one can believe to be true.

cross-link A covalent bond between different chains of atoms in a polymer or other complex molecule.

crude oil A mixture of hydrocarbons that originates from the remains of prehistoric marine micro-organisms. The organisms have been broken down by high temperatures and pressures over millions of years.

crystalline region A region where polymer molecules line up parallel to each other and pack closely together.

D

decalcification The removal or loss of calcium or calcium compounds.

denaturation The change of the secondary or tertiary structure of proteins, often caused by heat or a change in the pH of the surroundings.

dependent variable The variable that is measured or observed to determine the effect of changes in the independent variable.

detergent A synthetic compound that acts as a surfactant, used for cleaning.

dilution The addition of a solvent to a solution to reduce its concentration.

dilution factor The ratio of the final volume to the aliquot volume.

dimer A chemical structure formed from two similar sub units; for example, paired carboxylic acids that form hydrogen bonds with each other.

dipeptide An organic molecule that has been produced by the condensation reaction between two amino acids.

diprotic acid An acid that can ionise in water to form two H_3O^+ ions.

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 $Mg(s) + O_2(g) \rightarrow 2MgO(s)$.

dispersion force A very weak force of attraction between molecules due to temporary dipoles induced in the molecules. The temporary dipoles are the result of random fluctuations in the electron density.

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.

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

E number A code number used to identify food additives.

ecosystem A biological community of interacting organisms and their physical environment.

elastomer A rubbery material composed of long molecules that is capable of recovering its original shape after being stretched.

electrochemical cell A device that converts chemical energy into electrical energy (galvanic cells), or vice versa (electrolytic cells).

electrochemical series A list of half-equations, written as reduction reactions, arranged in order of reduction potentials, 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 causes a non-spontaneous redox reaction to occur by the passage of electrical energy from a power supply through a conducting liquid.

electrolyte A chemical substance that conducts an electric current as a result of dissociation into positively and negatively charged ions. In electrochemical cells, these ions migrate toward the negative and positive electrodes.

electrolytic cell A cell in which electrolysis can occur.

electromotive force The 'electrical pressure' between two points in a circuit, such as the electrodes of an electrochemical cell; defined as the energy given to electrons in a circuit. Measured in volts.

electronegative A measure of the ability of an atom of an element to attract electrons from within a covalent bond.

electroplating A process that uses electrolysis to deposit a layer of metal on the surface of another material.

elemental analysis A process that determines the mass of each element in a sample of a compound.

empirical formula A formula that shows the simplest whole number ratio of the elements in a compound, e.g. CH_2 is the empirical formula of propene (C_3H_6).

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 from the surroundings; ΔH is positive.

energy profile diagram A diagram that shows the energy changes during the course of a reaction.

enhanced greenhouse effect An increase in the temperature of Earth's surface due to an increased concentration of greenhouse gases, as a result of human activities.

enzyme A protein molecule that functions as a catalyst of a specific biochemical reaction. A catalyst increases the rate of a reaction.

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 equal.

equilibrium constant The value of the concentration fraction when equilibrium is reached; symbol K_c. 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 law The equilibrium law for the chemical equation:

$aW + bX \rightleftharpoons cY + dZ$

is given by the expression:

$$K_c = \frac{[Y]^c[Z]^d}{[W]^a[X]^b}$$

where K_c is a constant at a particular temperature.

equilibrium yield The amount of product obtained when a chemical reaction reaches equilibrium.

equivalence point The point during a titration when the reactants in solution are present in stoichiometric proportions, i.e. in the mole ratio shown by the reaction equation.

essential amino acid An amino acid that must be included in the diet as it cannot be synthesised in the human body.

ester The name of the homologous series of molecules that contain the ester (–COO–) functional group.

ester functional group The functional group that is the result of 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 Another name for the ester functional group, often used in the context of the polyesters, a type of condensation polymer.

esterification reaction The chemical reaction between an alcohol and a carboxylic acid to form an ester as the organic product.

exothermic An exothermic reaction releases energy to the surroundings; ΔH is negative.

extent of reaction The relative amounts of products compared with reactants. The extent of a reaction 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.

F

fatty acid A carboxylic acid that has a relatively long hydrocarbon chain.

fatty acid ester A carboxylic acid with a long hydrocarbon tail, usually containing 12–20 carbon atoms, derived from the reaction of an alcohol with a triglyceride.

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:

$C_6H_{12}O_2(aq) \rightarrow 2CH_3CH_2OH(aq) + 2CO_2(g)$

food chain A series of organisms from producer to consumer.

fossil fuel A fuel that has been produced over a long time by the breakdown of organic material. This process can take many thousands of years. Examples are coal, crude oil and natural gas.

fractional distillation The separation of the components in a mixture on the basis of their boiling temperatures.

fuel cell A type of electrochemical cell in which the reactants are supplied continuously, allowing continuous production of electrical energy.

functional group An atom or group of atoms in an organic molecule that largely determines the molecule's properties and reactions.

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.

geometric isomer A type of stereoisomer that can occur when there is restricted rotation in a molecule. Restricted rotation can occur about a carbon–carbon double bond or a ring. Stereoisomers of alkenes can be distinguished using the labels *cis*- and *trans*-.

global warming A gradual increase in the overall temperature of the Earth's atmosphere generally attributed to the greenhouse effect caused by increased levels of carbon dioxide, chlorofluorocarbons and other pollutants.

green chemistry The design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.

greenhouse effect The process by which heat radiation from Earth's surface is absorbed and re-radiated by gases in the atmosphere. The greenhouse effect maintains the temperature of Earth at conditions suitable for life.

greenhouse gas A gas that is able to absorb and re-radiate heat radiation. These gases contribute to the greenhouse effect. Examples are carbon dioxide, methane and water vapour.

H

Haber process The process for the industrial production of ammonia gas.

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 which shows the loss or gain of electrons by a species during oxidation or reduction. For example, the oxidation of magnesium is written as the half-equation $Mg(s) \rightarrow Mg^{2+} + 2e^-$.

halogen displacement reaction A redox reaction where an elemental halogen is reduced to its ions by a reaction with ions of another halogen.

hard water Water that requires a lot of soap to obtain a lather or froth.

heterogeneous reaction A chemical reaction in which at least two of the species are in a different state or phase.

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.

homogeneous reaction A chemical reaction in which all the species are in the same state or phase.

homologous series A series of organic compounds in which each member of the group differs from the previous member by a $-CH_2$ unit. Examples are alkanes, alkenes and alcohols.

hydration reaction A reaction that involves water as a reactant.

hydrocarbon A compound that contains carbon and hydrogen only. Examples include alkanes and alkenes.

hydrogen economy A proposed system of delivering energy for society using hydrogen as the source of energy.

hydrogen halide Diatomic molecules consisting of a hydrogen atom and a halogen atom joined by a covalent bond. HF, HCl, HBr and HI are hydrogen halides.

hydrogenation reaction The reaction of an organic compound with hydrogen so that it becomes more saturated.

hydrolysis A reaction involving the breaking of a bond in a molecule using water as a reactant. Two smaller molecules are usually formed.

hydrolysis reaction A reaction that occurs when a molecule or ion in aqueous solution reacts with water, either accepting or donating a proton.

hydrolytic reaction A reaction involving the breaking of a bond in a molecule using water as a reactant. Two smaller molecules are usually formed.

hydronium ion The $H_3O^+(aq)$ ion.

hydrophilic Describes molecules, or parts of a molecules, that form relatively strong intermolecular attractions with water molecules.

hydrophobic Describes molecules, or parts of a molecules, that tend to repel water. Hydrophobic substances are usually non-polar.

hydroxide ion The $OH^-(aq)$ ion.

hydroxyl functional group A functional group that consists of an oxygen atom covalently bonded to a hydrogen atom, –OH. This functional group is present in alcohols.

hypothesis A prediction based on previous knowledge; a possible outcome of the experiment.

I

ideal gas law The law that links the number of moles of a gas with its volume at a given temperature and pressure. It is commonly written as $PV = nRT$.

immiscible Describes a liquid that will not mix with or dissolve in another liquid; for example, oil in water.

independent variable A variable that is changed by the researcher.

indicator A chemical that has a different colour in acidic and basic solutions and is used to distinguish between acids and bases. Indicators are also used to determine the pH of a solution.

indicator range The range of pH values over which an indicator changes colour.

induced fit model A mechanism of the action of an enzyme where the active site on the enzyme to changes shape in response to the presence of the (reacting) substrate molecule.

inert A substance that is unreactive, such as platinum or graphite used in electrodes.

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 (in the form of graphite) are typically used as inert electrodes.

inorganic Of a compound that consists of elements other than carbon. Although certain compounds of carbon, such as carbon dioxide and carbonates, are also classified as inorganic.

internal circuit The part of an electrochemical cell in which ions move, e.g. solutions and salt bridge.

ion–dipole force The intermolecular attraction between a polar molecule (or polar section of a molecuke) and a positive or negative ion.

ionic product of water See *ionisation constant of water*.

ionisation either (i) The removal of one or more electrons from an atom or ion;

or (ii) 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 ion, e.g. $HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$.

irreversible reaction A reaction in which a significant reaction can occur in one direction only.

isomers Molecules that have the same molecular formula but a different arrangement of atoms.

IUPAC nomenclature A set of rules for naming organic molecules. It is usually systematic and gives the number of carbon atoms and the location and type of functional groups present. (IUPAC = International Union of Pure and Applied Chemists)

K

ketone A homologous series of organic molecules that contains the carbonyl functional group (C=O) within the carbon chain.

kinetic energy The energy that a particle or body has due to its motion $\left(KE = \frac{1}{2}mv^2\right)$

kinetic energy distribution diagram A graph of kinetic energy against number of particles that shows the range of energies in a sample of a gas or a liquid at a given temperature. Also known as a Maxwell–Boltzmann distribution curve.

krill Small crustaceans that live in the oceans.

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.

limiting reagent A reagent that is completely consumed in a reaction and which determines the amount of product.

lipid A class of organic compounds that includes fats, oils, waxes and steroids. They are insoluble in water but soluble in non-polar solvents.

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.

lock-and-key model A mechanism for the action of enzmes where only molecules with the correct shape and size can 'fit' into the enzyme.

low density polyethene (LDPE) A form of the polymer polyethene which has a high degree of short and long chain branching. This means the polymer chains do not pack together closely in the crystal structure. Therefore, it has weaker intermolecular forces, resulting in a lower tensile strength and increased ductility.

M

macroscopic property A property that can be seen by the naked eye, such as concentration, pressure, temperature and pH.

main group metal A metal in groups 1–3, such as lithium, sodium, potassium, magnesium, calcium, barium and aluminium.

Maxwell–Boltzmann distribution curve A graph of kinetic energy against number of particles that shows the range of energies in a sample of a gas or a liquid at a given temperature. Also known as a kinetic energy distribution diagram.

mean The sum of all the values in a data set divided by the number of values in the data set. It is commonly known as the average of a set of numbers.

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.

methyl orange A synthetic indicator often used in the analysis of weak bases. It is also used as a textile dye.

micelle A group of molecules, e.g lipids, in an aqueous solution, that arrange into clusters with the hydrophobic chains on the inside and the hydrophilic (polar) sections on the outside.

miscible Describes a liquid that will mix with or dissolve in another liquid; for example, ethanol and water.

mistake An avoidable error.

molar concentration The concentration of a solution expressed as moles of solute per litre of solutlion (mol L^{-1}).

molecular formula A formula that gives the actual number and type of atoms present in a molecule.

monomer A small molecule that is able to react to form long chains of repeating units, called polymers.

monoprotic acid An acid that can donate only one hydrogen ion.

monounsaturated fatty acid A fatty acid that contains one carbon–carbon double bond.

N

N-terminal The end of a protein or polypeptide with a free amine group ($–NH_2$).

neutral salt A salt that dissociates in aqueous solution and its ions are neither proton donors or proton acceptors.

nickel–metal hydride cell A rechargeable cell that generates an electric current by the oxidation of nickel metal hydride and the reduction of NiOOH.

non-rechargeable cell A primary galvanic cell.

non-renewable Non-renewable energy resources are those that are being used at a faster rate than they can be replaced.

non-polar Bonds or molecules that do not have a permanent dipole. They have an even distribution of charge.

non-spontaneous reaction A reaction that would not normally occur without the application of electrical energy. They are the reverse of spontaneous reactions, which produce energy.

O

ocean acidity The reduction in the pH of the ocean caused mainly by absorption of atmospheric carbon dioxide.

open system A system that allows matter and energy to be exchanged with the surroundings.

optimum pH The pH at which enzyme activity is greatest.

optimum temperature The temperature at which enzyme activity is greatest.

organic molecule An molecule that is based on a hydrocarbon skeleton. Organic molecules also commonly contain other non-metal elements, such as oxygen, nitrogen, sulfur and chlorine.

outlier A value that lies outside most of the other values in a set of data.

oxidant A chemical species (element, compound or ion) that accepts one or more electrons in an oxidation–reduction reaction. An oxidant causes another substance to be oxidised, and in the process the oxidant is reduced. Also called an oxidising agent.

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 is said to have occurred when there is an increase in an element's oxidation number during the reaction.

oxidation number A number assigned to an atom in a compound or as the free element, which represents the charge that 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.

oxidised The loss of electrons or an increase in oxidation number. When a substance is oxidised, the electrons are written on the right-hand side of the arrow in the half-equation.

oxidising agent A reactant that causes another reactant to lose electrons during a redox reaction. This reactant is, itself, reduced and gains electrons. The oxidation number of the oxidising agent decreases during the reaction. For example, in the reaction between magnesium and oxygen, the oxygen is the oxidising agent, as it causes magnesium to lose electrons and form Mg^{2+}.

P

parallax error The perceived shift in an object's position as it is viewed from different angles.

partial pressure The pressure exerted by one component of a mixture of gases. The total pressure of a mixture of gases is equal to the sum of the individual partial pressures of each component in the mixture.

peptide bond The bond between the carbon and nitrogen atoms in the amide group along a protein chain. This bond joins the amino acids in a polypeptide chain.

peptide link or peptide group The –CONH– functional group between amino acid units in a polypeptide chain; also called amide link.

percentage composition The proportion by mass of the different elements in a compound.

$$\%\text{ by mass of an element in a compound} = \frac{\text{mass of the element present}}{\text{total mass of the compound}} \times 100$$

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) Safety equipment such as safety glasses, lab coats, gloves and respirators worn to reduce risk in the laboratory.

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 $C_{15}H_{32}$.

pH curve A plot showing change in pH when an acid is titrated against a base. See also titration curve.

pH scale A measure of acidity and the concentration of hydronium ions, in solution. Acidic solutions have a pH value less than 7 at 25°C and bases have a pH value greater than 7 (at 25°C). Mathematically, pH is defined as $pH = -\log_{10}[H_3O^+]$.

phenolphthalein A synthetic indicator used in the analysis of weak acids.

phosphate buffer An important buffer system that operates in the internal fluid of all cells that works to stabilise the pH.

photosynthesis The chemical process by which oxygen and glucose are produced in plant cells in the presence of light. It can be represented by the equation:

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

pipette Glassware used for volumetric analysis to transfer a fixed volume of solution accurately.

plankton Aquatic microscopic algae and protozoa.

plastic A property of a material that can be reshaped by application of heat and pressure. In society, polymers are often referred to as plastics.

plasticiser Small molecules that soften a plastic by weakening intermolecular attractions between polymer chains.

polar Bonds or molecules with a permanent dipole. They have an uneven distribution of charge.

polyamide A condensation polymer consisting of monomers joined by amide linkages.

polyester A condensation polymer consisting of monomers joined by ester linkages.

polymer A natural or synthetic compound of high molar mass consisting of up to millions of repeated linked units known as monomers. There are many different types of polymers.

polymerisation The process of synthesising a polymer.

polypeptide An organic polymer molecule made from a condensation reaction between amino acids.

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

polyunsaturated fatty acid A fatty acid that contains more than one carbon–carbon double bond.

position of equilibrium The relative amounts of reactants and products at equilibrium. The position of equilibrium varies depending on the extent of the reaction.

positional isomers Isomers that arise from a functional group being in different locations on the carbon chain.

potential difference The electromotive force (measured as a voltage) between two points in a circuit, such as the electrodes of an electrochemical cell.

precise When repeated measurements of the same quantity give values that are in close agreement.

precision When repeated measurements of the same quantity give values that are in close agreement.

pressure The force exerted per unit area of a surface.

primary alcohol An alcohol in which the carbon that is bonded to the –OH group is only attached to one alkyl group.

primary amine An amine in which the nitrogen atom is bonded to one carbon and two hydrogen atoms.

primary cell A galvanic cell that is non-rechargeable because the products of the reaction migrate away from the electrodes.

primary source A source that is a first-hand account.

primary standard A substance used to make a standard solution. It is so pure that its amount, in moles, can be accurately determined from its mass.

primary structure The sequence (number, order and type) of amino acids in a polypeptide chain.

processed data Results, normally from an experiment, that have been manipulated in some way, such as grouping, averaging, sampling or graphing to help in the drawing of conclusions from the data.

protein An organic polymer molecule made from amino acids by condensation polymerisation. Proteins typically contain 50 or more amino acid units.

Protein Data Bank (PDB) An online database containing structural information about proteins.

Q

qualitative Relating to quality and not measured values.

quantitative Relating to measured values rather than quality.

quantitative analysis The determination of the quantities of particular components present in a substance.

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

random error An error that follows no regular pattern where measured results can be above or below the actual value. (The effects of random errors can be reduced by taking the average of many observations.)

rate of reaction The change in concentration of a reactant or product over a period of time (usually one second):

$$\text{rate of reaction} = \frac{\text{change in concentration}}{\text{time}}$$

raw data The information and results collected and recorded during an experiment.

reaction pathway A series of chemical reactions that converts a starting material into a product in a number of steps.

reaction quotient Another name for the concentration fraction. It is the ratio of concentrations of products to reactants in a reversible reaction, as expressed in the equilibrium law.

reactive electrode An electrode that is consumed in an electrochemical cell reaction.

reactivity series A ranking of metals in increasing 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.

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 The gain of electrons or a decrease in oxidation number. 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, itself, oxidised and loses electrons. For example, 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 or its oxidation number decreases. A reduction half-equation will show the electrons on the reactant side (left-hand side) of the equation.

reliability An experiment can be repeated several times with consistent results.

renewable Resources are considered to be renewable if they are not finite (e.g. wind power) or can be replenished (e.g. biochemical fuels) within a relatively short time span.

respiration A process in living things in which complex organic molecules are oxidised by oxygen with the release of carbon dioxide, water and energy, by which life is sustained.

reverse reaction The reaction that occurs in the opposite direction to the stated reaction.

reversible reaction A reaction in which significant reaction can occur in the reverse direction because the products are present and can react with each other under suitable conditions.

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 summary of the risks of using a particular chemical, including measures to be followed to reduce risk.

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.

saponification The process in which soap is produced by heating a fat or vegetable oil with alkali.

saturated Describes hydrocarbons composed of molecules with only carbon–carbon single bonds.

saturated ester An ester in which the hydrocarbon tail contains only carbon–carbon single bonds.

saturated fatty acid A fatty acid that contains carbon–carbon single bonds.

saturated molecule An organic compound in which all the atoms are joined by single bonds.

saturated solution A solution that cannot dissolve any more solute at the given temperature.

secondary alcohol An alcohol in which the carbon bonded to the –OH group is also bonded to two alkyl groups. The alkyl groups may be the same or different.

secondary cell An 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 source A source derived from the original data or account.

secondary structure Initial level of spatial arrangement of a polypeptide chain. There are two forms of secondary structure: α-helices and β-pleated sheets.

side group A group of atoms attached to a backbone chain of a long molecule.

significant figures Digits within a number that are used to express the accuracy of that number.

spontaneous redox reaction A redox reaction that occurs naturally.

self-ionisation An ionisation reaction of pure water in which water behaves as both an acid and a base.

semistructural formula A condensed formula that summarises the structural formula of a compound in a single line of text.

side chain The R group in an amino acid molecule; there are 20 different side chains on the α-amino acids used to make human proteins.

smelting The process where a metal ore is heated in order to separate the desirable components from the other parts of the ore.

soap A compound, normally derived from a fatty acid (long-chain carboxylic acid) that acts as a surfactant, used for cleaning or washing.

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.

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.

standard conditions Established reference conditions to compare testing of experimental activities. Conditions at which gas pressure is 100 kPa, the concentrations of dissolved species are 1.0 mol L^{-1} and the temperature is 25°C (298 K).

standard electrode potential The electromotive force that is measured when a half-cell, at standard conditions (gas pressures 100 kPa, 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 A $H^+(aq)/H_2(g)$ 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 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 of accurately known concentration.

stem name The name of a molecule derived from the number of carbon atoms in the longest continuous carbon chain in a hydrocarbon and the highest priority functional group present. For example, the stem name of 2-chlorobutane is butane.

strong acid A acid that readily accepts a hydrogen ion (proton) from an acid. A strong acid will completely ionise in water to produce H_3O^+ ions.

strong base A base that readily accepts a hydrogen ion (proton) from an acid. If the base is soluble, it will completely dissociate in water to produce OH– ions.

structural formula A formula that represents the three-dimensional arrangement of atoms in a molecule.

structural isomers Isomers are molecules that have the same molecular formulas but their atoms are bonded together in different ways.

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.

super acid An acid that has acidity greater than the acidity of 100% sulfuric acid.

surface area The area of all surfaces of the substance that are exposed to the other reactants. This is proportional to the amount of particles available at the surface to react.

surfactant A substance that causes non-polar and polar substances to mix due to the presence of hydrophilic and hydrophobic sections on molecules of the substance.

surroundings The environmment around a particular chemical reaction. The chemical reaction is the system. Energy moves between the system and surroundings in exothermic and endothermic reactions.

sustainable Able to support energy and resources into the future without depletion.

synthesis A process that results in the making of a new substance.

system In chemistry, a system is a chemical reaction. A system operates within its surroundings. Energy can move between the two. You always consider energy as being absorbed or released from the perspective of the system. For example, energy is absorbed into the system from the surroundings, or energy is released by the system to the surroundings.

systematic error An error that produces a constant bias in measurement – results are either always above, or always below the actual value. (Systematic errors are eliminated or minimised through calibration of apparatus and the careful design of a procedure.)

T

temperature A measure of the average kinetic energy of the particles in a substance, expressed in units (degrees) based on a standard scale.

tertiary alcohol An alcohol in which the carbon bonded to the –OH group is also bonded to three alkyl groups.

tertiary structure 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 apart as possible in three dimensions.

theoretical yield The mass of a 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.

thermoplastic A thermoplastic polymer will soften and melt when heated, allowing it to be remoulded or recycled. When heated sufficiently, the intermolecular bonds break, allowing the molecules to become free to move and be remoulded.

thermosetting When a thermosetting polymer is heated, it does not melt, but at high temperatures covalent bonds are broken and it decomposes or burns. It cannot be moulded into a different shape.

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 A graph obtained from a titration of pH against volume of reactant added from a burette. See also pH curve.

titre A variable volume of liquid measured in a burette by subtracting the final burette reading of a titration from the initial burette reading.

***trans* isomer** An isomer in which the highest priority groups attached to the carbons of a double bond are on opposite sides of the double bond plane.

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.

transition state An arrangement of atoms in a reaction that occurs when sufficient energy is absorbed for the activation energy to be reached. It represents the stage of maximum potential energy in the reaction. Bond breaking and bond forming are both occurring at this stage, and the arrangement of atoms is unstable.

trend line Line that represents the trend shown by a set of data; normally used to represent a clear relationship between two variables displayed on a graph.

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.

U

uncertainty An error associated with measurements made during experimental work.

universal gas constant The constant used in the ideal gas law, value is $8.314\,JK^{-1}\,mol^{-1}$.

universal indicator A widely used indicator for estimating 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 as the pH increases.

unsaturated Describes hydrocarbons composed of molecules containing one or more carbon–carbon double (or triple) bonds.

V

valence shell electron pair repulsion (VSEPR) theory A model in chemistry used to predict the shape of molecules based on electrostatic repulsion between electron pairs.

validity Refers to whether the evidence supports the argument.

variable Any factor that can be controlled, changed and measured in an experiment.

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 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

weak acid An acid that is partly ionised in water.

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 ($Fe_2O_3.xH_2O$), known as rust.

Z

zwitterion A dipolar ion formed when the amino and carboxyl groups in an amino acid or polypeptide are both charged.

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Periodic table

Groups

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hydrogen 1.008																	2 **He** helium 4.003
3 **Li** lithium 6.968	4 **Be** beryllium 9.012											5 **B** boron 10.82	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
11 **Na** sodium 22.99	12 **Mg** magnesium 24.31											13 **Al** aluminium 26.98	14 **Si** silicon 28.09	15 **P** phosphorus 30.97	16 **S** sulfur 32.07	17 **Cl** chlorine 35.45	18 **Ar** argon 39.95
19 **K** potassium 39.10	20 **Ca** calcium 40.08	21 **Sc** scandium 44.96	22 **Ti** titanium 47.88	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 72.59	33 **As** arsenic 74.92	34 **Se** selenium 78.96	35 **Br** bromine 79.90	36 **Kr** krypton 83.80
37 **Rb** rubidium 85.47	38 **Sr** strontium 87.62	39 **Y** yttrium 88.91	40 **Zr** zinconium 91.22	41 **Nb** niobium 92.91	42 **Mo** molybdenum 95.94	43 **Tc** technetium	44 **Ru** ruthenium 101.1	45 **Rh** rhodium 102.9	46 **Pd** palladium 106.4	47 **Ag** silver 107.9	48 **Cd** cadmium 112.4	49 **In** indium 114.8	50 **Sn** tin 118.7	51 **Sb** antimony 121.8	52 **Te** tellurium 127.6	53 **I** iodine 126.9	54 **Xe** xexon 131.3
55 **Cs** caesium 132.9	56 **Ba** barium 137.3	57–71 ***La** lanthanum 138.9	72 **Hf** hafnium 178.5	73 **Ta** tantalum 180.9	74 **W** tungsten 183.9	75 **Re** rhenium 186.2	76 **Os** osmium 190.2	77 **Ir** iridium 192.2	78 **Pt** platinum 195.1	79 **Au** gold 197.0	80 **Hg** mercury 200.6	81 **Tl** thallium 204.4	82 **Pb** lead 207.2	83 **Bi** bismuth 209.0	84 **Po** polonium	85 **At** astatine	86 **Rn** radon
87 **Fr** francium	88 **Ra** radium 226.0	89–103 ****Ac** actinium	104 **Rf** rutherfordium	105 **Db** dubnium	106 **Sg** seaborgium	107 **Bh** bohrium	108 **Hs** hassium	109 **Mt** meitnerium	110 **Ds** darmstadtium	111 **Rg** roentgenium	112 **Cn** copernicium	113 **Uut** ununtrium	114 **Fl** flerovium	115 **Uup** ununpentium	116 **Lv** livermorium	117 **Uus** ununseptium	118 **Uuo** ununoctium

key:

Atomic number
Symbol
Name
Standard atomic weight

* Lanthanide series	58 **Ce** cerium 140.1	59 **Pr** praseodymium 140.9	60 **Nd** neodymium 144.2	61 **Pm** promethium	62 **Sm** samarium 150.4	63 **Eu** europium 152.0	64 **Gd** gadolinium 157.3	65 **Tb** terbium 158.9	66 **Dy** dysprosium 162.5	67 **Ho** holmium 164.9	68 **Er** erbium 167.3	69 **Tm** thulium 168.9	70 **Yb** ytterbium 173.0	71 **Lu** lutetium 175.0
** Actinide series	90 **Th** thorium 232.0	91 **Pa** protactinium	92 **U** uranium 238.0	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium